BIODEGRADABILITY OF NONWOVEN FABRICS

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ABSTRACT

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The thesis was done in cooperation with Ahlstrom Oy, which is a high performance fiber-based materials company. The company wanted to test the biodegradability of their nonwoven filter fabrics and get information about standardized tests used to measure biodegradability. There were four different types of fabrics (EP 5334, EP 5395, EP 5396 and EP 5457) containing different compositions of various fibres. The tests were done as blind tests, i.e. the composition of the nonwoven fabrics was unknown to the person conducting the tests.

The thesis was done between January and May 2015 and it consists of two parts. In the experimental part the biodegradability of nonwoven fabrics was studied by composting and by measuring the oxygen consumption of the fabrics in soil with OxiTop®. A manual for OxiTop® soil respiration measurements was also written. The other part of the thesis is based on literature research. In this part, chosen standards for testing biodegradability and biodegradable polymers are introduced briefly.

The results of the composting experiment show that none of the fabrics were biodegradable in composting conditions. Surprisingly the average mass of all the fabric types was greater in the end of the experiment compared to the initial mass. However, the fabric EP 5457 showed clear visual changes suggestive of decay. Additionally some change in texture was observed with EP 5395. Similar results were gathered in the soil respiration experiment; of the fabrics, sample EP 5457 showed the highest oxygen consumption i.e. biodegradability activity in comparison with the blank soil sample. The second greatest oxygen consumption was measured with EP 5395. The results suggest that sample EP 5457 had the highest biodegradability potential, even though none of the samples were biodegradable in the tests.

Key words: biodegradation, composting, OxiTop® soil respiration, biodegradability standards, nonwoven fabrics

TIIVISTELMÄ

Tampereen ammattikorkeakoulu
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HARTIKAINEN, SALLA:
Kuitukankaiden biohajoavuus

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Toukokuu 2015

Opinnäytetyö tehtiin yhteistyössä Ahlstrom Oy:n kanssa. Ahlstrom Oy valmistaa kuitupohjaisia materiaaleja vaativaan käyttöön. Opinnäytetyön tavoite on testata yrityksen kuitusuodatinkankaiden biohajoavuutta sekä etsiä tietoa standardoiduista testeistä, joilla mitataan biohajoavuutta. Tutkittavana oli neljä erilaista, erityyppisistä kuiduista koostuvaa kuitukangasta (EP 5334, EP 5395, EP 5396 ja EP 5457). Biohajoavuustestit tehtiin sokkotestinä siten, että kuitukankaiden koostumusta ei tiedetty.

Opinnäytetyö tehtiin vuonna 2015 tammikuun ja toukokuun välillä, ja se koostuu kahdesta osasta. Kokeellisessa osuudessa Ahlstromin kuitukankaiden biohajoavuus testattiin kompostoimalla sekä mittaamalla kankaiden hapenkulutus OxiTop®-maahengityslaitteella. OxiTop®-laitteelle koostettiin myös käyttöohje. Kirjallisuusosiossa valittuja biohajoavuusstandardeja sekä biohajoavia polymeerejä esitellään lyhyesti.

Kompostointikokeen tulokset osoittavat, että mikään kuitukankaista ei ole biohajoava kompostiolosuhteissa. Oli yllättävää, että kaikkien kuitukangastyyppien massojen keskiarvo oli suurempi kokeen lopussa verrattuna alkuperäisiin massoihin. EP 5457 -kankaassa oli kuitenkin nähtävissä selviä visuaalisia muutoksia, jotka viittaavat biohajoamiseen. Kankaan EP 5395 tekstuurissa oli myös havaittamissa jonkin verran muutosta kokeen aikana. Samankaltaisia tuloksia saatiin maahengityskokeessa: kankaalla EP 5457 hapenkulutus oli suurin verrattuna kontrollimaanäytteeseen. Toiseksi suurin hapenkulutus mitattiin kankaalla EP 5395. Tulokset osoittavat, että näytteellä EP 5457 biohajoavuuspotentiaali oli suurin, vaikka yksikään näyte ei kokeessa ollut biohajoava.

Asiasanat: biohajoaminen, kompostointi, OxiTop® maahengitys, biohajoavuus standardit, kuitukankaat

CONTENTS

GLOSSARY

BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
ThOD	Theoretical oxygen demand
BA	Oxygen consumption
$M_R(O_2)$	Molar mass of oxygen
V_{fr}	Free gas volume
m_{ds}	Mass of dry sample
R	General gas constant
T	Temperature
ISO	International Organization for Standardisation
CEN	European Committee for Standardisation Institute
ASTM	American society for Testing and Materials
DIN	German Normalisation Institute
JIS	Japanese Institute for Standardisation
PHB	Poly(hydroxybutyrate)
PHBV	Poly(hydroxybutyrate-hydroxyvalerate)
PHAs	Polyhydroxyalcanoates
PLA	Polylactic acid
PGA	Polyglycolic acid
PCL	Polycaprolactone
PBS	Polybutylene succinate
PBSA	Polybutylene succinate adipate
PVOH	Polyvinyl alcohol
T_m	Melting temperature
T_g	Glass transition temperature
T_d	Decomposition temperature
M_w	Molecular weight
HDT	Heat deflection temperature

1 INTRODUCTION

The aim of the experimental part of this work was to determine the differences in the level of decay between different nonwoven filter fabrics. The biodegradation was studied in composting and in soil conditions. The aim of the literature part was to gather information about different aerobic biodegradation test methods and to gather information about biodegradable polymers applicable to use as fibre.

The literature research consists of two topics: Biodegradation standards and biodegradable materials. Biodegradation standards, presented in chapter 3, are developed to test biodegradability of materials. The research has been limited to aerobic biodegradation. The standards are divided according to testing conditions. The aerobic degradation method can be tested in aquatic, soil or in composting conditions. The field of biodegradable materials and biopolymers is vast and expanding. In chapter 4 chosen biodegradable polymers are introduced. The polymers are organized according to the production process. Polymers can be extracted from microorganisms, produced from natural monomers or produced synthetically from petroleum based materials.

The experimental part was conducted in TAMK laboratory. The composting was done in two composters (Biolan pikakompostori 220) for 3 months. The respiration experiment was done with OxiTop® device, which measures the pressure change in the measuring vessels due to consumption of oxygen by microorganisms. OxiTop® device had not been used before at TAMK to determine the respiration of samples in soil, thus there weren't any defined instructions how to do it. One of the aims of this work was to test the applicability of the device for biodegradability tests.

The experimental part consists of the composting experiment and the soil respiration experiment. Theory about biodegradation, composting and OxiTop® device can be found from chapter 2. The methods and experimental setup of these experiments is presented in chapter 5. The results and findings of the experiments are presented in chapter 6.

2 THEORY

2.1 Biodegradation process

Biodegradation is an irreversible process carried out by microorganism, such as bacteria and fungi, where organic material is broke down into simpler components. Microorganisms utilize the organic matter in their metabolic activities and growth. The end products of biodegradation, when the mineralization is complete, are CO_2, H_2O and minerals. Intermediate products of the process include also biomass and humic matter. (Bastoli 2005, 4.)

The focus of this thesis is on aerobic biodegradation, thus the testing done on nonwoven fabric samples was carried out in aerobic conditions. In aerobic conditions material is broken down by microorganisms in presence of oxygen. In the following equation (1) the biodegradable material is $C_{MATERIAL}$, indicating the material containing carbon, hydrogen and oxygen.

$$C_{MATERIAL} + O_2 \rightarrow CO_2 + H_2O + C_{RESIDUE} + C_{BIOMASS} \quad (1)$$

The material is oxidized into carbon dioxide (CO_2), water (H_2O) and some organic residue and biomass. The residue consists of non-degradable material and metabolites of microorganisms. The biomass is microbial carbon, i.e. carbon in microorganisms' structures. (Bastoli 2005, 151.)

Microorganisms biodegrade i.e. metabolise organic matter. In figure 1 the metabolism of microorganisms is described by using glucose ($C_6H_{12}O_6$) as an example. Glucose is metabolised in two ways; in dissimilatoric metabolism and catabolic metabolism. In dissimilatoric metabolism (lower chemical reaction in figure 1) glucose is mineralized to carbon dioxide (CO_2) and water (H_2O) at presence of oxygen (O_2). Energy is stored as ATP (adenosine diphosphate). In catabolic metabolism (upper chemical reaction in figure 1) glucose is transformed into cell structure ($C_4H_7O_2N$) with the energy derived from ATP. NADP (nicotinamide adenine dinucleotide phosphate) provides electrons if needed for both metabolisms. (Platen & Wirtz 1999a, 3.)

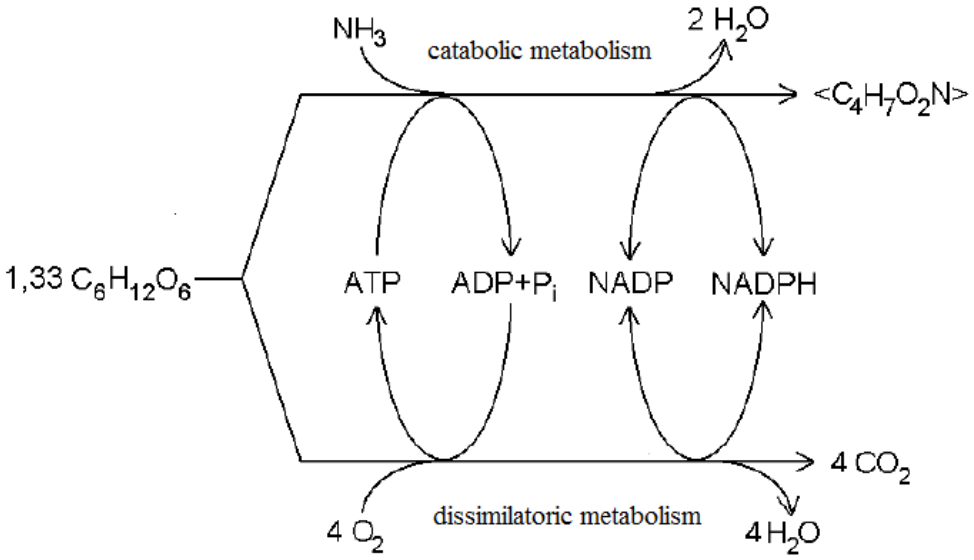


FIGURE 1. Decomposition of organic substance by aerobic organisms (Platen & Wirtz 1999a, 3)

2.2 Biodegradability of polymers

Biodegradation of polymers occurs usually in two steps: depolymerisation and mineralization. Depolymerisation happens outside the organism by hydrolysis, oxidation or extracellular enzymes. In the process polymer chains are broken into oligomers or monomers. In figure 2 the depolymerisation of cellulose polymer is presented. The monomer formed in the reaction is called glucose. Mineralization takes place inside the microorganisms. The monomeric and oligometric fragments are small enough for microorganisms to digest. These fragments are transferred inside the cell and consumed as energy by mineralization process. (Bastioli 2005, 20.)

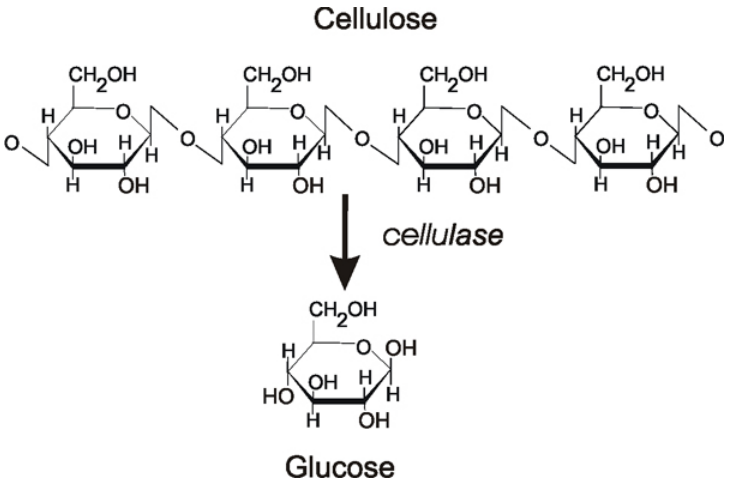


FIGURE 2. Depolymerisation of cellulose to glucose by cellulase enzyme (Held 2012)

The chemical structure and composition of the material affects the biodegradability. The relationships between the chemical composition and biodegradability are difficult to predict, but some general characteristics affecting biodegradability have been found. (Bastioli 2005, 20-21.)

Physical state and surface conditions (surface area and hydrophilic or hydrophobic properties) of the material have an effect on the accessibility of extracellular enzymes, which often start the degradation. High molecular structures, such as glass transition temperature (T_g), melting temperature (T_m), modulus of elasticity and crystallinity affect the biodegradability of the material. For instance crystallinity is an important factor concerning biodegradation, thus enzymes degrade first the amorphous regions of the material. Increasing crystallinity decreases the biodegradation rate. Melting temperature has an influence on biodegradability: the higher the melting temperature, the lower the rate of biodegradation. (Tokiwa et al. 2009.)

Chemical properties i.e. first order structures, such as chemical bonds and chemical groups affect the chemical activity and thus the degradability. Also molecular weight of the material affects the biodegradability: increasing the molecular weight decreases the biodegradability. Combining polymers, i.e. polymer blends, can change the biodegradation rates. Combining non-biodegradable polymers with biodegradable ones can produce a biodegradable polymer blend. (Bastioli 2005, 20-21; Tokiwa et al. 2009.)

The degradation of materials depends not only on the structure of the material, but also the environment in which the degradation takes place. The environmental conditions,

such as availability of water and oxygen, as well as temperature affect the activity of microorganisms. Different kinds of environments in which biodegradation takes place (disposal pathways) are described in table 1. The different environments are divided into groups according to the availability of oxygen and water. Concerning oxygen availability the environments can be divided into aerobic and anaerobic conditions. When the moisture content is taken into account, aerobic and anaerobic environments can be separated into aquatic and high solid environments. (Bastioli 2005, 11-12.)

TABLE 1. Different biodegradation environments (Bastioli 2005, 12)

	AQUATIC	HIGH SOLIDS
AEROBIC	• wastewater treatment plants (aerobic) • surface waters • marine environments	• composting plants • surface soils
ANAEROBIC	• wastewater treatment plants (anaerobic) • rumen of herbivores	• anaerobic sludge • anaerobic digestion • landfill

Degradation of materials in the environment includes various mechanisms. Apart from biodegradability, which was defined earlier in chapter 2.1, the material undergoes simultaneously several different processes regarding degrading. Biocorrosion of materials causes negative changes to the material properties, e.g. weakening the strength of the material. Microorganisms can participate to biodegradation of selected components in material. Biocorrosion can deteriorate the material into invisible particles without biodegrading the material completely into microorganisms' metabolic products. (Bastioli 2005, 308.)

Hydrolysis is a chemical process, in which the chemical bounds of material are broke into smaller fragments. In case of polymers' depolymerization hydrolysis or oxidation is essential in order to microbial biodegradation to take place. In depolymerization polymers are broken down into monomers and oligomers, which can be degraded by microorganisms.

Photodegradation is the decomposition of material by radiant energy, i.e. solar energy. Degradation happens often by oxidation weakening the mechanical properties of material. Bio-compatible materials degrade in living tissue and often this kind of degradation

is abiotic, i.e. non-enzymatic. Polymers with the ability to degrade in living tissue (e.g. PGA) are used in medical applications. (Bastioli 2005, 4, 308.)

The definite difference between environmental biodegradability and other material degradation processes is, that biodegradation is caused by micro-organisms and leads to complete biodegradation of microorganisms' metabolic end products (CO_2 water and mineral salts).

2.3 Composting

Composting is a biodegradation process, in which a mixture of waste in solid aerobic conditions is broke down by microbial community. The process is exothermal, thus it produces heat. The temperature of the compost varies during different phases in the process. End products of the composting process are CO_2, water, minerals and organic matter (compost). The organic end product, compost, is stabilized and sanitized in the process. The compost is not phytotoxic thus the amount of microbes (viruses, bacteria, fungi and parasites) has been reduced during the process. The compost can be used as organic fertilizer. (Diaz et al. 2007, 26.)

Composting is a complex process, thus several factors affect the functioning of a composter. In aerobic process the availability of oxygen and moisture content affect the activity of microbes; microbes need oxygen and moisture to function. If the concentration of oxygen is too low or if the mixture is too dry, the activity of organisms is inhibited. On the other hand, if the moisture content is too high, the air in the pores of the waste mixture is replaced by water causing anaerobic conditions. The quality of the end product is affected by several factors: quality of organic waste, ratio of carbon and nitrogen (C/N ratio), particle size, length of the process and temperature pattern during the process. (Diaz et al. 2007, 26.)

2.3.1 Operational principle of a compost

The composting process undergoes three degrading steps: rapid decomposition, stabilization and humification. The rapid decomposition is the initial oxidation of sugars and

proteins. Stabilization includes mineralization of slowly degrading compounds such as starch and cellulose. In humification process carbon in organic matter is converted into humic substance by microbes. Composting is seized during this last process, so that humification is incomplete and a part of organic matter is not degraded completely. (Diaz et al. 2007, 26.)

The composting process consists of four phases: first mesophilic phase, thermophilic phase, second mesophilic phase and maturation phase. The degrading processes mentioned in previous paragraph are undergone during the different phases of composting. (Diaz et al. 2007, 26.)

The first mesophilic phase is the starting phase of the composting process. The temperature of the compost in this phase rises to 25-40°C due to increasing microbial activity. Easily degradable compounds, such as sugars and proteins, are oxidized. Sugars degrade to organic acids and proteins are broken down to amino acids and ammonia. The compounds are degraded by mesophilic primary composters, such as fungi and actinobacteria. Mesophilic microorganisms function well in median temperatures (25-40 °C). (Diaz et al. 2007, 32.)

In thermophilic phase the temperature rises to 35-65°C. The mesophilic microbes are replaced by thermophilic microbes, which are adapted to higher temperatures. The degradation process accelerates until 62°C is reached. If temperature rises beyond 65°C, most mesophilic organisms are destroyed. High temperature sterilizes the compost from pathogens and weed's seeds. (Diaz et al. 2007, 32-34.)

The second mesophilic phase is the cooling phase, where the activity of thermophilic bacteria is inhibited due to the lack of substrates available. The mesophilic community of organisms recolonizes and starts to degrade larger compounds, such as starch and cellulose. (Diaz et al. 2007, 34.)

The last phase is maturation phase. The composition of the substrate has altered. In mature compost 50% of organic matter is utilized in metabolism of microbes as energy and cell material and turned into CO_2, water and mineral salts. The remaining organic matter consists of partially degraded organic compounds and humic-like substances. (Diaz et al. 2007, 34.)

When the composting process takes place in a composting container, such as Biolan pikakompostori 220, these four phases are ongoing in the container simultaneously in different layers. On the top of the composter the first mesophilic phase is initiated, when biowaste and blend component is added. In the middle of the composter the thermophilic phase, in which the temperature is the highest, takes place. At the bottom of the composter second mesophilic phase takes place and the temperature has cooled down. The bottom layer is compiled of mature compost that can be taken out from the hatch at the bottom of the composter. (Biolan® Pikakompostori 220, 2010.)

2.4 OxiTop® soil respiration device

OxiTop® is a manometric oxygen measurement device. It can be used to measure indirectly the activity i.e. the respiration of microorganisms in a sample. In the respiration process of microorganism oxygen (O_2) is consumed while carbon dioxide (CO_2) is produced. In reaction (2), the degradation of organic matter ($C_6H_{12}O_6$) in aerobic conditions is presented as a chemical reaction. When organic matter is degraded in presence of oxygen (O_2), carbon dioxide (CO_2) and water (H_2O) are formed. When organic matter is degraded in aerobic conditions, the equal molar amount of carbon dioxide (CO_2) is formed than oxygen (O_2) is consumed. (Platen & Wirtz 1999a, 4.)

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad (2)$$

The OxiTop® device measures the pressure change in the measuring vessel. The principle of the device is that the gaseous CO_2 produced by microbes is bound by an absorbing agent (e.g. sodium hydroxide) and oxygen remains in gaseous form being the only measured parameter. When oxygen is consumed by microbes, the amount of oxygen decreases resulting to a decrease in pressure according to the general gas equation (3):

$$\Delta p = \frac{\Delta n R' T}{V} \quad (3)$$

In the equation (3), Δp is the change in pressure, Δn is the change in amount of substance (in mol), R' is the ideal gas constant, T is temperature and V is volume. When

amount of oxygen (Δn) decreases, the pressure decreases if temperature and volume are constant. (Platen & Wirtz 1999a, 4.)

By measuring the change of the pressure in the measuring vessel the respiration of microorganisms in the sample, i.e. soil respiration can be determined by calculating oxygen consumption (BA). The unit of oxygen consumption (BA) is $mgO_2/kgTS$ and it is calculated with the following equation (4):

$$BA = \frac{M_R(O_2)V_{fr}\Delta p}{m_{DS}RT} \quad (4)$$

In the equation (4) $M_R(O_2)$ is molar mass of oxygen (32 000 mg/mol), V_{fr} is free gas volume of the measuring vessel (L), Δp is reduction of pressure in OxiTop® measuring device (hPa), m_{DS} is mass of dry sample (kg), R is general gas constant (83,14 J/molK) and T is measuring temperature (K).

In Oxitop® experiment the volume of the measuring vessel and the temperature are constant. In order to keep the temperature constant, OxiTop® experiments must be conducted in a dark and closed space. Hence the effect of changing temperature to the change of pressure in measuring vessels can be minimized. The measuring vessels must be airtight in order to ensure that the change in pressure in the vessels is only due to the decreasing amount of oxygen. The sealing of the measuring vessels is ensured by applying lubricant to the rubber seals and by fastening the lid properly. (Platen & Wirtz 1999a, 12.)

The absorbing agent, which absorbs the carbon dioxide, is alkaline e.g. sodium hydroxide, caustic soda solution, soda lime or potassium hydroxide. In the following reaction (5), the functioning of the absorbing agent is presented. Carbon dioxide (CO_2) in presence of absorbing agent, in this case sodium hydroxide (NaOH), is converted into sodium carbonate (Na_2CO_3) and water (H_2O).

$$CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(g) \quad (5)$$

According to Platen and Wirtz (1999a, 9), the best absorbing agent for measuring solid soil respiration is caustic soda solution, NaOH (aq). The absorption capacity is suffi-

cient and the absorption rate is high. Furthermore, the water content of the soil sample remains nearly constant, which is not the case with solid sodium hydroxide pellets. (Platen & Wirtz 1999a, 9.)

The OxiTop® device consists of a measuring vessel and a lid locking device, an OxiTop® -C measuring sensor and an OxiTop® OC110 controller, presented in picture 1. The soil and the sample are placed in the bottom of the measuring vessel. The absorbing agent is placed on a holder. The measuring sensors measure the pressure change in the measuring vessels in regular intervals and the data is gathered from the measuring sensors with the controller. The data from the controller is transferred to a computer with ACHAT OC PC communication software. The data can be further processed in Excel. Manual for OxiTop® device can be found in appendix 3. (Platen & Wirtz 1999a, 2.)

PICTURE 1. OxiTop® measuring vessel, lid, measuring sensor and controller

3 LITERATURE RESEARCH: BIODEGRADABILITY STANDARDS

There is a vast supply of different standards for testing biodegradability of materials and products. The purpose of this chapter is to introduce chosen standards for testing aerobic biodegradation. Test methods for aerobic biodegradation in aquatic, composting and soil conditions are introduced. There is limited amount of information available in the literature about the methods used in the standards. The information about biodegradability standards in this chapter has been gathered mainly from one source: Handbook of Biodegradable Polymers by Bastioli (2005).

3.1 The development of biodegradation standards

The development of standard measures for testing biodegradability of different materials became necessary in the 1980s due to the arrival of biodegradable plastics. There was a need for reliable tests to define the degree of biodegradability of plastics when the production and the demand of biodegradable plastics started to evolve. (Bastoli 2005, 145.)

It is important to have general rules in defining biodegradability in order to have reliable tests and norms. To achieve this, an international workshop on biodegradability was organised in 1992. The definition of biodegradability was introduced as follows: (1) biodegradation of material must relate to specific disposal pathway (composting, sewage treatment etc.), (2) the rate of degradation of biodegradable material must be consistent with the disposal pathway, i.e. degrade in a reasonable time frame, (3) the end products of complete aerobic biodegradation are CO_2, water and minerals, and intermediate products consists of biomass and humic matter, (4) biodegradable material should not have negative impact on the disposal process; no accumulation or toxic effects on the environment. Apart from these definitions for biodegradable materials, the material must be durable during the using period of the product. (Bastoli 2005, 2-3, 230.)

Today there are several normalization institutes working on biodegradability. Most nations have a normalization institute of their own, such as German Normalisation Institute (DIN), American society for Testing and Materials (ASTM) working in USA and

Canada as well as Japanese Institute for Standardisation (JIS). There are also international institutes working globally, such as International Organization for Standardisation (ISO) and European Committee for Standardisation Institute (CEN), which is working in EU and EFTA countries. (Bastoli 2005, 147.)

3.2 Biodegradability standards

In this section the most common biodegradability norms are introduced. The biodegradability standards are divided according to the disposal environment. Aerobic biodegradation can happen in different environments: aquatic, compost or soil. Apart from biodegradation, also disintegration of the material can be tested. There are also norms for compostability, in which the pass levels for the materials are defined as well.

3.2.1 Aquatic conditions

Testing biodegradability in aquatic conditions is relevant for materials, which can end up in wastewater treatment plants or in surface waters (lakes, rivers, marine environments). Such materials can be detergents, lubricates or other liquid organic compounds, as well as plastics fragments from laundry clothes or beauty products.

There are generally two methods for testing biodegradability in aquatic conditions: method measuring production of CO_2 and method measuring consumption of O_2. The two methods are introduced in this chapter using ISO standards as an example since most standards correspond to the ISO standards. Also other standards are mentioned briefly.

3.2.1.1 Methods by analysis of produced carbon dioxide

One well-known method for testing biodegradability is based on measuring the conversion of carbon to CO_2. In 1981 this method was first standardized as OECD 301B and in 1999 in standard ISO 9439. ASTM D5209 standard was published in 1992 and is similar to ISO 9439 but is no longer in use. These tests were suitable for materials with low

molecular weight. The testing conditions in these norms are not flexible; the test must be performed in ambient temperature (20-25ºC). (Bastioli 2005, 151.)

For materials with high molecular weight, such as polymers, another standard was developed in 1999, ISO 14852. The CEN norm EN 14047 (in 2002) is identical to ISO 14852, except that the CEN norm applies also for packaging materials, whereas the ISO norm can be applied only for plastics. ISO norm 12852 is applied also in Japan as JIS K 6951. The list of these standards is presented in table 2.

TABLE 2. Standards measuring production of CO_2

	Measuring method	Norm (year)	Info
AQUATIC CONDITIONS	Production of CO_2: method by analysis of evolved carbon dioxide	OECD 301B (1981)	Suitable for liquids and poorly soluble and absorbing materials
		ISO 9439 (1999)	Water quality, organic compounds
		ASTM D5209 (1992)	Corresponding standard: ISO 9439. Withdrawn in 2004
		ISO 14852 (1999)	Plastic materials
		EN 14047 (2002)	Corresponding standard: ISO 14852 (CEN)
		JIS K 6951 (2000)	Corresponding standard: ISO 14852

The ISO 14852 **(***ISO 14852 - Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by analysis of evolved carbon dioxide*) test is conducted in aqueus mineral medium, which provides nutrients (N, P, K and other) and buffering capacity. The medium can be activated sludge, compost eluate, soil eluate or a combination of these. The tested item is the sole source of organic carbon and thus the energy source for microorganisms in the test. The test is conducted as a batch test and is incubated at constant temperature. The test can be conducted in ambient (20-25ºC), mesophilic (30-40 ºC) or thermophilic (50-60 ºC) temperature conditions. The CO_2 is absorbed by an alkaline solution. The test mixture is stirred and aerated with CO_2 –free air during the test. The maximum duration of the test is six months. The test is continued until the plateau in activity is reached. (Bastioli 2005, 153.)

With this test method the amount of carbon in the test item converted to CO_2 is measured. The percentage of degradation is determined by titration or dissolved inorganic

(DIC) measurement. The rate of degradation can be determined depending how frequently the measurements are taken during the test. (Bastioli 2005, 153.)

3.2.1.2 Methods by analysis of oxygen consumption

Another test method for measuring biodegradability is based on measuring oxygen consumption instead of CO_2. The rate of biodegradation is determined by comparing biochemical oxygen demand (BOD) to chemical oxygen demand (COD).

In table 3 the norms measuring oxygen consumption are presented. The first standardized norm measuring oxygen consumption was OECD 301C. ISO standard ISO 9408 was published in 1999. In 1993 CEN standard EN 29408 was published and it is similar to ISO 9408. ASTM D5271 was published in 1992 but is no longer in use. In 1999 ISO 14851 was published. Japanese norm JIS K 6950 corresponds also to ISO 14851. (Bastioli 2005, 153.)

TABLE 3. Biodegradability norms measuring consumption of O_2 in aquatic environment

	Measuring method	Norm (year)	Info
AQUATIC CONDITIONS	Consumption of O_2: determination of oxygen demand in closed respirometer	OECD 301C (1981)	Chemical substances. Using activated sludge.
		ISO 9408 (1999)	Water quality, organic compounds.
		EN 29408 (1993)	Corresponding standard: ISO 9408 (CEN)
		ISO 14851 (1999)	Plastic materials
		EN 14048 (2003)	Corresponding standard: ISO 14851, applicable to packaging materials (CEN)
		JIS K 6950 (2000)	Corresponding standard: ISO 14851
		ASTM D5271 (1992)	Corresponding standard: ISO 14851. Withdrawn in 2011.

The ISO 14851(*ISO 14851 - Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium – Method by measuring the oxygen demand in a closed respirometer)* test method is similar to the ISO 14852 test. The difference is the

parameter used. In this test, oxygen consumption is measured instead of production of CO_2. The percentage of degradation is calculated by comparing biochemical oxygen demand (BOD) to chemical oxygen demand (COD) or to theoretical oxygen demand (ThOD). (Bastioli 2005, 153.)

3.2.2 Composting conditions

Testing the biodegradation of materials in composting conditions is relevant for materials that are likely to end up in composting plants when disposed. Biodegradation in composting is tested in controlled conditions. Disintegration of biodegradable material is tested to ensure the high-quality of the compost products. ISO test methods for controlled composing and compost disintegration are introduced in more detail as an example. Test procedure for compostability norms are introduced by going through EN and ASTM norms.

3.2.2.1 Controlled composting

In table 4 the standardized tests in controlled composting conditions are presented. Controlled composting test method was first standardized by ASTM in 1992, ASTM D5338. In 1999 ISO published a similar standard, ISO 14855. JIS K 6953 standard is adopted directly from ISO 14855. (Bastioli 2005, 154.)

TABLE 4. Biodegradability norms in composting conditions

	Measuring method	Norm (year)	Info
CONTROLLED COMPOSTING	CO_2 production: Method by analysis of evolved carbon dioxide	ASTM D5338 (1992)	Plastics
		ISO 14855 (1999)	Plastics
		EN 14046 (2003)	Corresponding standard: ISO 14855. Plastics and packaging
		JIS K 6953 (2000)	Corresponding standard: ISO 14855

In ISO 14855 (*ISO 14855 - Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions - Method by*

analysis of evolved carbon dioxide) norm the biodegradability is tested under controlled composting conditions. The test item (powder film) is mixed with mature compost, which acts as a carrier matrix, source of microorganisms and nutrients. The mixture is incubated at 58°C with controlled oxygen and moisture conditions. The mixture is aerated with CO_2 –free air. The CO_2 from the exhaust air is analysed. The layout of the test is sketched in figure 3. The maximum duration of the test is six months. (Bastioli 2005, 155.)

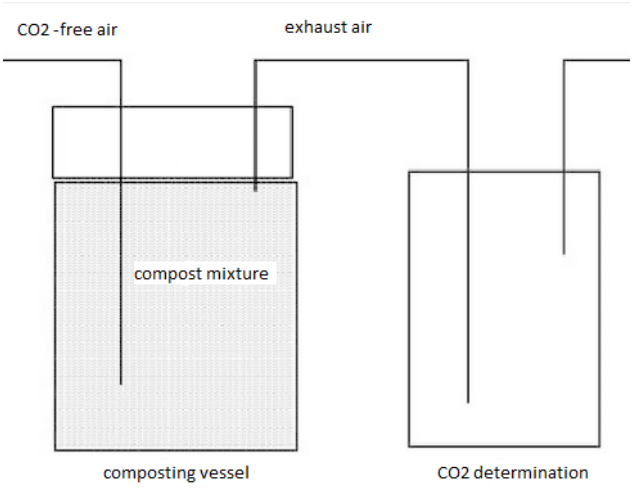


FIGURE 3. Layout of controlled composting test (Bastioli 2005)

CO_2 produced in the process is measured at regular intervals during the test. The production of CO_2 by the mature compost is determined by a blank inoculum test. The net CO_2 production by the test item is calculated by subtracting the CO_2 production of the mature compost. The activity of the inoculum is tested with positive reference control, cellulose. The percentage of degradation is determined in relation to the CO_2 production of the reference control. The rate of degradation can also be determined. (Bastioli 2005, 156.)

3.2.2.2 Compost disintegration

Measuring disintegration in compost is important for the quality of compost end-product. The biodegradable matter should disintegrate, i.e. blend in with the compost product and it should not influence negatively to the compost quality. There are two

kinds of disintegration tests by ISO: ISO 16929 is performed in pilot-scale and ISO 20200 in laboratory-scale, as presented in table 5.

TABLE 5. Compost disintegration norms in compost

	Measuring method	Norm (year)	Info
COMPOST DISINTEGRA-TION	Sorting and sie-ving	ISO 16929 (2002)	Plastics, pilot-scale test
		ISO 20200 (2004)	Plastics, laboratory-scale test

In ISO 16929 (*ISO 16929, Plastics - Determination of the disintegration of plastic materials under defined composting conditions in a pilot-scale test)* test the disintegration of the test item is evaluated. The test material is mixed with fresh biowaste. The mixture is placed in a composting bin (at least 140L) and the composting process starts naturally and the temperature starts to increase due to the microorganisms in the biowaste. The mixture is turned and mixed regularly. For instance temperature, pH, moisture, gas composition are monitored during the test and are required to stay within certain limits. After 12 weeks the disintegration is evaluated by sieving the mass to over 10 and 2 mm particles. The compost product can be analysed by chemical and ecotoxicity tests. (Bastioli 2005, 164.)

The ISO 20200 (*ISO 20200, Plastics - Determination of the disintegration of plastic materials under simulated composting conditions in a laboratory-scale test)* test method is used for primary screening, because it is much simpler than ISO 16929. T
he test material is mixed with synthetic waste in small containers (5-20L). The mixture is not actively aerated. The disintegration is evaluated manually by sorting and screening the mass to over 10, 5 and 2mm particles. (Bastioli 2005, 164.)

3.2.3 Compostability norms

Measuring biodegradability in composting conditions is not alone sufficient measure to evaluate the compostability of a material. When a material is disposed by composting, there are some requirements for the compost product as well. According to CEN, the three basic requirements for a compostable product are: (1) complete biodegradation, (2) disintegration into invisible particles and (3) high-quality compost product; the bio-

degradable material should not affect negatively to the quality of the end-product. (Bastioli 2005, 159.)

There are a few standards defining compostability. In table 6 the standards are presented. In 2000 a CEN standard (DIN V 54900) was published to fulfil the requirements of European Directive on Packaging and Packaging Waste (94/62/EC) on organic recovery of packaging waste. DIN V 54900 (testing of the compostability of plastics) is the oldest standard for compostability, but it has been replaced by another standard of CEN, EN 13432. (Bastioli 2005, 159; Rudnik 2007, 102.)

TABLE 6. Compostability norms

	Measuring method	Norm (year)	Info
COMPOSTABILITY NORMS	Biodegradation, disintegration and compost quality	EN 13432 (2000)	Packaging
		DIN V 54900 (2000)	Plastics
		ASTM D6400 (1999)	Plastics

Different norms have slightly different criteria for passing. In the following paragraphs the criteria of EN 13432 and ASTM D6400 are presented as an example.

EN 13432 – Packaging – Requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the final acceptance of packaging

Biodegradation is tested according to ISO 14855 (see chapter 3.2.2.1), 90% of material must biodegrade in six months. Disintegration is tested according to ISO 16929 pilot-scale test (see chapter 3.2.2.2). Maximum of 10% of material traced after 12 weeks. Compost quality is tested by ecotoxicological assessment as plant growth in compost. Also physical and chemical analysis is performed. If the material passes the requirements of EN 13432, it also meets the requirements of the Directive of Packaging and Packaging Waste. (Bastioli 2005, 160; Rudnik 2007, 102)

ASTM D6400 - Standard Specification for Labeling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities

A product consisting of single polymer is considered biodegradable if 60% of organic carbon is degraded in 180 days. For products containing more than one polymer, the

pass level is 90% in 180 days. Disintegration test is performed according to laboratory-scale test. Maximum of 10% of the product should remain. Compost quality is sufficient if the compost can support a plant growth and has low concentration of heavy metals. (Rudnik 2007, 102.)

3.2.4 Soil environment

Biodegradation in soil is less aggressive than in composting conditions due to the more moderate temperatures. However, soil as an environment is more favourable for degradation than water due to the higher concentration of microorganisms (e.g. fungi). Therefore biodegradability behaviour in soil cannot be predicted from test results in composting or aquatic conditions, and separate standards for soil environment are required.

In table 7 the norms for biodegradation in soil are presented. The first test method for biodegrading in soil was OECD 304A, which was published in 1981. Standard ISO 11266, published in 1994, is a test method for organic chemicals. First norm for plastics was ASTM D5988, published in 1996. In 2003 ISO published a standard for plastics, ISO 17556. This standard is introduced in the following paragraph as an example. (Bastioli 2005, 164.)

TABLE 7. Biodegradability norms in soil environment

	Measuring method	Norm (year)	Info
SOIL ENVIRONMENT	O_2 consumption or CO_2 production	OECD 304 A (1981)	Inherent biodegradability
		ISO 11266 (1994)	Soil quality: organic chemicals
		ASTM D5988 (1996)	Plastics
		ISO 17556 (2003)	Plastics

ISO 17556: Plastics – Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved

In ISO 17556 test method the test material is mixed in soil. The soil acts as a carrier matrix, the source of microorganisms and nutrients. The test is incubated at 20-25°C. The oxygen and moisture contents are controlled. The maximum duration of the test is

six months. Depending on the measurement parameter, the oxygen consumption or CO_2 production is monitored during the test. The activity of the soil is determined and eliminated from the measured parameter to determine the net amount of O_2/CO_2 from the test item. The percentage of biodegradation is calculated by comparing the net amount of test item to the theoretical oxygen demand (ThOD) if O_2 is measured or CO_2 production when CO_2 is measured. (Bastioli 2005, 165.)

4 LITERATURE RESEARCH: BIODEGRADABLE MATERIALS

The purpose of this chapter is to collect information from the literature about different polymers that are biodegradable. The aim is to offer objective information from several sources. Biodegradable polymers are intensively studied and new applications are discovered and new knowledge is gained all the time. Detailed information is gathered in this chapter from several sources. The most recent sources are Ghanbarzadeh & Almasi (2013), Tsuji (2013), Avérous & Pollet (2012) and Bergeret (2011). The information details about material properties, biodegradability and applications of the polymers differ according to the source.

In this chapter chosen biodegradable polymers are presented. The polymers presented below are selected according to the applicability as fibers. Biodegradable polymers are a vast and an expanding field, thus all biodegradable polymers cannot be presented in this chapter. The biodegradable polymers are selected for this chapter based on their applicability as nonwoven fabric fibers and based on availability of information. Some polymers are already produced commercially but some of the polymers are still under development.

Biodegradable polymers can be classified in many ways. In figure 4, the classification is done according to the origin and production process of the polymers which are presented briefly in this chapter. The biodegradable polymers are divided into natural and synthetic biodegradable polymers. Natural polymers are produced by microorganisms or synthetized from bio-derived monomers. Synthetic polymers are produced synthetically from e.g. petroleum-based materials.

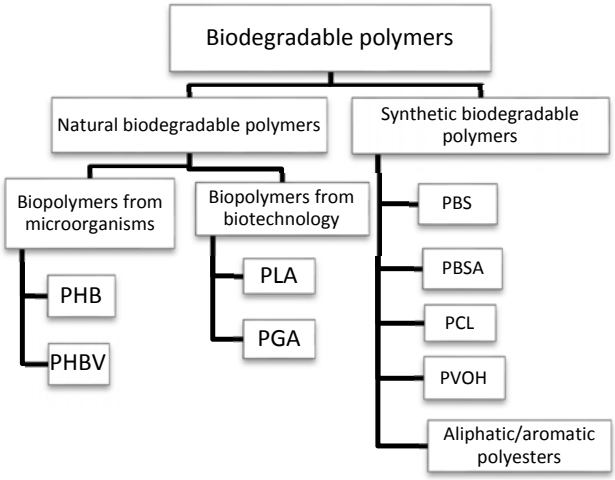


FIGURE 4. Classification of biodegradable polymers presented in this chapter

4.1 Biopolymers from microorganisms

Biodegradable polymers polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-co-valerate) (PHBV) are presented in this section. They are produced by biosynthetic function of microorganisms and are naturally enzymatically biodegradable. These polymers can be extracted from microorganisms.

4.1.1 Polyhydroxybutyrate (PHB)

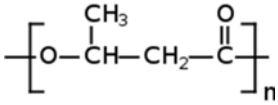


FIGURE 5. Poly(hydroxybutyrate) (PHB)
(http://commons.wikimedia.org/wiki/File:Polyhydroxybutyrate_structure.svg)

PHB is a polyhydroxyalkanoate (PHA). These aliphatic polyesters are produced by microorganisms during sugar fermentation. PHB is the primary product in the process. PHAs are naturally biodegradable due to their flexible chain structure. The chemical structure of PHB is shown in figure 5. (Bastioli 2005, 188; Ghanbarzadeh & Almasi 2013, 159.)

In table 8 the properties of PHB are listed. PHB is highly crystalline (>50%), it has high melting point, T_m, (173-180 °C) and glass transition temperature, T_g,, is about 5 °C. Due to crystallinity and high T_g the plastic products produced from PHB are brittle. Processing PHB is challenging due to degrading when temperature rises above the melting point. (Ghanbarzadeh & Almasi 2013, 160; Avérous & Pollet 2012, 30.)

TABLE 8. Properties of PHB

T_m	173-180 °C
T_g	5 °C
Tensile strength	40 MPa
Crystallinity	>50%

PHB is biodegradable both in aerobic and in anaerobic conditions. PHB-degrading microorganisms have been isolated from soil, activated sludge and surface waters. Most PHB-degrading microorganisms function in ambient (20-25°C) or mesophilic (25-40°C) temperatures. Degree of biodegradation for PHB of 90% has been detected. Biodegradation in living tissue takes years. (Tokiwa et al. 2009.)

4.1.2 Poly(hydroxybutyrate-co-valerate) (PHBV)

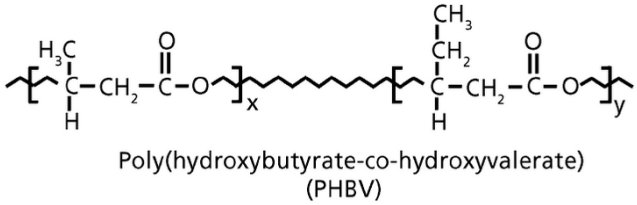


FIGURE 6. Chemical structure of PHBV (Bastioli 2005)

PHBV is a copolymer of PHB with hydroxyvaleric acid (HV). Certain bacteria can produce also copolymers such as PHBV. The chemical structure of PHBV is shown in figure 6. The copolymer is less crystalline and more flexible than PHB. Processing PHBV also is easier than PHB. The properties of the material can be altered by varying the type and proportion of monomers. By increasing HV content, there is a decrease in melting point, glass transition temperature, crystallinity, water permeability and tensile

strength. In table 9 some properties of PHBV with different HV contents are presented. (Luzier 1992.)

TABLE 9. Properties of PHBV (Luzier 1992)

	HV content (mol %)		
	0	10	20
T_m	177 °C	140 °C	130 °C
Crystallinity	80%	60%	35%
Tensile strength	40 MPa	25 MPa	20 MPa
Extension at break	8%	20%	50%

PHBV can be degraded by bacteria. In living tissue hydrolytic degradation is slow, thus PHBV is applicable in tissue engineering. (Ghanbarzadeh & Almasi 2013, 161.)

4.2 Biopolymers from biotechnology

Naturally biodegradable polymers can be synthetized for instance from bio-derived monomers. In this section polylactic acid (PLA) and polyglycolic acid (PGA) are presented.

4.2.1 Polylactic acid (PLA)

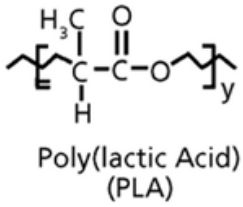


FIGURE 7. Chemical structure of PLA (Bastioli 2005)

Polylactid acid (PLA) is simple aliphatic polyester of lactic acid, which is extracted from starch. PLA is obtained from lactide by ring-opening polymerization catalyzed by stannous octoate. The chemical structure of PLA is shown in figure 7.

The properties of PLA can be altered by varying the L-lactic acid content. Some properties of PLA are listed in table 10. Crystallinity can vary from amorphous to semi-crystalline. Amorphous PLA contains 50-93% of L-lactic acid, while semi-crystalline PLA contains over 93% of L-lactic acid. (Bastioli 2005, 191, Bergeret 2011, 352.)

TABLE 10. Properties of PLA (Bergeret 2011, 352)

T_m	130-180 °C
T_g	50-80 °C
HDT	55 °C
Tensile strength	70 MPa
Elongation at break	6%
Crystallinity	0-40%

PLA has hydrolysable ester linkages which are prone to abiotic degradation. According to Tsuji (2013, 204) the biodegradation of PLA is slower than with other biodegradable polyesters. Biodegradation to lactic acid has been calculated to take over 40 years. This suggests that there are only few microorganisms capable of degrading PLA and that degradation of PLA is mostly abiotic. PLA degrades hydrolytically in human body, thus it is used in medical applications. PLA based films have been studied also for textile applications. (Bergeret 2011, 352; Tsuji 2013, 204.)

4.2.2 Polyglycolic acid (PGA)

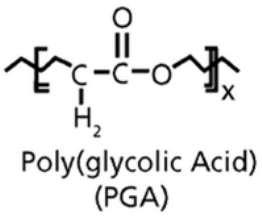


FIGURE 8. Chemical structure of PGA (Bastioli 2005)

Polyglycolic acid (PGA) is produced by polymerizing diglycolide with a tin catalyst.
In table 11 some properties of PGA are listed. PGA fibers have high strenght and modulus (7 GPa) and they are rather stiff. PGA is semi-crystalline. Melting temperature

and glass transition temperature are high. The chemical structure of PGA is shown in figure 8. (Ghanbarzadeh & Almasi 2013, 165)

TABLE 11. Properties of PGA (Ghanbarzadeh & Almasi 2013, 165)

T_m	225-230 °C
T_g	35-49 °C
Crystallinity	45-55%
Modulus (fibers)	7 GPa

PGA has hydrolysable ester linkages similar to PLA, which are degraded abiotically into monomers. The amorphous and crystalline regions of the monomers are degraded hydrolytically. The momoners can also be degraded enzymically by microorganisms. (Ghanbarzadeh & Almasi 2013, 165.)

PGA has the ability to biodegrade in human body, thus they are used in medical applications e.g. in surgical sutures and implants fixation of fractures. According to Park & Bronzino (2002, 108) the nonwoven textile structure is rather weak at least for tissue engineering. (Park & Bronzino 2002, 108.)

4.3 Synthetic biodegradable polymers

Synthetically produced biodegradable polymers are produced from synthetic artificial materials. In this section polycaprolactone (PCL), Polybutylene succinate (PBS), poly-butylene succinate adipate (PBSA) and polyvinyl alcohol (PVOH) are presented.

4.3.1 Polycaprolactone (PCL)

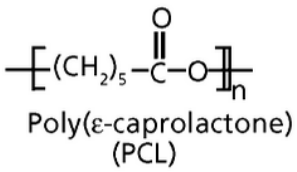


FIGURE 9. The chemical structure PCL (Bastioli 2005)

Polycaprolactone polymers belong to aliphatic polyesters. They can be obtained synthetically by ring opening polymerization, and the monomeric units are relatively cheap. The chemical structure of PLC is shown in figure 9. (Bastioli 2005, 193.)

In table 12 the properties of PLC are listed. PCL is semi-crystalline polymer and in room temperature it is rubbery. The polymer has relatively good thermal resistance; decomposition temperature is 350 °C. Melting temperature and glass transition temperature are low. Tensile strength is low, but elongation breakage is high. PCL is easily processible and it can be copolymerized with other monomers. (Avérous & Pollet 2012, 32.)

TABLE 12. Properties of PCL

T_m	57 °C
T_g	-62 °C
T_d	350 °C
Tensile strength	23 MPa
Elongation breakage	4700%
Crystallinity	semi

PCL can be degraded by aerobic and anaerobic microorganisms. Enzymes like lipases and esterase degrade PLC. The rate of biodegradation depends on crystallinity and molecular weight. Generally, the rate of biodegradation is relatively slow (2-3 years). PLC has applications in biomedicine (e.g. drug release) and in packaging (e.g. compostable bags). (Ghanbarzadeh & Almasi 2013, 161; Clarinval & Halleux 2005, 22; Tokiwa et al. 2009.)

4.3.2 Polybutylene succinate (PBS)

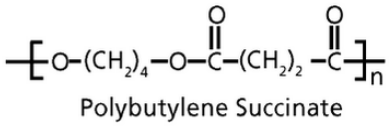


FIGURE 10. Chemical structure of PBS (Bastioli 2005)

PBS is aliphatic polyester and it is synthesized by polycondensation of 1,4-butanedial and succinic acid. The polymer is thermal and chemical resistant and has good mechanical properties (comparable to PET). The chemical structure of PBS is shown in figure 10. (Clarinval & Halleux 2005, 22; Ghanbarzadeh & Almasi 2013, 167.)

In table 13 some properties of PBS are listed. The melting point of PSB is around 108-115°C. It has excellent processing possibilities for nonwoven textiles. PSB is highly crystalline, which leads to relatively low biodegradation rate. To increase the biodegradability polymer blends and copolymerization have been studied. (Clarinval & Halleux 2005, 22; Ghanbarzadeh & Almasi 2013, 167.)

TABLE 13. Properties of PBS (Kabasci & Stevens 2013, 259)

T_m (single crystals)	115 °C
T_g	-38 °C
HDT	70-90 °C
Tensile strenght	30-35 MPa
Crystallinity	high
Elongation at break	350%

There are several microorganisms capable of degrading PBS, but the ratio of these microorganisms is rather low. (Tokiwa et al. 2009.)

4.3.3 Polybutylene succinate adipate (PBSA)

PBSA is synthesized by copolymerization of PBS by adipate. PBSA is synthesized from glycols and aliphatic dicarboxylic acids (succinic acid). Succinic acid is prepared by fermentation of sugars from sugarcane or corn. (Ghanbarzadeh & Almasi 2013, 168.)

In table 14 some properties of PBSA are listed. Melting and glass transition temperature are lower than of PBS's. Also crystallinity is lower than crystallinity of PBS.

TABLE 14. Properties of PBSA (Kabasci & Stevens 2013, 259)

T_m	90 °C
T_g	-45 °C
HDT	60 °C
Tensile strength	40 MPa
Elongation at break	800%
Crystallinity	low

The biodegradation rate is relatively high, thus it is applicable for products disposed e.g. in composters. PBSA degrades faster than PBS due to lower crystallinity of PBSA. (Ghanbarzadeh & Almasi 2013, 168.)

4.3.4 Aliphatic/aromatic co-polyesters

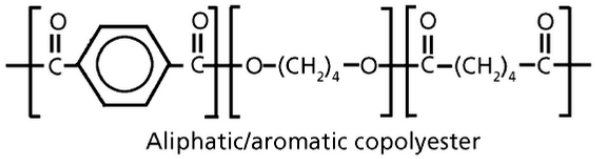


FIGURE 11. The chemical structure of one type of aliphatic/aromatic copolyester (Bastioli 2005)

Aliphatic/aromatic copolyesters have been developed to combine the good properties of both aliphatic and aromatic polyesters. Aromatic polyesters like PET have better material properties, whereas aliphatic polyesters are biodegradable. Combining these polyesters can be done by copolymerization of aliphatic monomers with aromatic polymers such as terephthalic acid. The chemical structure of one type of aliphatic/aromatic copolyester is shown in figure 11. (Bastioli 2005, 303.)

Aromatic polyesters are resistant to degrading by enzymes of microorganisms. Therefore the biodegradability of aliphatic/aromatic copolyesters depends on the length of aromatic sequence. For example polybutylene terephthalate oligomers with more than three sequences degrade very little, whereas sequences of 1 or 2 degrade in weeks. (Bastioli 2005, 304.)

Several companies market aliphatic/aromatic polyesters. Ecoflex® is a brand of BASF's and it contains butanediol, adipic acid and dimethyl terephthalate. Biomax® is a modified PET and it is marketed by DuPont. Eastar Bio is produced by Eastman Chemical Company in USA. EnPol is produced by Korean company called Ire Chemicals. (Bastioli 2005, 304.)

4.3.5 Polyvinyl alcohol (PVOH)

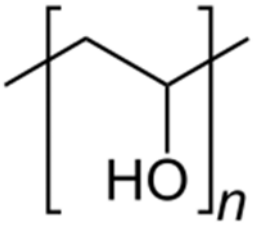


FIGURE 12. Chemical structure of PVOH (Wikipedia 2015)

Polyvinyl alcohol (PVOH) is produced in hydrolysis of polyvinyl acetate. By altering the molecular weight, the physical characteristics, water solubility and biodegradability can be controlled. The chemical structure of PVOH is presented in figure 12. (Ghanbarzadeh & Almasi 2013, 169.)

In table 15 some properties of PVOH are presented. Melting point of PVOH is 180-190°C and molecular weight is 26 300 - 30 000 g/mol.

TABLE 15. Properties of PVOH

T_m	180-190 °C
M_w	26 300 - 30 000 g/mol
Tensile strength	high

Biodegradation of PVOH happens through oxidation of hydroxyl group. Degradation of PVOH occurs mainly by hydrolysis, the degree of hydrolysis has studied to be 86,5 - 89%. Also enzymatic biodegradation has been studied. PVOH may be biodegradable. (Ghanbarzadeh & Almasi 2013, 169.)

5 METHODS

The biodegradability of the nonwoven fabric samples was studied by using two different means: composting and measuring the respiration activity. In the composting experiment the samples were in composting conditions for 12 weeks and the mass loss was measured and the visual changes were observed. The respiration experiment was implemented by using OxiTop® device and the biodegradation of samples was assessed from the oxygen consumption by microorganisms.

5.1 Composting experiment

The aim of the composting experiment was to test biodegradability of four different nonwoven fabric materials. The degree of biodegradability was measured in weight loss and also visually examining the samples. The phases in the experiment were: (1) filling the composters, (2) preparing the samples, (3) placing the samples in the composters and (4) documenting the changes in samples every 2 weeks.

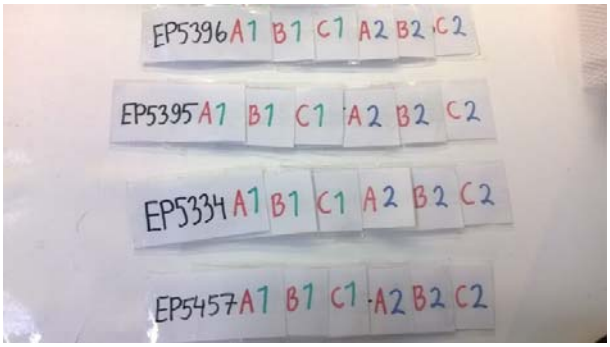
5.1.1 Preparation of composters

The composters (picture 2) were put in operation before inserting the samples to the composters. Two composters where first emptied through the unloading hatch. One quarter of old compost was left in the composters. The composters were filled with a mixture of biowaste from Campusravita kitchen and blend component (Biolan Kompos-ti- ja huussikuivike). Biowaste and blend component were added in 1:1 ratio in turns and mixed properly. 10 liters of bio waste was added in the composters approximately once a week and the mass was turned and mixed to ensure the availability of oxygen.

PICTURE 2. Biolan Pikakompostori 220 –composters

5.1.2 Preparation of samples

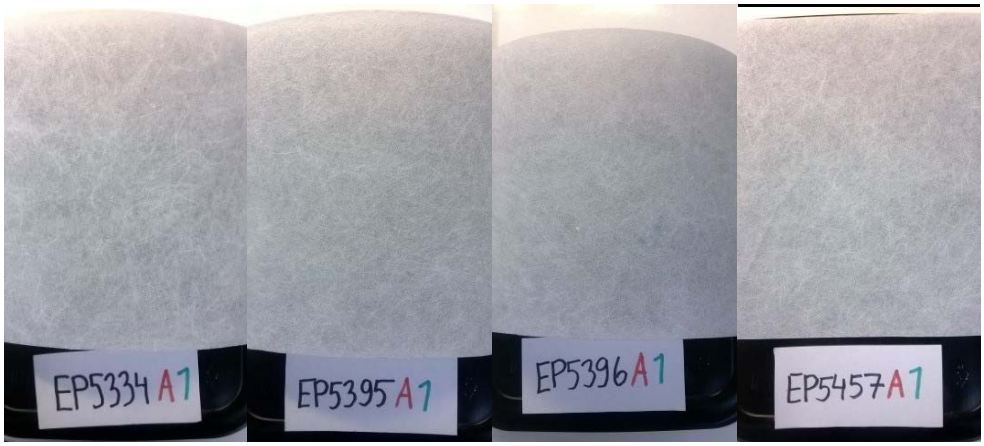
From the four types of nonwoven fabric, 6 identical samples of each type were prepared. The sizes of the samples were 20cm x 20cm. Each sample was labelled with the sample type, an alphabet corresponding the subsample and a number corresponding the composter. In picture 3 the 24 labels of the samples are shown. The labels were covered with non-biodegrading plastic.



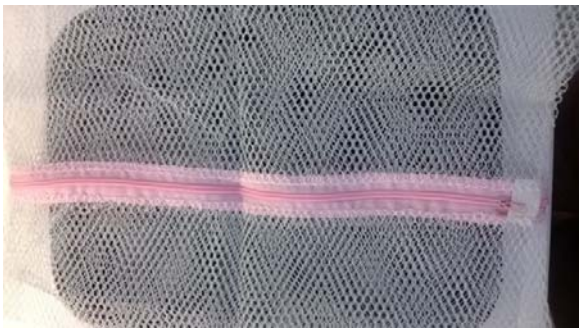
PICTURE 3. Sample labels for 4 fabric types and their 6 samples

PICTURE 4. Precisa XT 220A scale

The samples were weighed both with and without the laundry bag. The scale used for weighing was a Precisa XT 220A (picture 4). The masses were recorded as can be seen in appendix 1. Each sample type was also photographed on a black surface for further comparison. In picture 5 the A1 subsample from each fabric type is presented. The samples and labels were placed in laundry bags (picture 6) to ensure that the samples could be retrieved from the composter. The laundry bags were placed in the two composters in three layers, so that in each layer there were four samples of different fabrics.



PICTURE 5. Nonwoven fabric samples, subsamples A1



PICTURE 6. Laundry bag

5.1.3 Performing the experiment

During the 12 weeks of the experiment biowaste was added regularly approximately once a week to keep the composting process ongoing. The mature compost was removed from the composter through the hatch in the bottom to keep the volume of the waste mixture in composters appropriate.

The availability of oxygen was ensured by turning and mixing the compost regularly few times a week. The moisture content was evaluated by squeezing the compost in a fist. If, by squeezing the mixture, a couple of water drops dripped out, the moisture content was deemed appropriate. The moisture content was controlled by adding blend component into the mixture if it seeded to be too moist or by adding water if it was too dry.

Every two weeks the samples were recovered from the composters for weighting. First the samples were washed from dirt and dried overnight in room temperature. To ensure that samples were dry, they were still dried in an oven at 50^{o}C for two hours. When the samples were dry, they were weighted and photographed. After the procedures the samples were put back in the composters. This was repeated for 6 times over the three months.

5.2 Soil respiration experiment

The OxiTop® soil respiration measuring system has not been applied for determining biodegradability of solid sample in soil at TAMK before. The aim of the soil respiration experiment was to compare the respiration activity of nonwoven fabric samples in soil with each other and in relation to control samples. The aim was also to test the applicability of the test method for determining biodegradability.

The soil which was used in the experiment was Biolan Musta Multa. The mass of dry soil, m_{DS} (kg), required for calculating oxygen consumption was determined by drying 50g of moist soil. The moist soil was first weighed accurately and then put in an oven at 105^{o}C for 4 hours. The soil was then placed in an evaporation pan to cool down and after 30 minutes the dry soil was weighed. Three parallel tests were conducted in order to define the average value.

The free gas volume, V_{fr}, was determined by measuring the volume of the measuring vessel, excluding the volume of moist soil and the volume of the absorption vessel and the absorption agent. The volume of the measuring vessel was measured by first weighing the empty vessel with the lid and then filling the vessel with distilled water and weighing it again. The weight of distilled water corresponds directly to the volume.

40mL of 1M NaOH solution was used in the experiment. According to Platen and Wirtz (1999a, 5) the amount of NaOH needed to absorb CO_2 completely is 0,334g for a measuring vessel of 0,96L. In 40mL of 1M NaOH there are approximately 1,6g of NaOH, thus over four times above the required amount of NaOH.

5.2.1 First trial

In the first trial 6 measuring vessels were used. About 50g of moist soil was accurately measured into each vessel. A sample of nonwoven fabric was added in to four of the vessels. Two 4,5cm x 4,5cm pieces were cut from each type of fabric and the samples were weighed. The recorded masses of soil and samples are presented in table 16. The samples were then buried in the soil in the measuring vessels.

TABLE 16. The masses of soil and fabric in first trial

FIRST TRIAL (7 days)		
SAMPLE	Mass of soil (g)	Mass of fabric (g)
blank 1	50,30	no sample
blank 2	50,08	no sample
EP5334	49,97	0,26
EP5395	50,13	0,22
EP5396	50,19	0,26
EP5457	50,03	0,26

The preparation of the measuring vessels was done according to the OxiTop manual in appendix 3. After the soil and the fabrics were placed in the measuring vessels (picture 7), 40 mL of absorption agent, 1M NaOH, was measured to a plastic cup, which was placed on the holder of the lid-locking device. The sealing of the measuring vessels was ensured by applying lubricant to the rubber seals on the lid and by fastening the lid with 6 clips. The OxiTop® -C censor was screwed on.

PICTURE 7. Blank sample in OxiTop® measuring vessel

The prepared measuring vessels were put in an incubation cabin (picture 8) and the experiment was started with the OxiTop® controller (picture 9) according to Operating Manual: System OxiTop® Control (2006). The duration of the first trial was set to 7 days. After the measuring period the data was recovered from the measuring heads with

OxiTop® OC110 controller and the information was processed in Excel. The manual for OxiTop® soil respiration can be found in appendix 3.

PICTURE 8. Soil respiration samples in incubation cabinet

PICTURE 9. OxiTop® OC110 controller

5.2.2 Second trial

The second experiment included two blank samples and two parallel samples from each nonwoven fabric type. In total 10 measuring vessels were used. In blank vessels there was about 50 g of moist soil measured accurately. The rest of the vessels included also a fabric sample. In this trial the mass of fabric sample was increased to get more variation in the results. Masses of soil and samples in each vessel are presented in table 17. The preparation of the measuring vessels was done according to OxiTop® manual in appendix 3.

TABLE 17. The masses of soil and fabric in second trial

SECOND TRIAL (30 days)		
SAMPLE	Mass of soil (g)	Mass of fabric (g)
Blank 1	49,90	no sample
Blank 2	50,06	no sample
EP5334 A	49,91	0,63
EP5334 B	50,10	0,61
EP5457 A	50,03	0,59
EP5457 B	50,03	0,57
EP5395 A	50,10	0,58
EP5395 B	49,95	0,58
EP5396 A	50,05	0,65
EP5396 B	50,10	0,61

During the second experiment, on the 9th day of the experiment, the location of the measuring vessels was changed from an incubation cabinet to a plastic box with a lid, because the incubation cabinet was needed elsewhere. On the 11th day the results were called up from the OxiTop® measuring head to analyze the results gathered so far. The plastic box was noticed to have insufficient insulation properties to keep the temperature in the box constant. The plastic box was replaced with a Styrofoam box.

On the 14th day of the experiment, the pressure in some of the vessels had decreased under -80 hPa. According to Platen and Wirtz (1999b, 3) the measuring vessels have to be treated if warning pressure (-100 hPa) is undercut. Hence the measuring vessels were aerated and the absorption agent (NaOH) was refilled to maximize the absorption capacity. The measuring head of one of the EP 5334 fabric samples had run out of battery during the experiment, thus the pressure for that sample was not recorded.

5.2.3 Third trial

The third trial was executed with same sample arrangement than the second trial; 10 measuring vessels of which 8 contained a fabric sample. From each fabric type there was 2 samples. Two measuring vessels contained the blank samples. The soil used in this trial was different than in the first two, thus the dry mass of the soil (m_{ds}) and the volume of the moist soil were determined. About 50g of accurately measured soil was used in the measuring vessels. The weight of the fabric samples were approximately the same as in the second trial. The weights of the soils and fabrics are listed in table 18. The preparation of the measuring vessels was done according to OxiTop® manual in appendix 3.

TABLE 18. The masses of soil and fabric in third trial

THIRD TRIAL 14 days		
SAMPLE	Mass of soil (g)	Mass of fabric (g)
Blank 1	49,92	no sample
Blank 2	49,96	no sample
EP5334 A	50,01	0,60
EP5334 B	49,96	0,55
EP5457 A	50,00	0,58
EP5457 B	49,96	0,59
EP5395 A	49,95	0,63
EP5395 B	50,08	0,59
EP5396 A	49,95	0,60
EP5396 B	49,98	0,60

The measuring period in the third trial was set to 14 days. The measuring period of 30 days in the second trial was too long, because the pressure was dropping under the warning pressure (-100 hPa). The aim of the third trial was to get a smooth pressure graph without any disturbance (temperature changes or treating of measuring vessels).

6 RESULTS

6.1 Composting experiment

The changes in the nonwoven fabrics were observed every two weeks by photographing the fabrics during the experiment. In appendix 2 there are the pictures of subsample A1 from each fabric type as an example. During the experiment the pictures of all samples were sent to the company. The visual changes in the fabrics during the experiment can be observed from the pictures. The physical changes and the structure of the fabrics cannot be seen in the pictures.

The only fabric that showed visual changes during the composting experiment is EP 5457. It started to get brittle and it started to rip easily towards the end of the experiment. The other fabrics (EP 5334, EP 5395 and EP 5396) seemed to maintain their fabric structure. When handling the fabrics, also other changes were observed. The surface of fabric EP 5395 started to get fluffy and the fabric felt softer after the experiment. The fabrics EP 5334 and EP 5396 maintained their stiffness throughout the experiment.

The mass of the nonwoven fabrics was measured every two weeks during the composting experiment. The duration of the experiment was 12 weeks. In table 19 the average mass of 6 samples from each fabric type (EP 5334, EP 5395, EP 5396 and EP 5457) are presented. In appendix 1 the masses of each sample are presented. In figure 13 the average masses of the fabrics are presented in graphical form. From the figure 13 can be seen, that surprisingly the mass of all fabrics increased during the first 6 weeks. Only the fabric EP 5457 started to lose mass after 6 weeks.

TABLE 19. Average mass change of six samples from each fabric during 12 weeks

	Average mass (g)						
SAMPLE	Initial	2 weeks	4 weeks	6 weeks	8 weeks	10 weeks	12 weeks
EP 5334	2,91	3,12	3,21	3,47	3,54	3,65	3,69
EP 5395	2,31	2,37	2,46	2,63	2,64	2,74	2,76
EP 5396	2,54	2,66	2,82	2,97	3,02	3,13	3,17
EP 5457	2,64	2,79	2,96	3,14	3,08	2,93	2,86

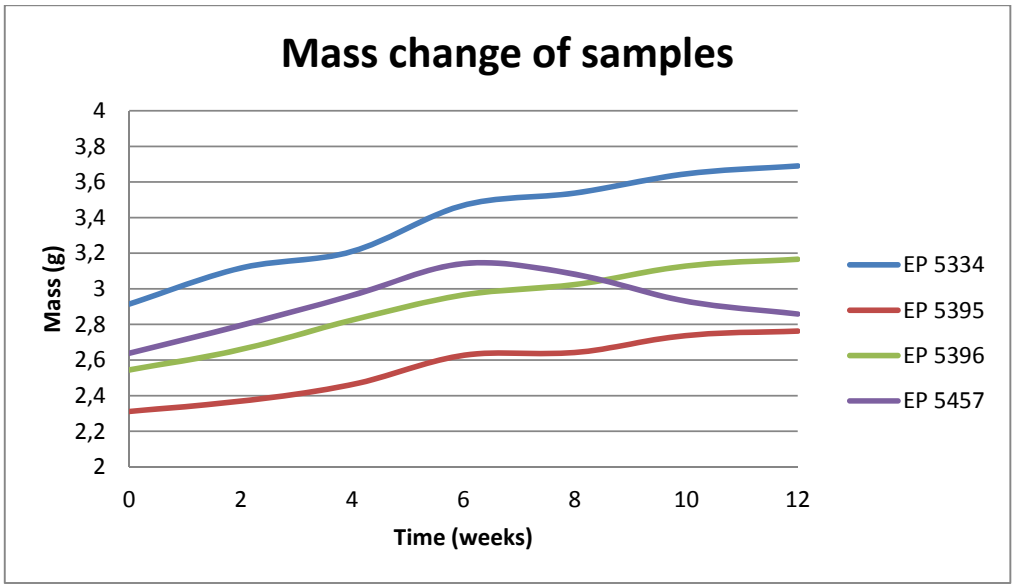


FIGURE 13. Change in mass of fabrics during the 12 weeks

In figure 14 the mass change of the fabrics has been presented by comparing the initial mass to the mass of the fabrics after 12 weeks. The mass increase was the greatest with fabric EP 5334 and EP 5396, approximately 25%. The mass of EP 5395 increased approximately 20% from the initial mass. The mass of EP 5457 after 12 weeks is also 8% greater than the initial mass even though the mass started to decrease compared to the highest value at week 6.

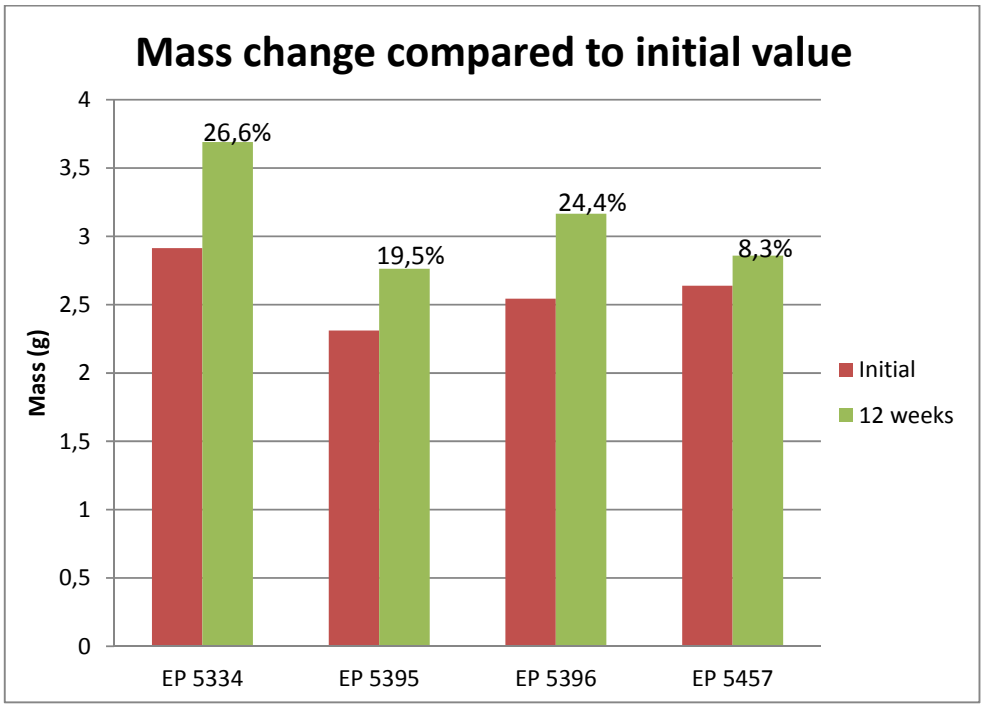


FIGURE 14. Mass change of each fabric type compared to initial value.

6.2 Soil respiration experiment

The free gas volume, $V_{fr,}$ consists of the volume of the measuring vessel excluding the volume of the lid, the volume of moist soil and the volume of absorption vessel and absorption agent (equation 6).

$$V_{fr} = V_{vessel} - V_{moist\ soil} - V_{absorption\ agent} \quad (6)$$

In the first and in the second trial, the free gas volume of the vessel was calculated followingly:

$$V_{fr1} = 0{,}943L - 0{,}120L - 0{,}040L = 0{,}783L$$

In the third trial, a different soil was used and the volume of the soil was measured to be 160mL, thus the free volume in the third trial was:

$$V_{fr2} = 0{,}943L - 0{,}160L - 0{,}040L = 0{,}743L$$

The mass of dry soil in equation 6 includes the mass of dried soil and the mass of the fabric sample. The dry mass of the soil was determined as the average of three parallel samples. In the first and second experiment the same soil was used. From the table 20 can be seen that in first and second trial in average the dry weight of soil is 27,18g. In the third trial different soil was used, the average dry weight of this soil is 9,85g as can be seen in table 21.

TABLE 20. Average mass of dry soil used in first and second trial. The average is calculated from three individual samples

MASS OF DRY SOIL		
Sample	Mass of moist soil (g)	Mass of dry soil (g)
1	50,00	27,13
2	50,10	27,57
3	49,96	26,83
AVERAGE	50,03	27,18

TABLE 21. Average mass of dry soil used in third trial

MASS OF DRY SOIL		
Sample	Mass of moist soil (g)	Mass of dry soil (g)
1	49,94	9,83
2	50,05	10,08
3	49,97	9,65
AVERAGE	49,99	9,85

The temperature of the incubation cabin was 21°C or 294,15K.

The oxygen consumption (BA) is calculated by using the following formula:

$$BA = \frac{M_R(O_2)V_{fr}\Delta p}{m_{DS}RT} \quad (4)$$

For instance, in the first trial the oxygen consumption of blank sample ($Blank_1$) was calculated as follows:

$$BA_{blank\,1} = \frac{32000\ mg/mol \times 0{,}783\ L \times 35\ hPa}{27{,}1765\ g \times 83{,}14\ L\ mbar/molK \times 294{,}15\ K} = 1{,}3195\ mgO_2/kgTS$$

6.2.1 First trial

The graphical presentation of the pressure change for each sample during the 7 days (10080 min) is present in figure 15. The pressure has decreased steadily during the whole experiment and there are no sudden peaks in the graph. The more the pressure is decreased, the more the sample consumes oxygen in the sample vessel.

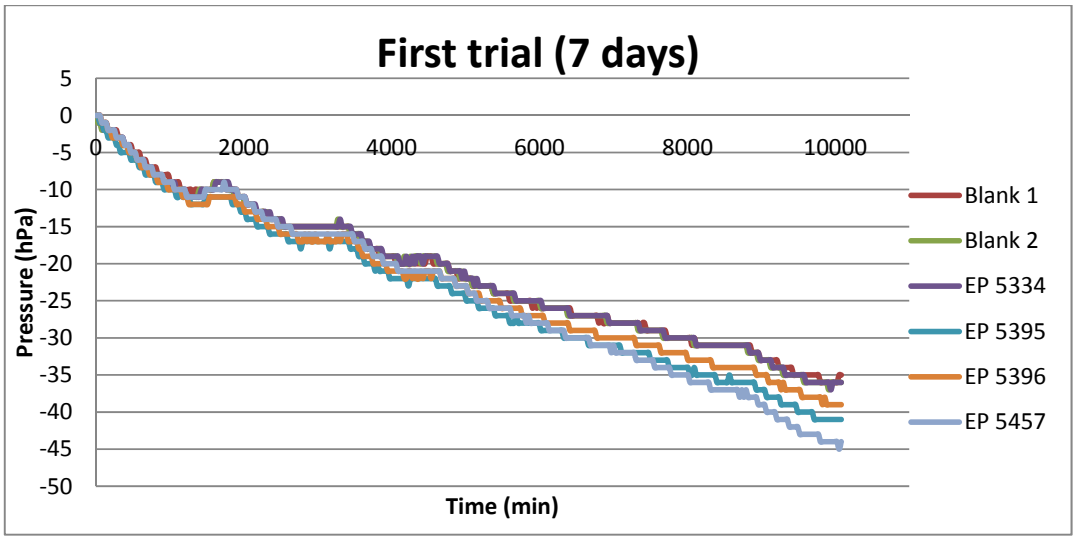


FIGURE 15. Graphical presentation of the pressure change in the first trial

In table 22 and in figure 16 the results for each sample of the first trial are presented. The duration of the first trial was 7 days. The change in pressure (Δp) in table 22 is the final value after 7 days. The oxygen consumption (BA) in table 22 is calculated by using formula 4.

TABLE 22. Oxygen consumption of first trial in 7 days

SAMPLE	Δp (hPa)	BA ($mgO_2/kgTS$)
Blank 1	-35	1,32
Blank 2	-36	1,36
EP 5334	-36	1,34
EP 5395	-41	1,53
EP 5396	-39	1,46
EP 5457	-44	1,64

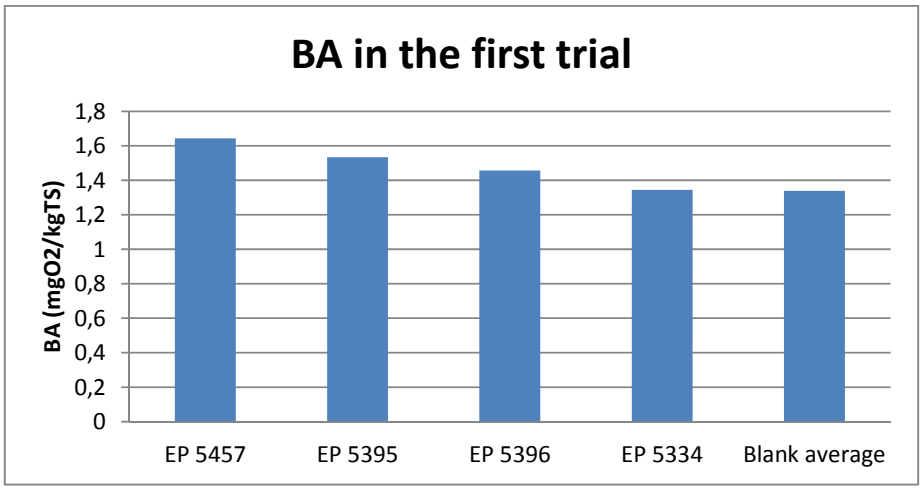


FIGURE 16. Oxygen consumption of the first trial after 7 days

In figure 17 the oxygen consumption of the fabric samples is compared to the average of the blank samples, which was calculated to be 1,34 $mgO_2/kgTS$. The BA of EP 5457 fabric is highest, about 23% greater than BA of blank sample. BA of EP 5395 is about 15 % above the blank average, BA of EP 5396 is 9% above blank and EP 5334 is only about 0,4% greater than the blank average.

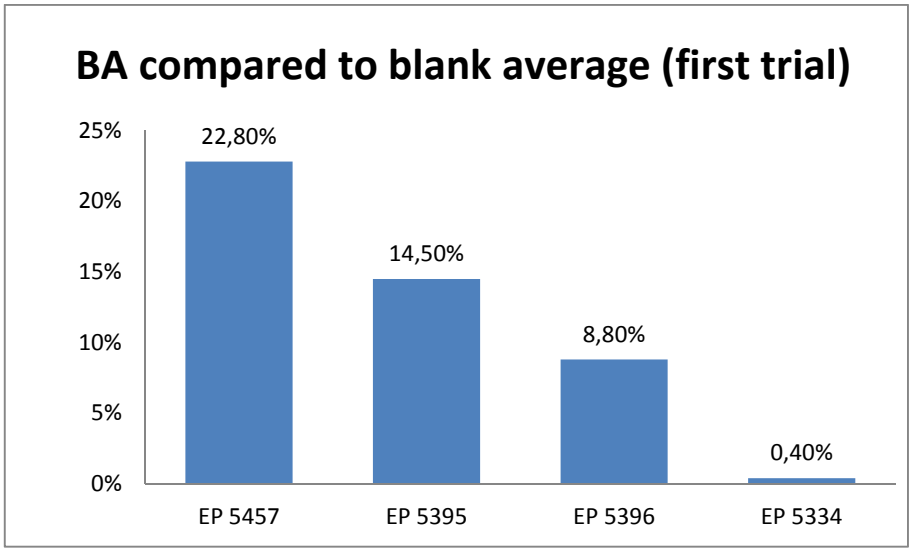


FIGURE 17. Oxygen consumption of fabric samples compared to blank sample in the first trial after 7 days

6.2.2 Second trial

The pressure changes in the measuring vessels during the 30-day experiment are shown in figure 18. The decrease in the pressure is for the most part due to consumption of oxygen in the vessel due to microbial activity. However, there is a lot of fluctuation in the pressures. In figure 18 the black circle indicates the period when the measuring vessels were in a plastic box (see chapter 5.2.2). The regular wave fluctuation of the pressure is probably due to temperature change in the room temperature, which the plastic box was not able to stabilize. In constant-volume an increase in temperature results to an increase in pressure and vice versa (see chapter 2.4).

The yellow arrow in figure 18 points the moment when the measuring vessels were treated to prevent the pressure from decreasing under the warning value (see chapter

5.2.2). Aeration of the measuring vessels resulted to a sudden increase in pressures. After the aeration the pressures started to decrease again.

The blue arrows point the other sudden peaks in the pressure. There is no obvious reason for the peaks, but it is likely that there has been a momentary temperature change in the room temperature which has changed the pressure temperately.

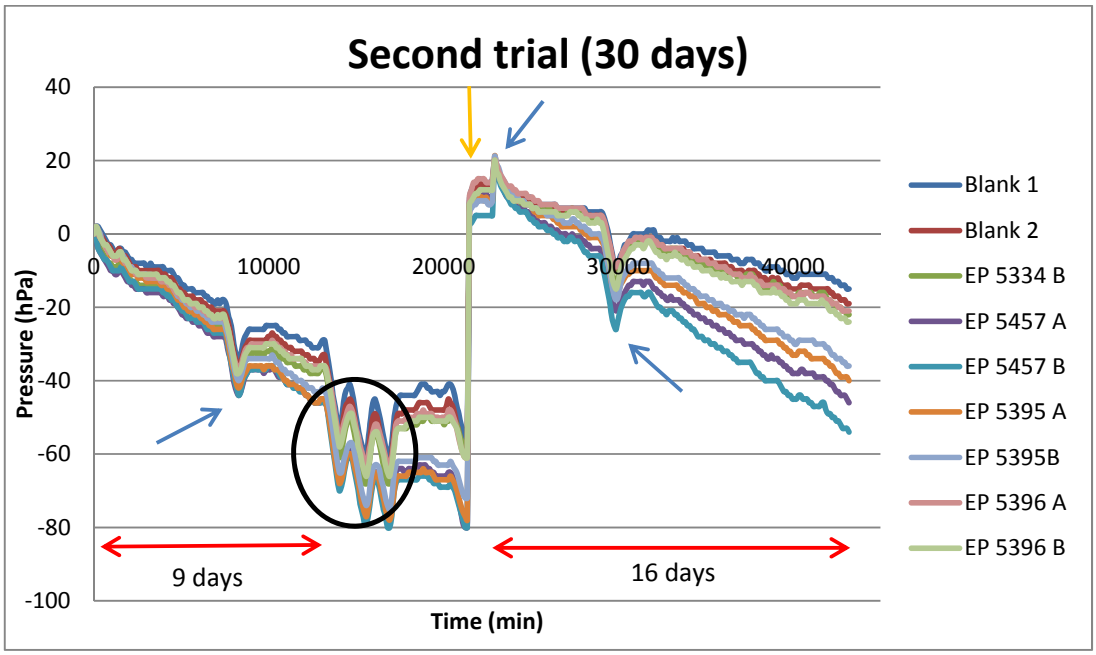


FIGURE 18. Change in pressure during the second trial. The yellow arrow points the moment, when measuring vessels were treated. Blue arrows point sudden peaks in the pressure. The circle points the period, when measuring vessels were in a plastic box.

The second trial consists of two parts; first part includes data from 9 days gathered before changing the placement of the measuring vessels in plastic boxes (4.3.–13.3.2015). The latter part includes the data recovered after the aeration (18.3.–3.4.2015). The results of these two parts are presented separately next.

6.2.2.1 First part of the 2nd trial

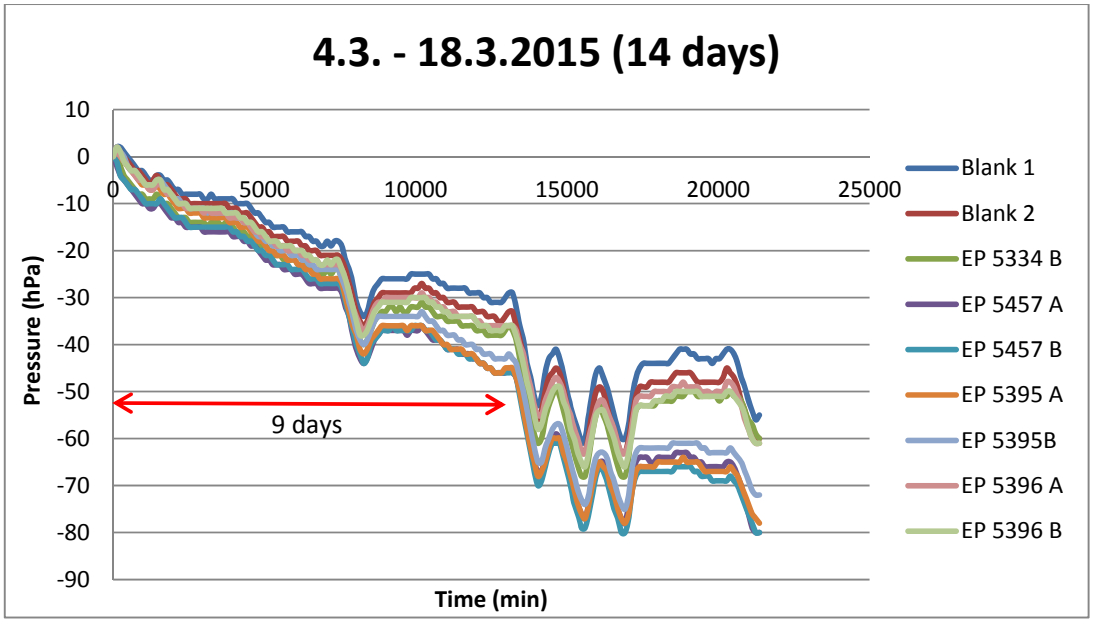


FIGURE 19. Change in pressure during the first 14 days of the second trial

In figure 19 the pressure change during the first part of the second trail is presented in graphical form. The oxygen consumption (BA) during the first 9 days can be calculated, because the pressure has decreased steadily. In table 23 the average pressure and average BA has been calculated by using formula 4 for each fabric type after 9 days of the experiment. In figure 20 the BA values are presented in columns from highest to lowest.

TABLE 23. Average oxygen consumption of blank samples and each fabric sample after 9 days

SAMPLE	Average pressure (hPa)	Average BA ($mgO_2/kgTS$)
Blank	-33	1,24
EP 5334	-38	1,40
EP 5457	-46	1,70
EP 5395	-44,5	1,64
EP 5396	-36,5	1,34

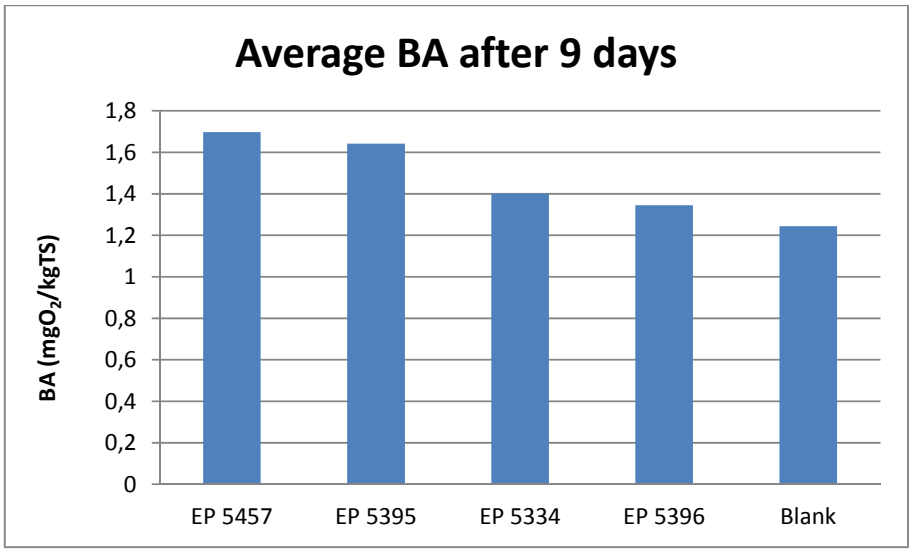


FIGURE 20. Average oxygen consumption after 9 days in the second trial

The average oxygen consumption values of the four different fabrics were compared with the blank average, which was the control sample. In figure 21 the results are presented in columns. The BA of EP 5457 and EP 5395 are roughly 30% higher than the blank average. The BA of EP 5334 and EP 5396 are approximately three times lower, only about 10% higher than the blank average.

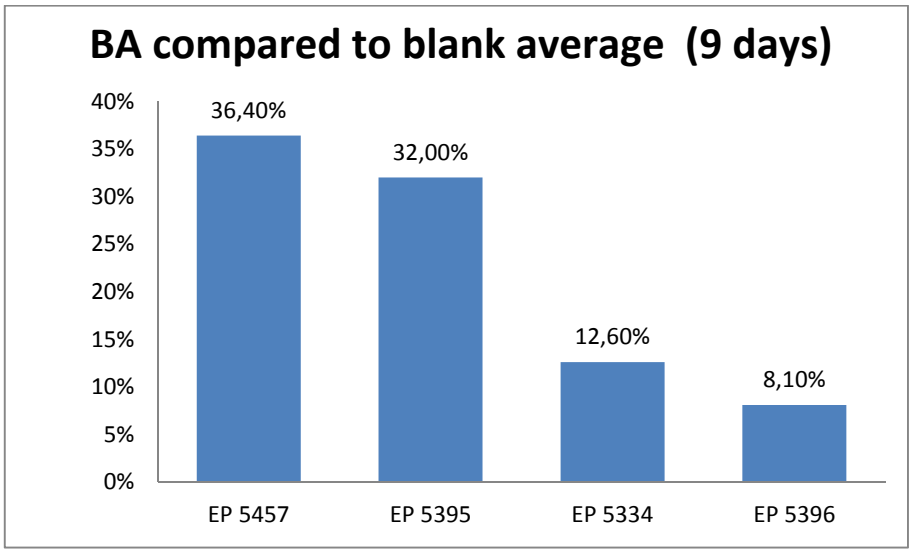


FIGURE 21. Average oxygen consumption of fabric samples compared to blank sample after 9 days of the second trial

6.2.2.2 Latter part of the second trial

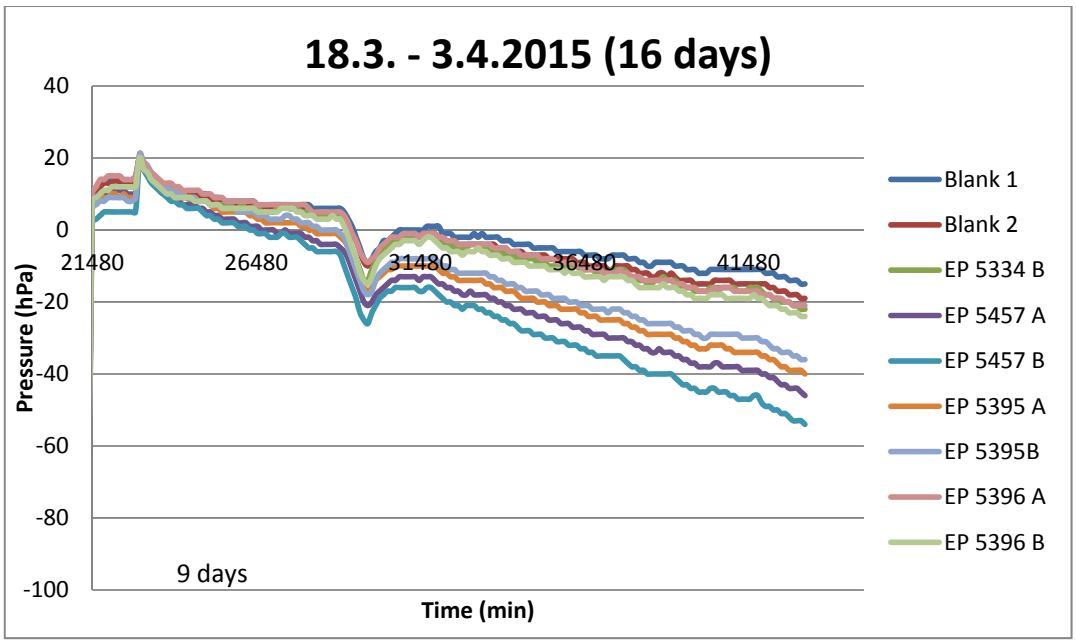


FIGURE 22. Change in pressure after aeration in the second trial (latter part)

In figure 22 the pressure change during the latter part of the second trial is presented in graphical form. In table 24 the average oxygen consumption (BA) from each of the two parallel samples in the end of the second trial is calculated by using the formula 4. Fabric EP 5334 had only one sample. In figure 23 the BA values are presented in a column from the highest value to the lowest. The oxygen consumption is the highest for EP 5457 and 5395 fabrics. The oxygen consumption of EP 5396 and EP 5334 fabrics is close to the BA value of the blank samples.

TABLE 24. Average oxygen consumption of blank samples and each fabric samples

SAMPLE	Average pressure (hPa)	Average BA ($mgO_2/kgTS$)
Blank	-17	0,64
EP 5334	-22	0,81
EP 5457	-50	1,85
EP 5395	-38	1,40
EP 5396	-22,5	0,83

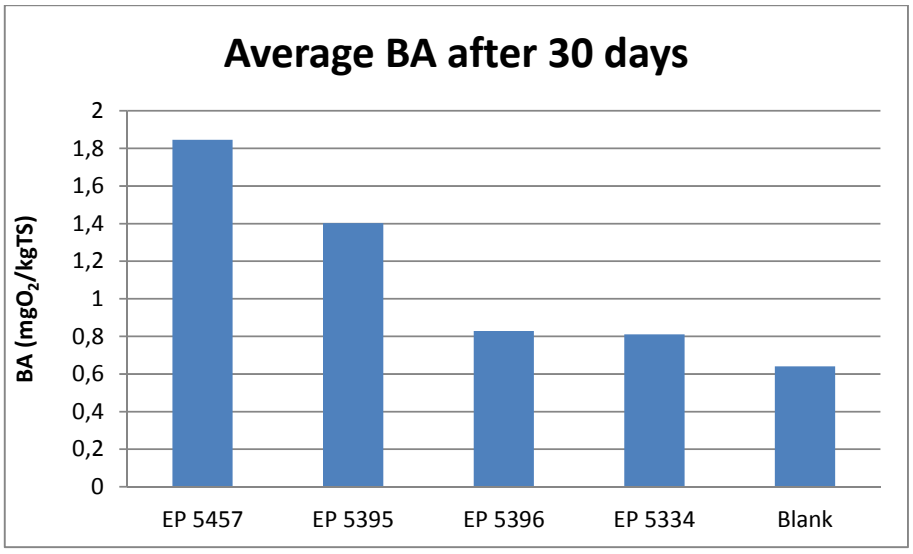


FIGURE 23. Average oxygen consumption of samples after 30 days of the second trial

The average BA values of the four fabric samples were compared with the blank average (zero level). In figure 24 the results are presented. The figure shows, that BA of EP 5457 is almost twice as high as BA of blank average. BA of EP 5395 is also relatively high, 1.2 times higher than blank average. The BA of EP 5396 and EP 5334 are more moderate, the oxygen consumption of these two is about 30% higher than blank average.

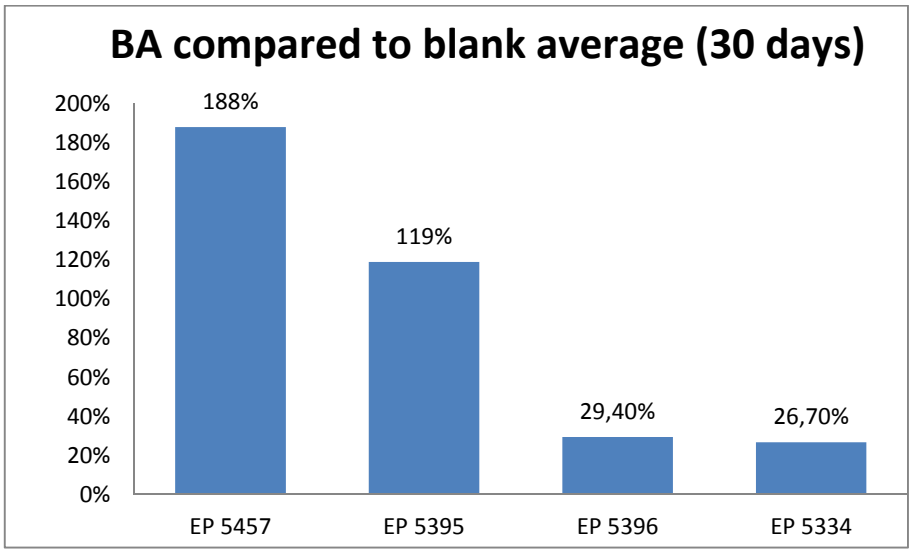


FIGURE 24. Average oxygen consumption of fabric samples compared to blank sample in the end of the second trial

6.2.3 Third trial

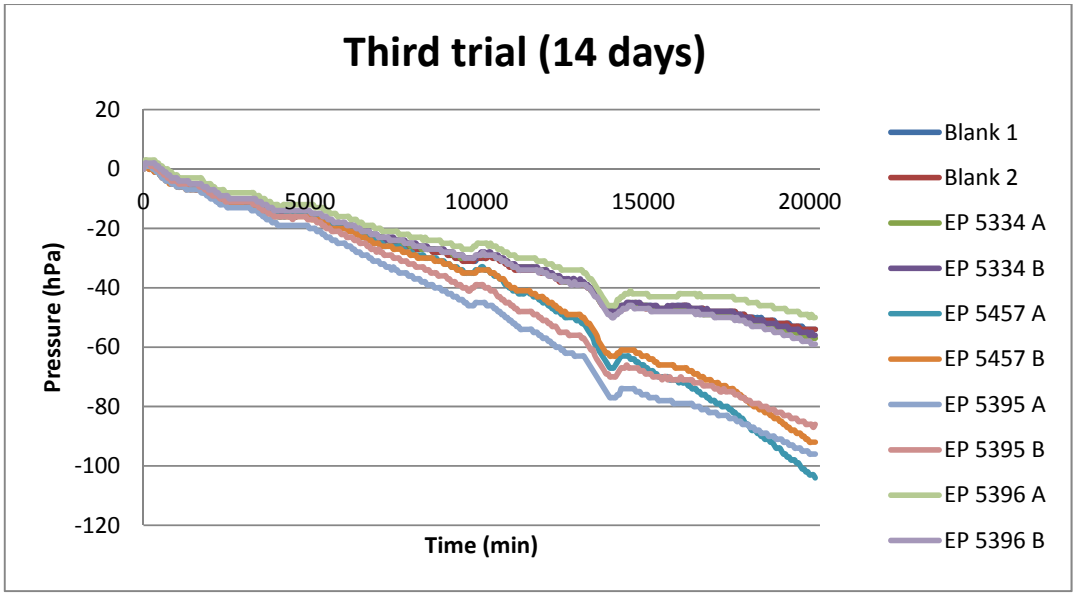


FIGURE 25. Change in pressure during 14 days in the third trial

In table 25 the average pressure and calculated oxygen consumption (BA) are presented. In figure 26 the BA is presented in columns and the samples are arranged according BA value from highest to lowest. The BA of EP 5457 and EP 5395 are clearly higher than Ba of other samples. Actually, the BA of EP 5396 and EP 5334 are even lower than BA of blank sample.

TABLE 25. Average oxygen consumption of blank samples and each fabric samples

SAMPLE	Average pressure (hPa)	Average BA ($mgO_2/kgTS$)
Blank	54	5,33
EP 5334	51,5	4,81
EP 5457	98	9,13
EP 5395	91	8,45
EP 5396	54,5	5,07

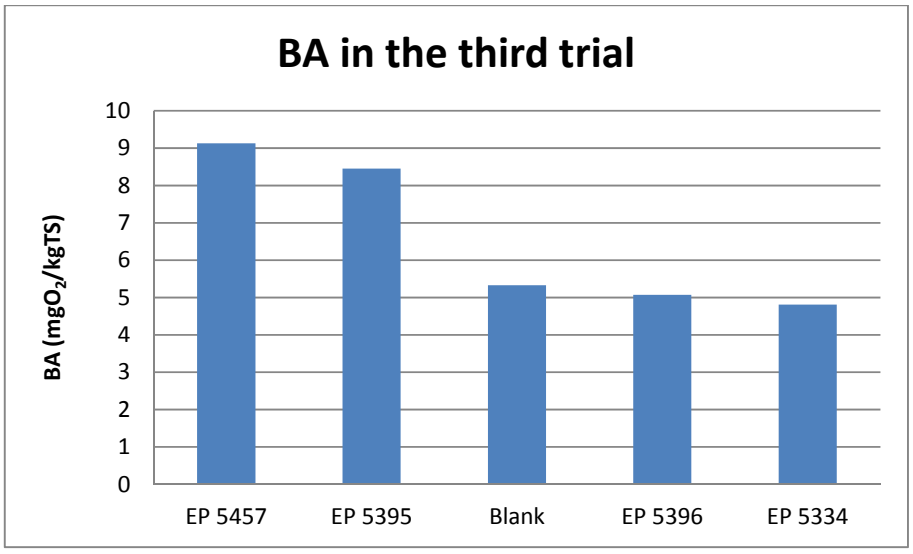


FIGURE 26. Average oxygen consumption of samples after 14 days in the third trial

In figure 27 the BA of the fabric samples are compared to the average of the blank samples. Oxygen consumption of EP 5457 is about 70% higher than compared to blank samples. BA of EP 5395 is about 60% higher than average BA of blank samples. From the figure 27 can be seen, that the calculated BA of EP 5396 is about 5% lower and BA of EP 5334 is almost 10% lower than the BA of blank average.

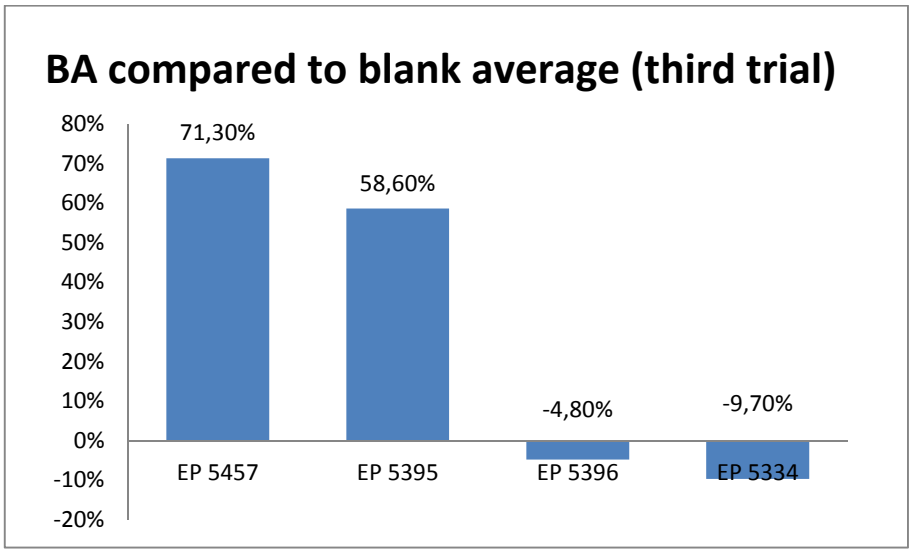


FIGURE 27. Average oxygen consumption of fabric samples compared to blank sample in the end of the third trial

7 CONCLUSIONS AND DISCUSSION

In chapters 7.1 and 7.2 the topics of the literature research are discussed. In chapters 7.3 and 7.4 the results of the experimental part, the composting experiment and the soil respiration experiment are concluded and discussed. The error evaluation and proposals how to improve the test methods are also discussed.

7.1 Biodegradability standards

There are many standards available for determining biodegradability. The challenge is how to select the most suitable test method for measuring the biodegradability of a certain material. When considering the appropriate test method for a certain material or a product, the disposal pathway must be taken into consideration. For example if the product is likely to end up in a marine environment, the biodegradability in those conditions must be studied. It is important that the product is durable throughout its useful life. If the product is designed for outdoor use and to be used in contact with soil, the biodegradation in soil conditions should be tested. And even if the product would be designed to be durable in soil, it could degrade for instance in more aggressive composting conditions.

In the biodegradation test methods the degree of biodegradation is determined. The tests do not determine whether the material is biodegradable or not. There are compostability norms, which determine also the pass levels for the material. In most cases the pass level for degree of biodegradation is 90% in a certain time period. It is debatable if a material can be determined as biodegradable, if 10% of it doesn't degrade. (Bastioli 2005, 160.)

Standardized test methods only model the possible disposal pathways – the degree of biodegradability tested in laboratory or even in pilot-scale tests do not correspond perfectly with real-life conditions. In reality the conditions in the disposal pathways can vary and differ from the optimum conditions. The functioning of the disposal pathways is based on the activity of microorganisms, which means that it is impossible to control which microorganisms are present in the disposal pathway. Especially in the case of

polymers the abundance of the right microorganisms capable of degrading a certain polymer is crucial for the biodegradation.

7.2 Biodegradable polymers

Many factors affect the biodegradation of polymers. Biodegradable polymers are intensively studied and new compounds and polymer blends are constantly produced. Some of the biodegradation mechanisms are studied and understood, but there are many cause-and-effect relationships that are yet unknown.

Naturally occurring polymers in the environment have greater potential to biodegrade, because different microorganisms are evolved to biodegrade these materials that have been present in nature for a long time. Polymers that are synthetically produced and have been discovered only some decades ago do not possess the same advantage; most microorganisms have not yet evolved to digest these polymers. (Tokiwa et al. 2009.)

Some polymers are biodegradable by only few species of bacteria. When the polymer product is disposed, it is not certain that these microorganisms are abundant in the environment of the disposal pathway. This means that even if a polymer has tested to be biodegradable by some microorganisms, the polymer does not biodegrade if the microorganisms capable of degrading the polymer are not present in the disposal pathway. (Tsuji 2013)

Hence the determination of a biodegradable polymer is problematic; even if the polymer has been studied to biodegrade by a certain bacteria, it doesn't directly mean that the polymer is biodegradable in practice. This is why standardized test for biodegradability are specific to a certain disposal pathway – to see whether the polymer or a product is biodegradable in practice.

7.3 Composting experiment

The aim of the composting experiment was to study whether the nonwoven fabrics are biodegradable and which fabrics biodegrade the best. According to the results, none of

the fabrics are biodegradable. The fabric EP 5457 was the only one showing some signs of biodegradation due to the visual changes as can be seen in appendix 2.

During the first 6 weeks of the composting experiment the mass of all fabric types increased. After 6 weeks the mass of EP 5457 started to decrease, while the mass of all other fabric types continued to increase. However, in the end of the experiment the mass of all fabric types was greater than in the beginning of the experiment. This was not an expected result. The mass of the fabrics should not have been increasing. The results indicate that there are some other substances, which are accumulated in the fabric during the composting process and which cannot be rinsed off with water. The composition and properties of the nonwoven fabrics are unknown, thus I cannot explain the increasing mass of the fabrics.

The comparison of the initial mass of the fabric with the final mass cannot be used to evaluate the degree of biodegradation. What caused the increase in the mass is ambiguous, but it can be discussed. As explained in chapter 2.3, there are different phases in the composting process and in each of these phases different microorganisms are present (Diaz et al. 2007). It is possible, that the biodegradable parts in the nonwoven fabrics start to degrade only by certain microorganisms that are not present in the compost at all times and temperatures. It is probable that microorganisms capable of degrading materials in fabric EP 5457 were present only after 6 weeks of the experiment, when the fabric started to lose its mass. However, it is not certain that the weight loss of the fabric EP 5457 is due to the biodegradation of the material. It is possible, that the material has degraded only into smaller fragments.

The evaluation of the biodegradability of the fabric samples was also done by taking pictures of each sample every two weeks. Before the experiment there was no idea of how much the samples would degrade and how visible the changes in the samples would be. During the experiment it became obvious that taking pictures of the samples was not sufficient measure to evaluate the rate of degradation; one could not see the change from the pictures. In most cases the fabrics retained their shape and the loss in fabrics' mechanical properties was only observable when handling the fabrics. By evaluating visually the changes in the fabrics' properties, fabric EP 5457 had become fragile and the structure was brittle. The fabric EP 5395 felt softer and more pliable.

In the future with the composting experiment it would be worth considering evaluating the biodegradation and the changes in the properties of material also by other means apart from measuring the change in mass. The changes in the properties of the material could be evaluated by endurance tests, for instance by measuring the tensile strength.

As a conclusion, none of the four nonwoven fabric types are biodegradable in composting conditions according to the experiment. Some differences and trends between the samples could be observed, yet the differences were not substantial. Only the sample EP 5457 showed both visually and by mass change a trend of decay.

7.3.1 Error evaluation of composting experiment

There were two composters in use and, as expected, the conditions in the composters varied. During the composting experiment the conditions in the composters were not optimum; the temperature didn't stay constant at 58°C, which is the set temperature determined in controlled composting test methods for determining biodegradability (Bastioli 2005, 155). The temperature stayed more moderate, at 35-45°C. The reason for the low temperature could be that the composter itself didn't function properly due to a malfunction.

The evaluation of the moisture content of the compost mixture had to be done when bio waste was added to keep the composters running. If moisture content rose too high, the compost started to smell and the temperature started to decrease. It is possible that the moderate temperature prevented the activity of some microbes that could have contributed to the decomposition process. All in all, it was quite challenging trying to keep the conditions in the composters optimum for the process.

7.4 Soil respiration

The aim of the experiment was to determine the oxygen consumption of fabric samples compared to blank soil samples in order to determine the ranking according to the biodegradability of the fabric samples. The test method measures indirectly the biodegradability activity of the samples, which allows comparison regarding biodegradability of

different samples with each other. The results however do not show the degree or rate of biodegradability of the fabrics and the results cannot be compared with the results of standardized test methods.

The results indicate that the oxygen consumption, i.e. the biodegradation activity is highest for sample EP 5457. Also EP 5395 had clearly higher BA than the other two fabric samples, EP 5396 and EP 5334. The BA of EP 5396 and EP 5334 are at the same level with the blank samples indicating that the activity of biodegradability is not different from soil itself. In all trials the ranking was the same from the highest BA to the lowest: EP 5457, EP 5395, 5396 and EP 5334. The ratio of the fabric sample and blank sample varied between the trials.

The OxiTop® soil respiration device has not been used at TAMK before and one of the aims of this work was to test the applicability of the device for this kind of biodegradability tests. There is limited amount of information available for the appropriate parameters, for instance for the ratio of soil and sample or the measuring period. Three trials were conducted with slightly different parameters to see how the parameters affect the results. Because all of the three trials were slightly different they cannot be compared with each other. However, they gave important information to develop the test procedure. If the experiments were to conclude with exactly the same parameters, it might be possible to compare the results with each other.

In the first trial the ratio of soil and sample was lower than in the other two trials. The measuring period was only 7 days. There was only small difference between the oxygen consumption of the samples. In the second trial the measuring period was increased to 30 days and the ratio of soil and sample was also increased. The measuring period was too long, thus the pressure was dropping too low. However, after the aeration there were clearer differences between the samples. In the third trial a different soil was used to see how it affects the oxygen consumption. The dry mass of this soil was significantly lower than the dry mass of the soil used in the first two trials. This affected the BA calculation and the BA values were significantly higher than in the first two trials.

According to the this experiment, the OxiTop® device is applicable for testing biodegradability of samples, but the optimum sample and soil ratio and the measuring period should be studied and determined in the future. In this experiment, the most suitable

measuring period for these samples was 14 days. However, the measuring period depends on the activity of the sample. The mass of soil in this experiment was 50g and the volume of the measuring vessel was approximately 1L. It is important that there is enough free volume in the measuring vessel for the gases. The free gas volume in the experiments was approximately 0,7L, which I think was enough, because the pressure didn't drop too low too quickly. The mass ratio of sample and soil in this experiment was low; 50g of soil and roughly 0,5g of sample. I would assume that clearer differences between the blank soil samples and the samples containing both soil and sample could be recorded if the soil/sample ratio was higher, i.e. more sample in relation to soil.

The amount of absorbing agent was 40mL and according to my experience this was enough to absorb the gaseous CO_2 – the pressure dropped quite steadily in all trials, i.e. the gas amount in the vessels was degreasing steadily. If the absorbing agent would not absorb the produced CO_2, the pressure in the vessels would have started to increase.

There are many factors affecting to the result when measuring the pressure and calculating the oxygen consumption (Platen & Wirtz 1999a, 4). Two of the factors that affect the results are the temperature conditions and the constant volume of the measuring vessels. In the recorded pressure curve there were sudden peaks in the pressure especially when the measuring vessels were kept in a Styrofoam box during the second and third trial (see chapters 6.2.2 and 6.2.3). The incubation cabin should keep the temperature constant. In the first trial (see chapter 6.2.1), when the vessels were in another incubation cabin, no sudden peaks in the pressure were observed.

The sudden peaks in the pressure curve could also be due to the changing volume in the measuring vessels, i.e. the measuring vessels might not have been completely airtight and some gas exchange could have occurred. In this experiment, the timing of the sudden peaks in the pressure was the same with all of the samples. If the measuring vessel would not be airtight, the peak in the pressure would be likely to happen only in one of the vessels at a time. The peaks in the pressure should be able to prevent; the measuring vessels should be in a proper incubation cabin and the airtightness of the vessel should be ensured by following the instructions enclosed in appendix 3.

The moisture content of the soil affects also the results. The dry mass of the soil should be accurately determined in order to get accurate results from the calculations. If several

trials are conducted, the moisture content of the soil should be constant in all trials in order to be able to compare the results with each other.

In all three trials the ranking was the same even though the parameters varied. Hence the method and the result are quite reliable. Oxygen consumption was the highest with sample EP 5457. The second highest oxygen consumption was measured from sample EP 5395. EP 5396 and EP 5334 showed more moderate BA than the two other fabrics. BA of EP 5396 was slightly higher than oxygen consumption of EP5334.

7.4.1 Error evaluation of soil respiration

The masses of the fabric samples were not equal (see tables 16-18). This might and should affect the results of oxygen consumption, thus increase the error of results. The mass of the fabric samples in the second trial were approximately 3 times greater than in the first trial. Still, when the results from the 7th day of first trial were compared to the results on 9th day of second trial, the magnitude of the BA values were approximately in the same range. Thus the increase in the mass of the fabric samples didn't show in the results.

In the second trial, the data gathered during 13.3.-18.3. (5 days), when the measuring vessels were in the plastic boxes, was not used. The pressure change didn't correlate the activity of microbes, but the change is more likely to correlate the changes in the room temperature, though this cannot be confirmed with the performed measurements.

REFERENCES

Avérous, L. & Pollet, E. 2012. Environmental Silicate Nano-Biocomposites, Green Energy and Technology. London: Springer-Verlag.

Bastioli, C. 2005. Handbook of Biodegradable Polymers. Shrewsbury, GBR: Smithers Rapra.

Bergeret, A. 2011. Environmental-Friendly Biodegradable Polymers and Composites, Integrated Waste Management - Volume I. Kumar, S (Ed.). InTech.

Biolan® Pikakompostori 220 – asennus- käyttö- ja huolto-ohjeet. 2010. Biolan Oy. Available at:
http://www.biolan.fi/image/ymparisto/kayttoohjeet/5726_34_kayttoohje_fi.pdf (accessed 22.5.2015)

Clarinval, A-M. & Halleux, J. 2005. Biodegradable polymers for Industrial Applications. Classification of biodegradable polymers. Smith, R. (ed.) England: Woodhead Publishing Limited.

Diaz, L.F., De Bertoldi, M., Bidlingmaier, W. & Stentiford, E. 2007. Compost Science and Technology. Amsterdam: Elsevier Ltd.

Ghanbarzadeh, B. & Almasi, H. 2013. Biodegradable polymers, Biodegradation – Life of Science. Chamy, R. & Rosenkranz, F. (ed.).

Held, P. 2012. Enzymatic Digestion of Polysaccharides (Part II). BioTek Instruments, Inc. Available at:
http://www.biotek.com/assets/tech_resources/Cellulosic_App_Note_Part_II.pdf (accessed 28.5.2015)

Kabasci, S. & Stevens, C. 2013. Wiley Series in Renewable Resource: Bio-Based Plastics: Materials and Applications. John Wiley & Sons.

Luzier, W.D. 1992. Materials derived from biomass/biodegradable materials. USA: Proc. Nati. Acad. Sci.
Available at: http://www.pnas.org/content/89/3/839.full.pdf (accessed 29.4.2015)

Operating Manual: System OxiTop® Control. 2006. Wissenschaftlich-Technische Werkstätten GmbH.
Available at: http://www.globalw.com/downloads/WQ/oxitop_oc_100.pdf (accessed 9.3.2015)

Park J.B. & Bronzino, J. D. 2002. Biomaterials: Principles and Applications. CRC Press LLC.

Platen, H. & Wirtz, A. 1999a. Application analysis no. 1. Measurement of the respiration activity of soils using the OxiTop® Control measuring system. Basic principles and process characteristic quantities.

Platen, H. & Wirtz, A. 1999b. Application analysis no. 2. Measurement of the respiration activity of soils using the OxiTop® Control measuring system. Standard test preparation.

Rudnik, E. 2010. Compostable Polymer Materials. Google eBook. Available at: https://books.google.fi/books?id=ZrQwn8XzKlEC&pg=PA101&lpg=PA101&dq=DIN+V+54900&source=bl&ots=kX9mCeNZyO&sig=zAY4sInzyIE9sitBRBbHW6Q93Wg&hl=en&sa=X&ei=r8UTVcHaE8_natKYgYAM&ved=0CCcQ6AEwAQ#v=onepage&q=DIN%20V%2054900&f=false (accessed 22.5.2015)

Tokiwa, Y. Calabia, B. P. Ugwu, C. U. Aiba, S. 2009. Biodegradability of plastics. Switzerland: Molecular Diversity Preservation International.

Tsuji, H. 2013. Wiley Series in Renewable Resource: Bio-Based Plastics: Materials and Applications. Poly(Lactic Acid). Kabasci, S. (ed.). John Wiley & Sons.

Wikipedia. 2015. Strurturausschnitt Polyvinylalkohol. Available at: http://en.wikipedia.org/wiki/Polyvinyl_alcohol#/media/File:Polyvinyl_Alcohol_Structural_Formula_V1.svg (accessed 28.5.2015)

APPENDICES

1(2)

Appendix 1. The mass loss of fabric samples in the composter.

			Mass of fabric (g)			
		SAMPLE	EP5334	EP5395	EP5396	EP5457
Initial 18.2.	Compost 1	A1	2,8342	2,2019	2,4221	2,6211
		B1	3,043	2,598	2,6499	2,6568
		C1	2,8556	2,432	2,6319	2,61898
		AVERAGE (g)	2,9109	2,4106	2,5680	2,6323
	Compost 2	A2	2,8443	2,4009	2,4331	2,6287
		B2	2,8112	2,011	2,6487	2,6623
		C2	3,098	2,2231	2,4797	2,6432
		AVERAGE (g)	2,9178	2,2117	2,5205	2,6447
	TOTAL AVERAGE		2,9144	2,3112	2,5442	2,6385

			Mass of fabric (g)			
		SAMPLE	**EP5334**	**EP5395**	**EP5396**	**EP5457**
After 2 weeks	Compost 1	A1	3,1550	2,2211	2,7201	2,7298
		B1	3,0358	2,4776	2,6573	2,7037
		C1	3,0012	2,4987	2,6681	2,7696
		AVERAGE (g)	3,0640	2,3991	2,6818	2,7344
	Compost 2	A2	3,1051	2,5657	2,5335	2,7907
		B2	3,0727	2,1932	2,6449	2,7271
		C2	3,3295	2,2566	2,7275	3,0424
		AVERAGE (g)	3,1691	2,3385	2,6353	2,8534
	TOTAL AVERAGE		3,1166	2,3688	2,6586	2,7939

			Mass of fabric (g)			
		SAMPLE	**EP5334**	**EP5395**	**EP5396**	**EP5457**
After 4 weeks	Compost 1	A1	3,2476	2,3444	2,7653	2,8919
		B1	3,1652	2,5137	2,7631	2,8337
		C1	3,0527	2,5966	2,7399	2,7946
		AVERAGE (g)	3,1552	2,4849	2,7561	2,8401
	Compost 2	A2	3,1557	2,7159	3,0431	3,1382
		B2	3,2662	2,3066	2,7676	2,9167
		C2	3,3728	2,2952	2,8682	3,2035
		AVERAGE (g)	3,2649	2,4392	2,8930	3,0861
	TOTAL AVERAGE		3,2100	2,4621	2,8245	2,9631

2(2)

			Mass of fabric (g)			
		SAMPLE	**EP5334**	**EP5395**	**EP5396**	**EP5457**
After 6 weeks	Compost 1	A1	3,4687	2,5598	2,9974	3,0791
		B1	3,2931	2,5949	2,9186	2,9793
		C1	3,1985	2,6336	2,8407	2,7972
		AVERAGE (g)	3,3201	2,5961	2,9189	2,9519
	Compost 2	A2	3,8069	2,8299	3,1347	3,4818
		B2	3,4973	2,5615	2,8779	3,2058
		C2	3,5513	2,5791	3,0255	3,3084
		AVERAGE (g)	3,6185	2,6568	3,0127	3,3320
	TOTAL AVERAGE		3,4693	2,6265	2,9658	3,1419

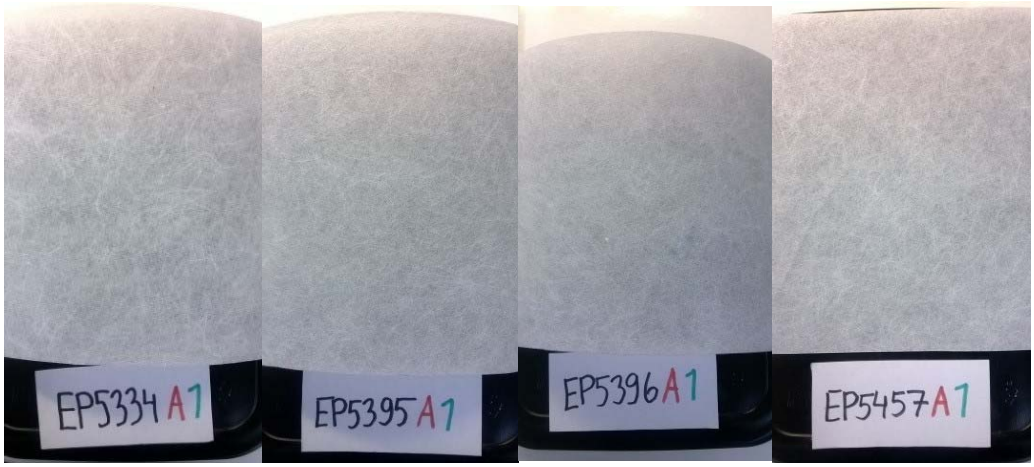
			Mass of fabric (g)			
		SAMPLE	**EP5334**	**EP5395**	**EP5396**	**EP5457**
After 8 weeks	Compost 1	A1	3,7280	2,6381	3,0861	3,0281
		B1	3,3307	2,6400	2,9465	3,0193
		C1	3,2325	2,6462	2,9208	2,7958
		AVERAGE (g)	3,4304	2,6414	2,9845	2,9477
	Compost 2	A2	3,7384	2,8848	3,1077	3,2937
		B2	3,5794	2,4723	2,9887	3,2004
		C2	3,6186	2,5716	3,0933	3,1525
		AVERAGE (g)	3,6455	2,6429	3,0632	3,2155
	TOTAL AVERAGE		3,5379	2,6422	3,0239	3,0816

			Mass of fabric (g)			
		SAMPLE	**EP5334**	**EP5395**	**EP5396**	**EP5457**
After 10 weeks	Compost 1	A1	3,7960	2,8311	3,1323	2,9047
		B1	3,5836	2,7462	3,0788	2,9757
		C1	3,4110	2,8357	3,0653	2,7319
		AVERAGE (g)	3,5969	2,8043	3,0921	2,8708
	Compost 2	A2	3,7190	2,9325	3,1330	3,0729
		B2	3,6326	2,4848	3,1109	2,9496
		C2	3,7341	2,597	3,2506	2,9445
		AVERAGE (g)	3,6952	2,6714	3,1648	2,9890
	TOTAL AVERAGE		3,6461	2,7379	3,1284	2,9299

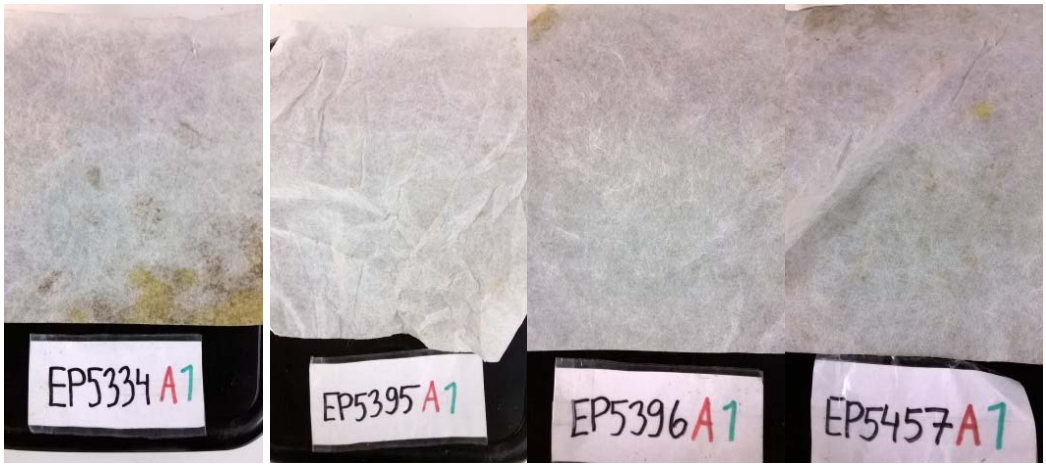
1(3)

Appendix 2. Pictures of the fabric samples in the composter.

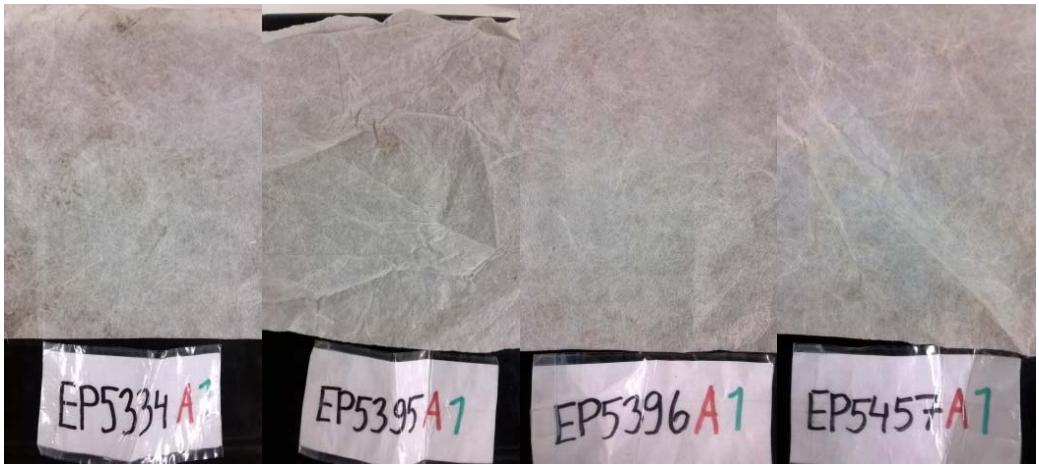
Initial



2 weeks



4 weeks

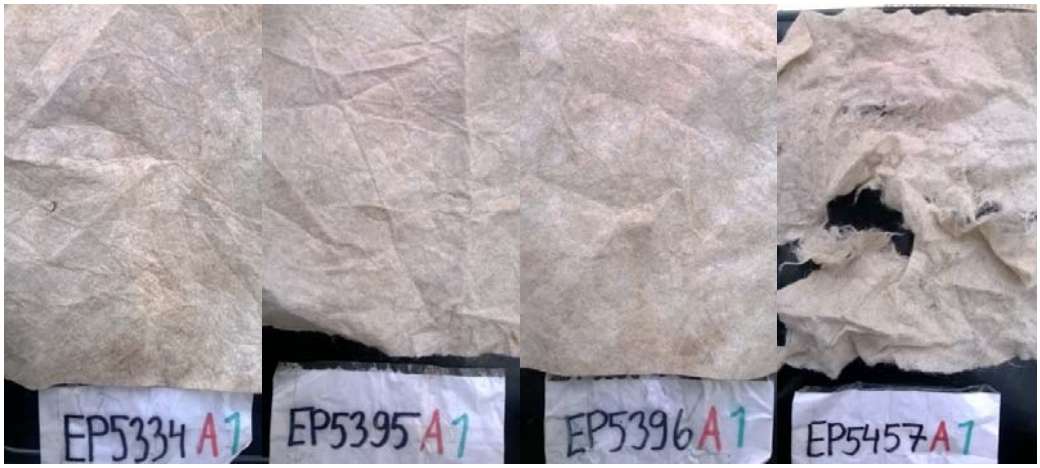


6 weeks 2(3)

8 weeks

10 weeks 3(3)

12 weeks



Appendix 3. OxiTop soil respiration manual

OxiTop soil respiration device measures the pressure change due to consumption of oxygen. The oxygen consumption can be calculated from the results. Oxygen consumption is an indirect measure of biodegradation.

The device can be used to compare oxygen consumption of different materials with each other. The samples are compared to a blank soil sample. The materials can be ranked according to biodegradability. Degree of biodegradation is not determined.
In an experiment there should be at least one blank soil sample and the samples including soil and material of which biodegradability is studied. When several parallel samples are used, the average value of the material can be determined and the results are more accurate.

Preparation of sample

1. Measure the dry mass of the soil and sample. For example weight accurately the amount of moist soil used in the experiment. Dry the soil in oven at 105°C for couple of hours. Place the soil in evaporation pan for 30 minutes to cool down. Measure the weight again. Repeat the procedure until weight of soil remains constant.
2. Measure the free volume of the measuring vessel. The free gas volume, $V_{fr,}$ consists of the volume of the measuring vessel excluding the volume of the lid, the volume of moist soil and sample and the volume of absorption vessel and absorption agent.

$$V_{fr} = V_{vessel} - V_{moist\ soil\ and\ sample} - V_{absorption\ agent}$$

   - Measure the volume of soil, sample and absorbing agent.
   - The volume of vessel with the lid can be measured by filling the vessel with distilled water to the top and placing the lid on top. The weight of vessel and lid is recorded first empty and then filled. The mass of distilled water in kilograms corresponds to the volume in liters.
3. Weight an appropriate amount of soil (e.g. 50g of mature compost) and sample in the measuring vessel. Make sure there is enough free volume in the measuring vessel.

Preparation of measuring vessel 2(5)

1. The components of the measurement should be at room temperature.
2. Apply lubricant to both sides of the rubber sealing of the lid to ensure airtight lid.
3. Measure 40ml of 1M NaOH in a plastic cup and place it to the holder under the lid.
4. Place soil in the bottom of the measuring vessel and bury the sample in the soil.
5. Place the lid on and fasten it with 6 clips.
6. Place a black rubber stopper in the hole on the lid.
7. Screw the measuring head tightly on the lid.
8. Place the measuring vessels in incubation cabin with constant room temperature (e.g. styrofoam box).

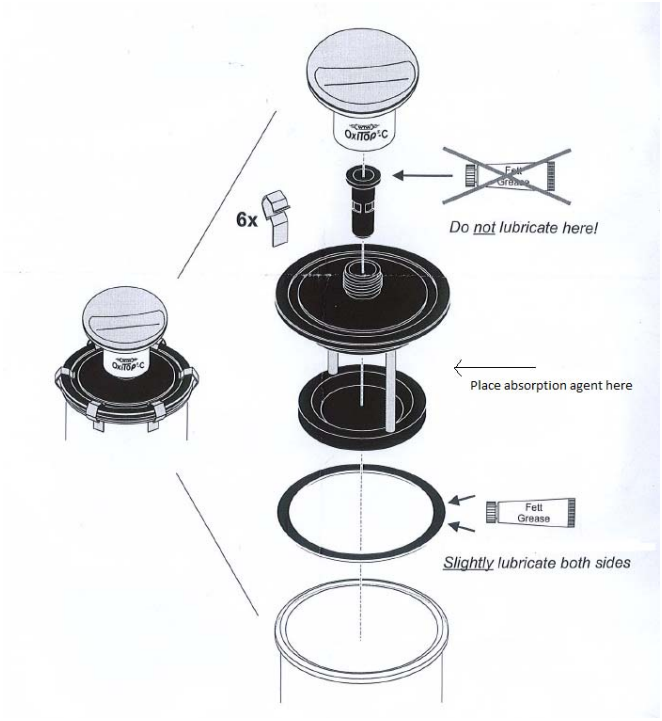


FIGURE 1. Assembly of the device.

Starting the measurement 3(5)

1. Check that the measuring heads are available and functioning:
   - Press “GLP” and select “Check” and press “RUN/ENTER”.
   - Select “info” and press “RUN/ENTER”. Point the controller to the measuring head.
   - INFO appears on the screen (picture). If “Batteries: OK” and “Status: free”, the measuring head is ready for use. If batteries are low, don’t use the measuring head. If Status is not free, empty the memory (next step).

2. Empty the measuring heads if necessary:
   - Press “GLP” button, select “Maintenance” and press “RUN/ENTER”.
   - Select “Reset/release” and press “RUN/ENTER”.
   - “Reset/release” appears on the screen again, press “RUN/ENTER” and point the controller towards the measuring head. The Ser. no. of the measuring head appears on the screen.
   - Select “Reset/release” and press “RUN/ENTER” while pointing the controller towards the measuring head. “Reset performed!” appears on the screen when the measuring head is emptied.
   - Select “continue” by pressing “RUN/ENTER” to empty the next head.
3. Select the operation mode:
   - Press “GLP” button.
   - Select “Settings” and further “Operation mode”.
   - Select “Mode” by pressing “RUN/ENTER” and select “pressure p” with up and down buttons.
   - Accept the operation mode by pressing “RUN/ENTER”.
4. Select the measuring period:
   - Press “GLP” button.

- Select “Settings” and further “Measuring time”.
- Adjust the measuring time (in days) with up and down buttons. The measuring time depends on the quality of the soil and sample, for example 7-30 days.
- Press “RUN/ENTER” to accept

5. Start sample:
   - Press button with “picture of controller and measuring head” 
   - Select “Start sample” by pressing “RUN/ENTER”.
   - The information of the sample appears on the screen, check that settings are correct.
   - Identification number can be changed by selecting “I.D. number” and pressing “RUN/ENTER”. Change the number with arrow buttons. Save the change by pressing “RUN/ENTER”.
   - Remember to write down the details of the measurement for example in the OxiTop lab log.
   - Select “Start” and press “RUN/ENTER” and hold controller to the measuring head. When sample is started “!started!” appears on the screen.

During the measurement

Check the momentary value of the samples regularly to avoid the pressure to drop below warning pressure (e.g. 100 hPa). The momentary value of the sample can be checked with the controller:

- Press “ON/OFF” and then press “table button” and the list of measurements appears on the screen.
- Select a sample with arrow buttons and press “RUN/ENTER”.
- Select “Momentary value” and hold controller to the measuring head and press “RUN/ENTER”, the current pressure value appears on the screen.
- Select “Stop” and press “RUN/ENTER”.
- Press ”table button” to go back to the list of measurements. 

Gathering the data from the measuring heads

1. To call up data from the measuring heads press “button with controller and measuring head”.

2. Select “Call up all data” and press “RUN/ENTER” while holding the controller approximately 40cm from the measuring heads.
3. The number of called up measuring heads appears on the screen. If the number corresponds to the number of samples, all data has been called up. If the number doesn’t correspond to the number of samples, repeat the procedure.
4. When all samples have been called up, select “Stop” and press “RUN/ENTER”.

Transferring the data from controller to PC

1. Connect the controller to a PC with OxiTop –cord (the cord is in I1 –laboratory) and switch on the controller by pressing “ON/OFF” button.
2. Start the A Chat OC –programme. The programme is at least in some of the I1 –laboratory computers.
3. Press “File” and select “Fetch sample list”. The sample list appears on the screen. To open the sample information double click the sample. Copy all data in Excel. Repeat this with all samples.

Calculating the oxygen consumption

Oxygen consumption is calculated with the following formula:

$$BA = \frac{M_R(O_2)V_{fr}\Delta p}{m_{DS}RT}$$

In the equation $M_R(O_2)$ is molar mass of oxygen (32 000 mg/mol), V_{fr} is free gas volume of the measuring vessel (L), Δp is reduction of pressure in OxiTop® measuring device (hPa), m_{DS} is mass of dry sample (kg), R is general gas constant (83,14 J/molK) and T is measuring temperature (K).