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Reverse Engineering on Biodegradable Pegs on the Market

-An early stage study of biodegradable plastics for Husqvarna

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Department of Chemistry and Chemical Engineering

CHALMERS UNIVERSITY OF TECHNOLOGY

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Abstract

This thesis is a pre-study for the possible development of biodegradable plastics at Husqvarna AB. An application for these kinds of materials at Husqvarna, are pegs that secure the Automower cables. The cables are laid out along the garden during installation of the mower. Biodegradable pegs with similar application and formation already exist on the market. Three kinds of commercially available pegs were investigated in this thesis.

The purpose of the thesis was to conduct reverse engineering on the purchased biodegradable pegs in order to determine their material composition. Literature studies was also made to lay a broad foundation about the subject.

Characterization using DSC, TGA, FTIR and NMR was conducted in order to determine what material the peg are made of. The analysis showed that one of the pegs consisted of poly lactic acid (PLA) and the other two of polypropylene (PP).

Since PP is not a biodegradable plastic, it is not a relevant material for this kind of application. PLA could be a suitable material for the pegs. Its monomers are non-toxic and it can be produced from renewable sources. However, PLA biodegrades slowly, complete degradation in soil conditions can take several years. Thermoplastic starch (TPS) is another biodegradable material that has been studied in this thesis. Its monomers are non-toxic and the material is produced from renewable sources. However, the material is highly sensitive to moisture and is therefore rarely used alone. Blending it with other polymers or additives might improve its properties. The biodegradation process of TPS is fast, the material can biodegrade within months.

The biodegradation process of PLA is slow, that might lead to problems with pollution and micro plastics. However, that would have to be further investigated. In order to assess the complete environmental impact of the materials, life cycle analysis (LCA) would have to be conducted.

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1 Introduction

1.1 Background

In the 1990s biodegradable plastics were introduced on a industrial scale [1]. The reasons were because of environmental concerns, dumping of waste in the ocean caused litter problems on beaches and affected the marine life [2]. Today, that problem still exists and accumulation of plastic occurs everywhere. Conventional plastics not only create debate on pollution but also on greenhouse gas emissions. According to Intergovernmental Panel on Climate Change (IPCC), the greenhouse gas (GHG) emissions have to decrease to 40-50% compared to the 2010 values before 2030 in order to limit a global warming above 1.5 °C [3]. Among other things, these issues has lead to increasing interest of biobased and biodegradable plastics.

It is important to separate the terms biobased and biodegradable. Biobased plastics mainly or partly consists of biological products that derive from biomass [4]. Biodegradable plastics can fully degrade into carbon dioxide, water and biomass under action of microorganisms [1]. From Figure 1, it can be obtained that biodegradable plastics can be based on both renewable and petrochemical sources.

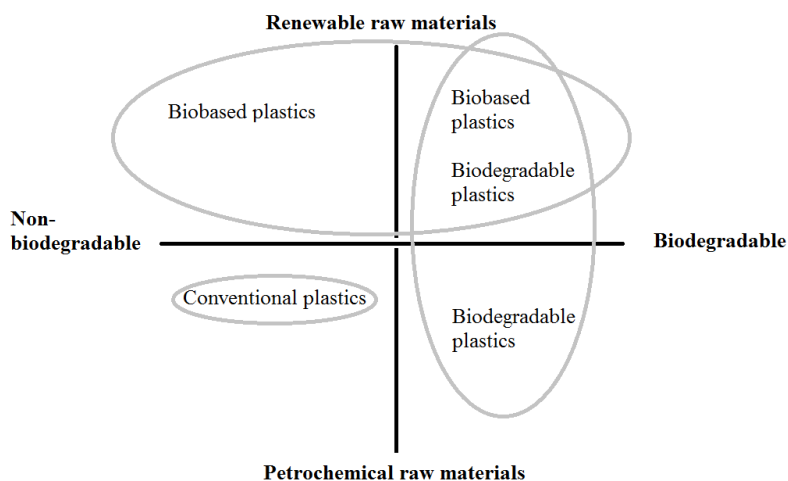


Figure 1: The different windows of biobased and biodegradable plastics. Bioplastic is a wide concept and includes three of these windows. The picture is developed based on information from Bio Based Press [5].

An application for biodegradable materials at Husqvarna, are the pegs used to secure Automower (robotic mowers) boundary cables, see Figure 2. They are pushed into the ground to prevent the cable from moving around. Even though the purpose of the pegs is fulfilled as soon as the grass has grown over the cable, they

are usually left in the ground by the customers.



Figure 2: Picture of the current pegs used to secure Automower boundary cables

Biodegradable pegs already exist on the market today, sold as tent pegs and pegs to secure germination blankets. Since their shape, appearance and application are very similar to the pegs that are used with Automower, it would be interesting to see what kind of material they are made out of. Three kinds of pegs from the market were purchased for this project.

1.2 Purpose of the thesis

The purpose of the thesis is to conduct reverse engineering on pegs that are purchased from the market. The goal is to determine what materials they are made of. Literature studies of biodegradation and biodegradable plastics will also be made. Some assessment on the suitability of the materials for this application will be made as well.

1.3 Scope of the thesis

In this thesis, the focus of biodegradation processes will be on soil conditions.

2 Theory

2.1 Pegs for securing Automower cables

Currently, Europe is the main market for Husqvarna’s pegs and they are made from rest products that are left when Husqvarna’s other plastic parts are manufactured. They mainly consist of polypropylene (PP), acrylonitrile butadiene styrene (ABS) and acrylonitrile styrene acrylate (ASA).

The pegs could be seen as a disposable product if they are used once and the cable is never moved. To leave the pegs in the ground could therefore be seen as contributing to pollution. On the other hand, there are customers who would like to be able to move the cable. In that case, the pegs must keep its mechanical properties to be able to be used sufficient number of times. Therefore it would not be an alternative for Husqvarna to fully exchange the pegs for biodegradable ones. However, the biodegradable pegs could be an alternative for the customers.

Some possible advantages with biodegradable pegs are convenience for the customers, the pegs would decompose when their purpose is fulfilled. Another advantage could be to decrease pollution. PP is not susceptible to biodegradation as it has high molecular weight (M_w), is hydrophobic and do not have active functional groups [6]. A third reason is to reduce distribution of chemicals in the environment. The monomers of ABS and ASA is listed at Chemsec’s sin list [9]. The plastics are considered as potentially problematic throughout their life cycle by Naturskyddsöreningen [7]. Acrylonitril especially, is CMR-classed by Chemsec [9]. As the current pegs mechanically degrades, these harmful chemicals are released into the environment.

2.1.1 Biodegradable pegs

The purchased pegs for this thesis has been compiled in Table 1.

Table 1: Commercially available pegs that have been analyzed

Company	Declared material	Proposed degradation time
Product from getcamping.se	Degradable PLA	-
Yellowstone	-	6 months
Tildenet	Starch based	-

No information about materials were found for the Yellowstone product. For the Tildenet product, it was stated that the material was starch based. That could mean that it is the raw material. It is possible that the materials that the pegs are made out of are a blend with other polymers. Analysis will be made on these

pegs in order to get as much information about the materials as possible.

During a previous Bachelor thesis at Husqvarna [10], Automower pegs were produced in PLA. This proves that it is possible to produce PLA pegs with Husqvarna's current equipment. These pegs has also been tested as a reference for PLA as one of the pegs were stated to be made out of it.

2.2 Plastics

Pure polymers are rarely used as they are, they need some kind of modification before they can be commercially used. The modification is usually in the form of additives. Plastic is the term for the material the polymers and additives form together. The amount of additives in plastics varies widely, from 0.01 % to 90% depending on application [1].

Fillers are an example of additives, they can either be organic or inorganic. The fillers that improve properties of the plastic is called functional fillers. The fillers that dilute the materials and lower the cost are called extenders [1].

Plasticizer are another kind of additives. They lower the glass transition temperature (T_g) of the material, reduce reformation tension and increase the flexibility of the polymer chain. The plasticizers usually have low molecular weight and they are therefore able to diffuse into the material and take up cavities in the structure. This allow the materials to flow better at lower temperatures and improves the dispersion of fillers [11, 12].

Polypropylene (PP) is a conventional plastic, its melting point (T_m) is around 165 °C [13]. PP is almost insoluble in most organic solvents [14].

2.3 Biodegradable plastics

2.3.1 Definition

There is a difference between degradable and biodegradable polymers. According to the European Committee for Standarization, the definition of biodegradation is "degradation of a polymeric item due to cell-mediated phenomena" [15]. IUPAC defines a biodegradable polymer as; "Polymer susceptible to degradation by biological activity, with the degradation accompanied by a lowering of its molar mass" [16].

A polymer is degradable when it goes through cleavage and molar mass decrease without interactions of microorganisms [4]. Polymers can be mechanically degraded into small invisible pieces and appear to have disappeared, but that does not mean that the material has biodegraded [1]. Microplastic is a term for all pieces of plastics that are less than 5 mm long [17].

2.3.2 General biodegradation of polymers

The biodegradation process can be divided into two main steps, depolymerization and mineralization. In the depolymerization step, the polymer chains are cleaved into smaller pieces [15, 18]. The scission can be on both the main chain and the side chains [19]. Depolymerization usually occurs outside of organisms and can be initiated by enzymes or presence of certain chemicals like acids or peroxides, both which are usually secreted by organisms [15]. However, chemical and physical processes also effect the biodegradation and can even initiate it. Some factors are, chemical hydrolysis, thermal degradation, oxidation and photo degradation [20].

Mineralization is when microorganisms digest the smaller polymer pieces generated from the depolymerization. The water-solubility of the polymer chains are limited and they are too big to directly be consumed by the microorganisms. This means that mineralization occurs when the polymers are sufficiently cleaved to generate water-soluble intermediates that can be transported into the cells [20]. Then, the monomeric or oligomeric fragments are metabolized into adenosine triphosphate (ATP), gases, water, minerals and biomass [15, 18]. The mineralization can be either aerobic or anaerobic. The aerobic process results in formation of carbon dioxide and the anaerobic of methane [1].

2.3.3 Complexity with biodegradation

As mentioned earlier, plastics usually contain some additives and even though a product is made out of biodegradable polymers, the plastic might still not be biodegradable if the additives do not biodegrade [15].

The biodegradation of a polymer might not be homogeneous which means that the degradation is not the same throughout the whole molecule [15]. Enzymatic degradation is an example of this. The material gradually degrades under impact of enzymes, from the surface and inwards since macromolecular enzymes cannot diffuse through the polymer [18].

The biodegradation process of a polymer depends on presence of microorganisms which are affected by the surrounding environment. Therefore factors like humidity, temperature, pH, access of oxygen, presence of

nutrients and other factors that affect the access of microorganisms, should be considered for the intended place of biodegradation of the material [20]. Other factors that also have impact on the process, are the chemical and physical properties of the polymer. Cross linking, purity, chemical reactivity, porosity etc. affects the accessibility of the material for depolymerization [19].

2.3.4 Methods for measuring biodegradability of a material

There are several ways to measure if a material undergoes biodegradation. The following methods are just a few examples.

- **Respiration test** For biodegradation to happen there must be a supply of oxygen. By putting a substrate and soil in incubation, the amount of consumed oxygen can be measured. The biological oxygen demand (BOD) can be expressed as a percentage of the theoretical oxygen demand (TOD) [18].
- **CO₂ or CH₄ evolution test** The evolved amount of CO₂ or CH₄ from a substrate during the mineralization process can be measured by measuring increased pressure or volume due to evolved gases. Gas chromatography analysis (GC) of the gas can also be conducted to analyse its composition [18]. The set up for this method could be a two-flask system. In the first flask the substrate is mixed with soil, the other flask contains CO₂ sorbant. It is important that the system contains enough oxygen to sustenate the biodegradation process [18]. Some of the evolved carbon from the substrate convert into biomass. To get the total amount of evolved CO₂ from the substrate additional analyses of soluble and solid material has to be made [18].

2.4 Polylactic acid

Polylactic acid (PLA) is polymerized from lactic acid(α -hydroxypropionic acid), it is biodegradable and can be produced from renewable sources, such as corn, potato and sugarcane [21]. The melting point for PLA is around 140-175 °C, and the glasstransition temperature is 58°C [1]. The lactic acid molecule is chiral, there are two stereoisomers of it L-lactic acid and D-lactic acid, see Figure 3 [23].

There are therefore three possible ways of combining the optically active forms when PLA is produced; combining two L-lactates to form LL-lactide, combining two D-lactates to form DD-lactide or lastly, combining L-lactate with D-lactate to retrieve DL-lactide (also called meso-lactide). They give PLLA, PDLA and PDLLA respectively [21].

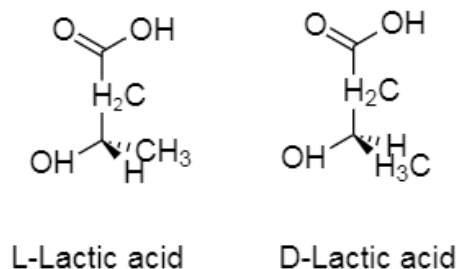


Figure 3: Stereoisomers of lactic acid

2.4.1 Production

Lactic acid can be produced in two ways, either by bacterial fermentation or by chemical synthesis. Bacterial fermentation is preferred due to better production capacity and both stereoisomers of lactic acid can be produced [24].

The raw materials for fermentation are starch and sugar. Depending on the bacteria that fulfills the fermentation, the process can either be homofermentative (one product is produced) or heterofermentative (multiple products are produced). To prevent unwanted by-products and to get the optimum yield of lactic acid, the homofermentative method is more commonly used in the industry. Unlike the heterofermentative process that yields around 50% lactic acid, the homofermentative process yields more than 80% lactic acid which means that 1 mole of glucose yields 2 moles of lactic acid [25].

During chemical synthesis of lactic acid, hydrogen cyanide is firstly base catalyzed with acetaldehyde and lactronitrile is produced. The other steps are hydrolysis from lactronitrile to produce lactic acid, esterification of lactic acid with alcohol and lastly purification by distillation [26].

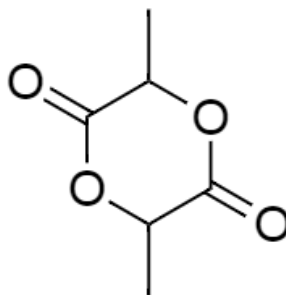


Figure 4: Lactide molecule

The produced lactic acid is then polymerized to produce PLA. This can occur either by direct polycondensation (DP) or by a ring-opening polymerization (ROP) from lactide [27, 25], see picture 4 for structure. The different manufacturing techniques affect the M_w of the produced PLA. Usually the high M_w is the most desired product as it has the highest commercial value in fibre, textile and packaging industries [24].

DP is an example of polycondensation. During the process, the carboxyl and hydroxyl groups are connected as water molecules are eliminated [27]. However, DP is considered to be the most cost efficient method to produce high M_w PLA. But addition of coupling agents are needed to increase the molecular weight of the product which increases cost and complexity of production [24].

During production via ring-opening polymerization, the purity of lactide is easier to control which makes it possible to produce polymers with specific properties. This also means that polymers with a wide range of molecular weight can be retrieved [27].

PLA is sensitive to higher temperature, at 230-260 °C it decomposes and at temperature above 60°C it loses its structural properties. The usage of PLA is therefore limited to room temperature [25].

2.4.2 Polymer blends with PLA

PLA is rather brittle, has low impact strength and has low heat resistance, therefore it could be of interest to enhance its properties by blending it with other polymers [1]. To obtain a good polymer blend, the polymers have to be melted together at a certain temperature. For PLA the lower temperature limit should be about 180°C. This has to be taken into consideration when choosing the polymers to blend with PLA, since PLA risks undergoing thermal degradation at temperatures above 270°C [25].

It is also important to obtain good interfacial adhesion of the blending polymers, which means that the added polymers should be compatible with PLA. To retain the biodegradability of the polymer blend, the added polymers should also be biodegradable [25].

2.4.3 Biodegradation

For PLA the depolymerization step occurs in the form of hydrolysis of the ester linkages in the polymer chain [28]. This step could also occur by enzymatic attack [21].

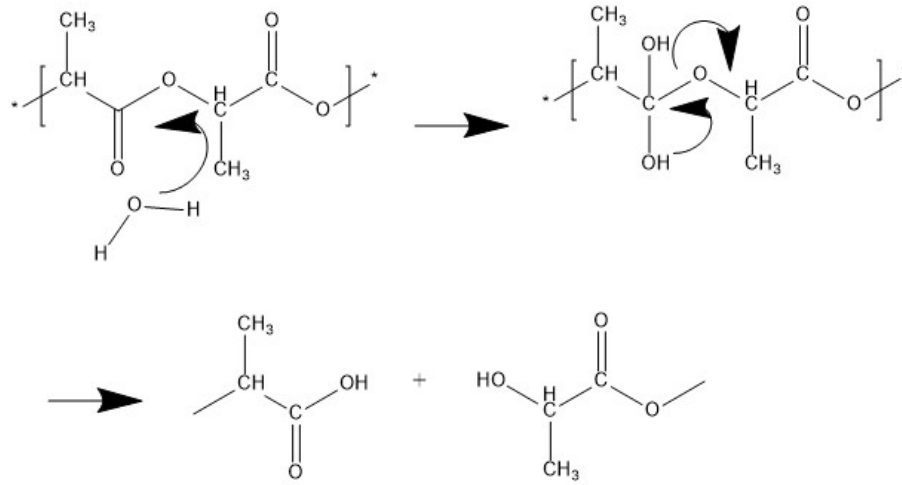


Figure 5: Hydrolysis of PLA

Figure 5 shows the hydrolysis and how the fragmentation of the PLA chain happens. This fragmentation leads to a higher number of carboxylic end-groups, when these acid end-groups dissociate the environment becomes acidic and the hydrolysis is further catalyzed. The rate of hydrolysis can be described with Equation 1 and it is dependent of the concentrations of carboxylic acid, esters and water,

$$\frac{d[COOH]}{dt} = k[COOH][H_2O][E]. \quad (1)$$

Since reaction 1 is further catalyzed with increased dissociation, it is seen as an autocatalyzed reaction [29].

2.4.4 Biodegradation in real soil environment

Reports were biodegradation of PLA has been tested in real soil environments has been studied. PLA films of different thicknesses and PLA fibers were tested in Mediterranean soil conditions for 11 months. The temperature of the site varied between 5-30 °C during the test period. The first significant visual signs of degradation was observed after 7 months. The thinner the film, the more pronounced signs of degradation were observed, but the general degradation was low [30]. Films of PLLA were buried outdoors in soil in the south of Finland during 2 years. The study showed that degradation by hydrolysis happened between month 12-24 and that migration and assimilation of low molecular weight compounds occurred between month 20-24. No samples did completely biodegrade during this period [31]. In Costa Rica, PLA-films were buried outdoors during 3 months. The average soil temperature was 27 °C and the average humidity level was 80%. The result showed that the average degradation rate of the plastic films were 7675 M_w /week and an estimated visible degradation time of 6 months was presented [32]. Among other biodegradable plastics, PLA films were buried in soil at 19 different sites in Japan for a year. The study showed that PLA was the plastic that degraded the slowest of the biodegradable plastics. The only two sites where the PLA were completely degraded after 9 months was in greenhouses. None of the PLA films that was buried outside completely degraded after 12 months [33].

2.4.5 Optimal parameters for biodegradation in soil

A study investigated the biotic and abiotic effects of degradation of PLA. They concluded that the highest rate of biodegradation in soil occurred in an environment rich of microorganisms and with high temperature (45-50 °C). The results also showed that after 1 year in 25°C or 37°C, no signs of changes in tensile stress was found. This can be interpreted as a risk for PLA pollution in the future [34].

For a successful hydrolysis of PLA to happen, the presence of water is necessary. The amorphous parts of a polymer has a higher water solubility than the crystalline parts which means that amorphous parts will hydrolyse more rapidly since there is a greater access of water there [28, 1].

For PLA the level of L-lactide in the plastic seems to affect the biodegradation of PLA [22].

2.5 Starch

Starch is produced in plants from the glucose that is produced during photosynthesis. It is stored in the plants as carbohydrate reserves in the form of crystalline granules. Some crops that has a high starch content are potato, maize and cassava [12].

Starch is made out of two biopolymers, amylose and amylopectin. Amylose is made out of α -D-glucose units that are linked to each other with $\alpha(1 \rightarrow 4)$ glycosidic bonds, creating a helical structure, Figure 6. The amylopectine contains both $\alpha(1 \rightarrow 4)$ glycosidic bonds and branched $\alpha(1 \rightarrow 6)$ bonds, see Figure 7. The ratio between the two depends on the origin of the starch, but an average number for native starches are 85-70% amylopectin [36, 37, 12].

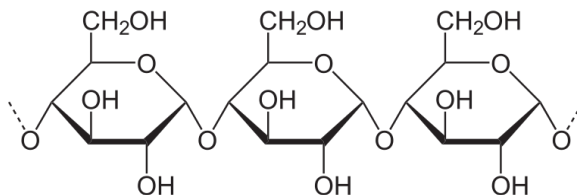


Figure 6: Structure of amylos. Used with licence rights. Source: <https://de.wikipedia.org/wiki/Datei:Amylose3.svg>

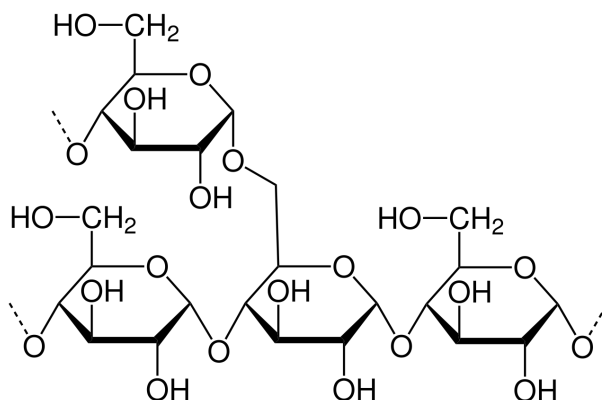


Figure 7: Structure of amylopectin. Used with licence rights. Source: https://commons.wikimedia.org/wiki/File:Amylopektin_Haworth.svg

Starch is naturally found in plants in the form of granules. These are partly crystalline (about 20-45%) with amorphous parts formed by amylose. Native starch is not thermoplastic, the melting point is higher than the temperature for thermal degradation. This means that pyrolysis occurs before the material reaches its melting point [38].

2.5.1 Structure of starch

The primary structure of starch is the linkage of amylopectin and amylose. The branches of amylopectin form a secondary structure in form of double helices and together they form a superhelix [39].

In plants, starch appears in the form of granules. The shape and size of these varies, but normally the diameter varies from 1 μm to 100 μm [40].

The helical structures crystallize and form granules, which are hydrophilic. Hydrogen bondings are formed with the hydroxyle groups leading to strong intermolecular association [37].

2.5.2 Polymer blends with starch

Pure starch is brittle and highly water sensitive. Products made in starch can swell when they come in contact with moisture. therefore it has been of interest to combine starch with other polymers. Various attempts has been made to blend starch with traditional synthetic polymers to increase the biodegradability and reduce costs. However, it is difficult to achieve a good blend since most of these polymers are hydrophobic and thermodynamically immiscible with starch [41]. A blend between the two will most likely result in phase separation and poor mechanical properties. However, simple mixing without any reactions does not lead to phase separation under certain percentages. Starch can also be blended with polymers by reactions which generates certain bonds as carboxyl, anhydride or epoxy. Graft copolymerization is another way to obtain starch based mixtures. The synthetic monomers bind to hydroxyl groups on the starch molecules to at last be polymerized [42].

2.5.3 Thermoplastic Starch

Starch granules can be processed by heat and plasticizers to form a viscous melt called thermoplastic starch (TPS). Limited amount of water combined with heat is used to disrupt the order and crystallinity of the granules [38]. Common plasticizers that are used to produce TPS are water and glycerol [11].

Retrogradation is a crystallization process that happens when starch that has been heated is cooling down, and the hydrogen bonds and alignment of molecular chains rearranges to form a more crystallized state. This makes the material more brittle, but the process can be limited by the addition of plasticizers [11, 12].

To process the melt of the starch granules, extrusion and injection molding can be used [37]. The thermoplastic starch can be re-melted and re-extruded [12]. In DSC it shows a gelatinisation peak at 60-70 $^{\circ}\text{C}$, if the material has 15-25 wt% water [39].

2.5.4 Biodegradation of thermoplastic starch in soil environments

In a study, it was desired to decrease the water absorption and delay the biodegradation of TPS by adding two kinds of fillers, eggshell and commercial calcium carbonate. The result showed that the lowest absorption was retrieved with eggshell fillers and the highest without any fillers. Both fillers managed to delay the biodegradation. During biodegradation of TPS without fillers, 71.55% weight were lost after 15 days [40].

A study was made on polypropylene blends with starch in the form of agricultural waste and its degradation. In the study it was concluded that the starch phase of the blends did biodegrade, but the polypropylene parts did not. The rate of biodegradation depended among others, on the on the ability to absorb water which was directly linked to the ratio of amylopectine in the material [43].

Degradation of different polystyrene (PS) and starch blends were analyzed in another study. The purpose of the study was to see if starch improved biodegradation of PS in the samples. The biodegradation of the starch in the blends did not lead to a significant effect on the degradation of polystyrene [44].

2.6 Standards for biodegradation of plastics in soil

During this thesis ISO 17556 for biodegradation of plastics in soil has been studied, it is equivalent to the American standard ASTM D5988. Two other standards for ecotoxicity (DIN 38412 and EN 13432) has also been examined.

2.6.1 ISO 17556

This standard is designed to yield the optimum degree of biodegradation of plastic material in test soil. The described method can also be used to determine potential biodegradability of the material. Depending on the soil used in this test, it could simulate the biodegradation process of a material in a natural environment.

The soil and plastic material are mixed together. The amount of consumed oxygen or evolved amount of CO₂ is determined. The test is terminated when a constant biodegradation level has been achieved or at the latest, after six months. The mixture of soil and plastic should take place in a dark place maintained at a constant temperature within 20-28 °C. In this standard they suggest that either natural soil from the surface layer of fields, forests or standard soils could be used. If it is desired to look at a degradation process similar to the one that would happen in a natural environment, a non-adapted soil could be used as an inoculum.

In that way, the bacteria that mineralize the samples in the test, are naturally occurring.

In the test, a reference material and a negative control is needed. The reference material should be a well-defined biodegradable polymer and the negative control should be a non-biodegradable polymer.

Experiments has shown that the degree of biodegradation is almost independent of form and shape of the test material. However, the rate of degradation depends on this. For the test, the test material should preferably be in powder but may also be in the form of films, fragments or shaped articles.

2.6.2 Standards for ecotoxicity

Polymers are generally considered as an inert material. During biodegradation however, intermediates and are released from the material. Water-soluble chemicals has a tendency to spread to groundwater or transport via watercourses and they are easily absorbed by organisms. therefore it is important to assure that these produced intermediates are not harmful for the environment. [18].

DIN 38412 is a standard for examining toxicity of waste water by conducting tests on Daphnia. Different concentrations of the water-soluble intermediates are mixed with a numbers of Daphnia to see what concentration they can recover from.

EN 13432 is a standard to ensure that a material (including colours and glues etc) is industrially compostable. In this standard a plant toxicity test is also included where the composts effects on plant growth is tested. The compost is mixed with reference soil and seeds from OECD guidance 208 are planted.

3 Method

3.1 Differential scanning calorimetry (DSC)

During DSC analysis, changes in enthalpy are detected which show melting points, T_g 's and crystallization temperatures. These values can be compared to literature values, to estimate what kind of material the pegs are made of.

The temperature program for the DSC analysis was -10-220 °C, 10 °C/min heating rate with nitrogen gas for all four samples. Standard aluminum 40 μ l pans were used and the samples were prepared by cutting of small pieces from the pegs.

3.2 Thermogravimetric analysis (TGA)

In TGA analysis the mass of the sample is continuously measured as the temperature changes over time. Material characterization of the samples can be performed by looking at decomposition patterns and mass loss steps of the materials.

The first segment of the temperature program for the TGA analysis was 25-600 °C with 20 °C/min nitrogen gas. The second was 600-900 °C with 20 °C/min oxygen gas. A third isothermic segment at 900°C with oxygen gas was also used to burn of the sample.

The pans used were Alumina standard 70 μ l and the samples were prepared by cutting off small pieces from the pegs.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

During FTIR, a spectra that contain peaks of absorbance for different chemical bonds of the sample, is retrieved. Evaluation of these peaks will be made by analysing the peaks and by using the software program OMNI spectra that compares the spectra to different ones in its database.

The wave numbers of the instrument ranges from 400 to 4000 cm^{-1} . The crystal was ATR and the angle of incidence was 45°.

3.4 Nuclear magnetic resonance (NMR)

Some nuclei have a spin that generates a magnetic field. By applying an external magnetic field, the nuclei will align to that field. By irradiating the nuclei they can shift and return to their original state which emits energy. This energy can be translated into a spectra. How likely the nuclei are to flip and at what wavelengths they do that, depends on nearby atoms. NMR can therefore be used for qualitative measurements.

Only the getcamping and PLA samples were able to be dissolved in common organic organic solvents at ambient conditions. Therefore this method could not be performed on the other two samples. The solvent used for getcamping and PLA was chloroform.

4 Results and discussion

4.1 FTIR

The three commercially available pegs and the peg from a previous Bachelor thesis (BT) at Husqvarna that is made of PLA, were tested with FTIR analysis. The result are shown in Figure 8 and Figure 9.

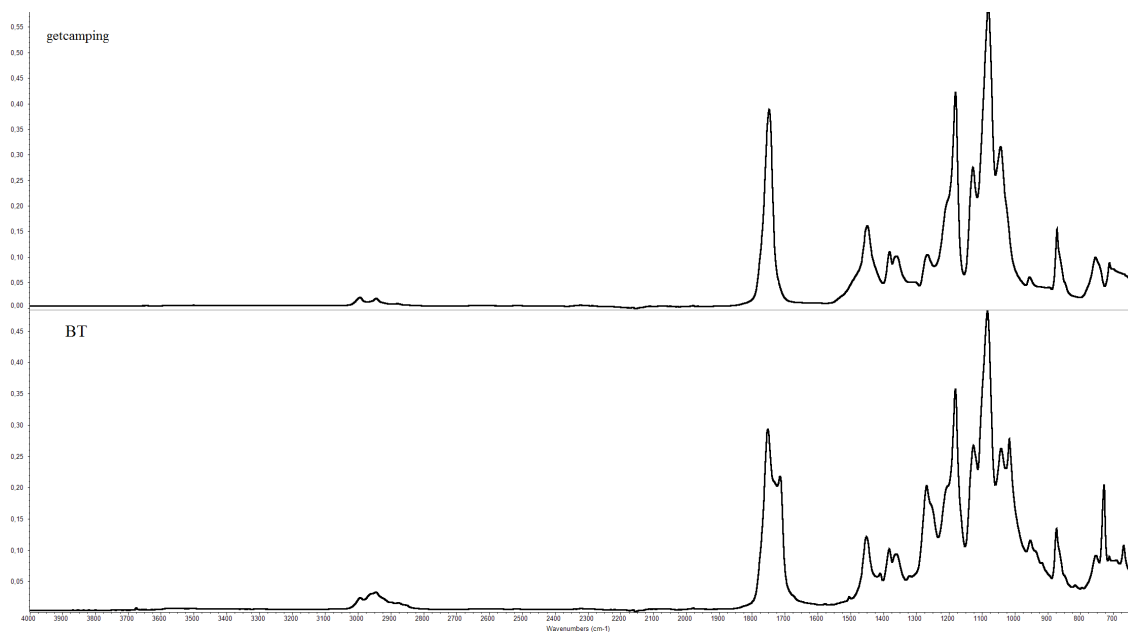


Figure 8: FTIR results of BT and getcamping. Note the similarities in peaks of the two samples.

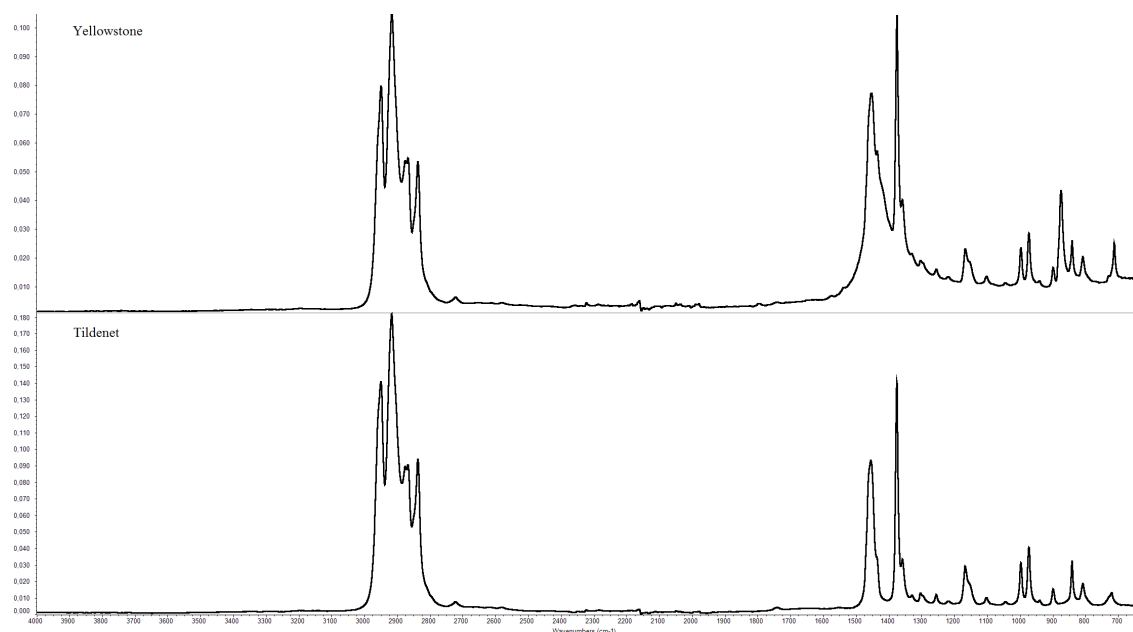


Figure 9: FTIR results of Yellowstone and Tildenet. Note the similarities in peaks of the two samples.

When the samples from the FTIR analysis were done, OMNI spectra was used to conduct the evaluation, see Table 2.

Table 2: Matches in OMNI spectra software program

Sample	Highest match in database %	Matched substance
Tildenet	93.76	Polypropylene
Yellowstone	88.01	Polypropylene
getcamping	67.66	α -Methoxyphenylacetic acid
BT	62.46	α -Methoxyphenylacetic acid

The matches in the software program is based on existing FTIR curves from different databases. These test matched with samples from the following databases: "Hummel polymer and additives" and "Hummel polymer sample library".

The getcamping product showed characteristic frequencies for PLA, C=O ester stretching at 1750, C-H bending alkane methyl group at 1450 and C-O stretching in the area from 1080 to 1180. The spectra also corresponded well with the spectra from the BT sample that also showed these characteristic peaks. The database match for both these samples was low, around 60-70%. Searches for polylactic acid, PLA and α -hydroxypropionic acid did not get any hits which indicated that PLA was not included in the database

which explain the low matches.

The sample from Yellowstone and Tildenet correspond well with the characteristic spectra for PP. The peaks ranging from 2800-3000 show C-H stretching vibration, CH₂ bending vibration around 1450, CH₃ bending vibration around 1376 and CH₂ rocking vibration at 973. Both these samples matched well (over 90%) with polypropylene in the database as well.

4.2 NMR

The two samples of pegs that were dissolved in chloroform (BT and getcamping) was tested with NMR analysis, see Figure 10.

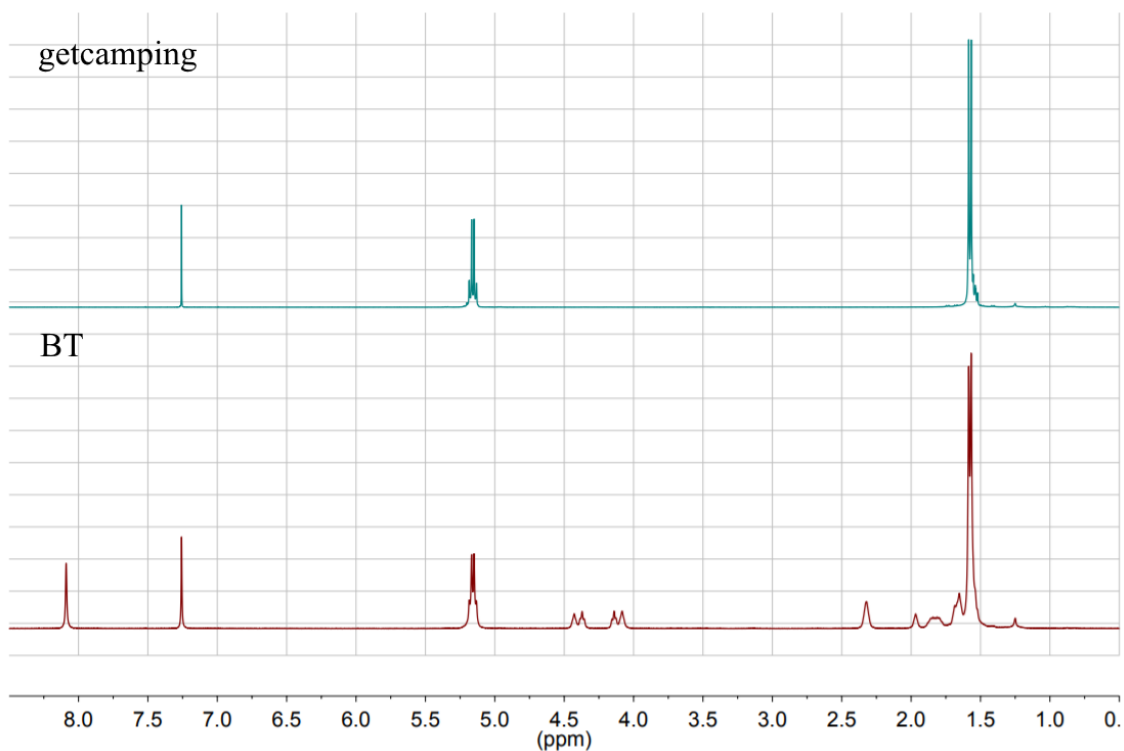


Figure 10: NMR results for BT and getcamping products. Note the corresponding peaks around 7.3, 5 and 1.5

The getcamping product and BT sample showed characteristic peaks for PLA at 1.5 and 5. The peak around 7.3 in both spectra, is due to chloroform.

4.3 DSC

DSC was conducted on all four samples of pegs, and the respective curves are gathered in Figure 11.

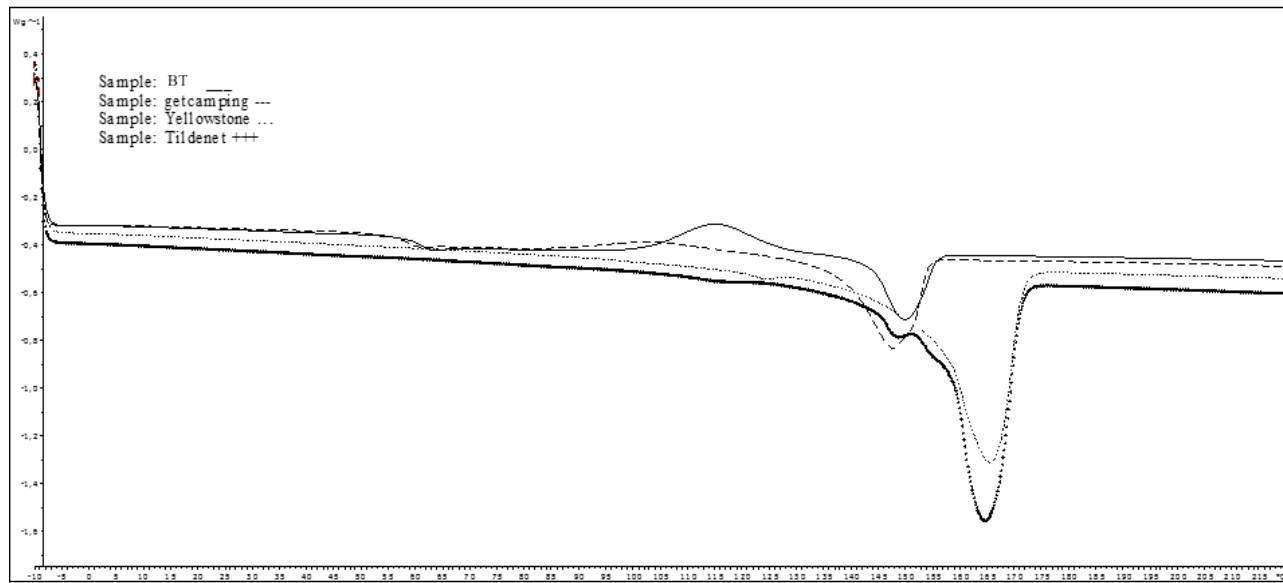


Figure 11: DSC curves for samples from getcamping, Tildenet and Yellowstone and for BT. Note that only two samples (BT and getcamping), show distinct T_g 's

The T_m for Yellowstone and Tildenet were 165 °C and 164°C respectively which correlate well with the literature value for PP [13].

The getcamping sample showed T_m at 148°C and T_g at 59°C which corresponds well with data from the PLA sample, T_m at 150 °C and T_g at 59°C and with the literature value [1].

4.4 TGA

The four samples of different pegs were analyzed with TGA. The result is found in Figure 12.

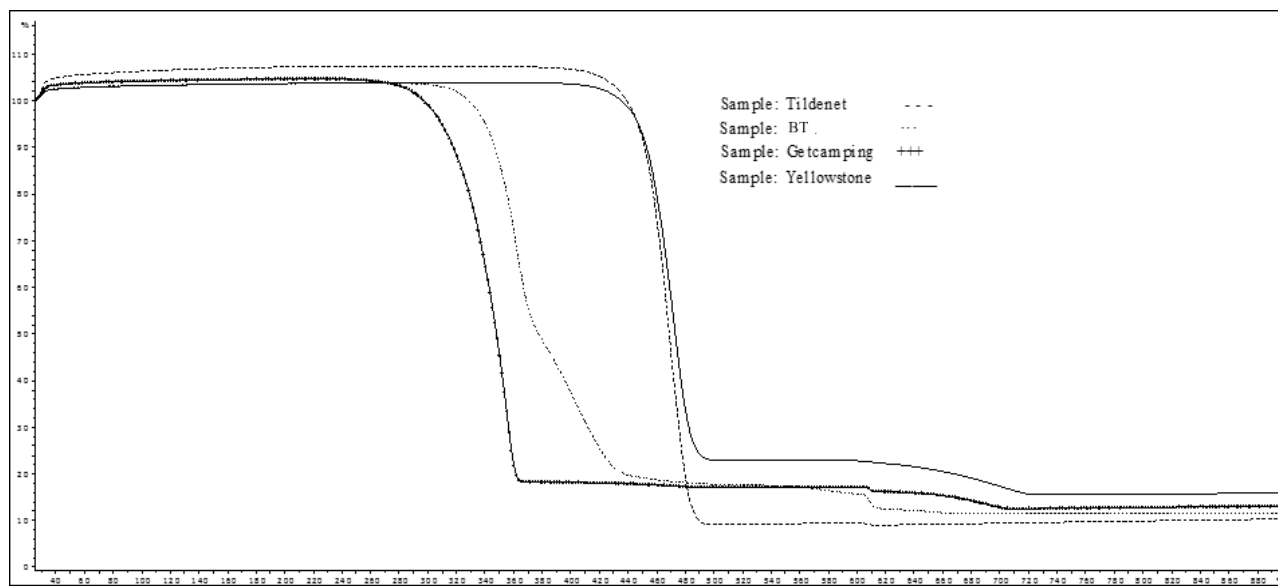


Figure 12: TGA curves for samples from getcamping, Tildenet and Yellowstone and for BT

Tildenet and Yellowstone showed single degradation steps with a major step around 470 °C. This is consistent with the thermal degradation pattern of PP. The result shows that Tildenet consists of a higher part of PP (around 10 percentage points) than Yellowstone.

The sample from getcamping showed a single mass loss step around 340°C. The BT sample could possibly show a second degradation step but based on this result it is difficult to confirm that.

4.5 Discussion of materials for the pegs

The studies of biodegradation of pure PLA in outdoor conditions in soil that were presented in chapter 2.4.4, show that biodegradation under these conditions is slow. In all the studies, the tests has been conducted on small plastics films. Since the pegs are much thicker and enzymatic degradation is not homogenous, the biodegradation can be expected to be even slower for the pegs. The studies of biodegradation of PLA-films in outdoor conditions also show that degradation is faster in humid and warm environments like in greenhouses and in the study made in Costa rica. Studies show that high temperature (up to 50 °C) and high humidity combined with rich environment of microorganisms is optimal for degradation of PLA. But this environment can still require a long degradation time. Since these conditions are rare during winter in most parts of Europe, it is likely that the degradation process is even slower, up to several years.

Since the biodegradation of PLA is slow, the usage of this plastic could lead to pollution problems. For this application this might not be a problem since the pegs will be buried anyways. However, for some applications this might lead to increased pollution as people might not pick up the litter since it is biodegradable.

The biodegradation process of TPS is much faster than the one for PLA. Even if the biodegradation studies also are made on films, it seems to be unlikely that the degradation process should take several years. However, TPS high sensitivity to moisture makes it an unattractive material for the application. Eventual swelling of the material due to moisture leads to loss of mechanical properties. It would be difficult to push the pegs into the ground if their mechanical properties are impaired. However, the right choice of additives or polymer blends might be able to improve the properties of TPS.

PP is a non-biodegradable material and it is therefore not a suitable material for the application biodegradable pegs.

5 Conclusion

The conducted analysis show that the getcamping product is produced from PLA, the Tildenet and Yellowstone products are made of PP.

PLA could be a suitable material for the pegs. It is possible to manufacture from biobased sources and it is biodegradable. The degradation process has shown to be quite slow, the optimal parameters for biodegradation are not fulfilled outside in Europe. The monomers of PLA are non-toxic and would not contribute to spreading harmful chemicals in the environment.

TPS biodegrades fast and is produced from non-toxic monomers. However solely TPS does not seem to be a good material for the pegs as it is sensitive to moisture. That might be able to correct with blends or additives.

It has to be noted that eventual polymer blends and additives also affect whether the material is biodegradable or not. The complete plastic with additives would have to be tested according to standards to assess its biodegradability. Additives might also affect the toxicity of the material and release harmful chemicals during degradation.

6 Further studies

This scope for this thesis has been on biodegradation processes in soil. As the depolymerization of the polymer chains proceeds, shorter pieces of the original chain are produced. These could be transported by water and eventually end up in water courses. Therefore it is important to establish whether the polymers biodegrades in water as well. If they do not, that would probably lead to microplastic problems.

The current pegs are manufactured from rest products. It is difficult to assess if biodegradable pegs would be better for the environment or not. Based on this study, it is not possible. A lifecycle analysis (LCA) has to be conducted in order to assess that.

References

- [1] Ullmann's Polymers and Plastics - Products and Processes, 4 Volume set [e-book]. John Wiley Sons;2016 [Cited: April 30]. Available from: http://app.knovel.com/web/toc.v/cid:kpUPPPPVs1/viewerType:toc//root_slug:ullmanns-polymers-plastics/url_slug:table-6-properties-biodegradable?b-q=PLA%20Tg%2C%20melting%20point&b-subscription=true&b-group-by=true&b-sort-on=default&b-content-type=all_references&include_synonyms=yes
- [2] Huang JC, Shetty A S, Wang MS. Biodegradable plastics: A review. Advances in Polymer Technology [internet] 1990 [Cited: May 22];10(1):23-30. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/adv.1990.060100103>
- [3] Intergovernmental panel on climate change. Global Warming of 1.5°C [internet]. Switzerland: Intergovernmental panel on climate change; 2018 [Cited 23 May]. Available from: https://report.ipcc.ch/sr15/pdf/sr15_spm_final.pdf
- [4] Lundblad RL, Macdonald FM. Handbook of Biochemistry and molecular biology. 5th edition. London: CRC press; 2018.
- [5] van der Hoeven D. Bioplastics: end the confusion [internet]. Bio Based Press; 2017[April 5; cited May 23]. Available from: <https://www.biobasedpress.eu/2017/04/bioplastics-end-confusion/>
- [6] Arkatkar A, Arutchelvi J, Sudhakar M, Bhaduri S et al. Approaches to Enhance the Biodegradation of Polyolefins. The Open Environmental Engineering Journal [internet]. 2009 [cited May 28];(2):68-80. Available from: <https://benthamopen.com/ABSTRACT/TOENVIEJ-2-68>
- [7] Naturskyddsföreningen. Allt du (inte) vill veta om plast [internet] SIDA;2014.[Cited: April 29]. Available from: <https://www.naturskyddsforeningen.se/allt-du-inte-vill-veta-om-plast>
- [8] Chemsec SINLIST [internet]. [Cited: April 30]. Available from: <https://chemsec.org/sin-list/>
- [9] Chemsec SINLIST [internet]. Acrylonitril. [Cited: April 30]. Available from: <https://sinlist.chemsec.org/search/search?query=acrylonitril>
- [10] Fritz D. Technischer Stand ökologischer Kunststoffe, Einsatzmöglichkeiten und Grenzen. Hochschule Aalen. April 2018
- [11] Wypych G. Handbook of Plasticizers[e-book]. 3rd Edition. ChemTec Publishing; 2017[cited May 20] Available from: <https://app.knovel.com/hotlink/toc/id:kpHPE00024/handbook-plasticizers/handbook-plasticizers>

- [12] Prabhu T N, Prashantha K. A review on present status and future challenges of starch based polymer films and their composites in food packaging applications. *Polymer Composites* [internet]. October 2016[Cited: May 14];39(7)2499-2522. Available from: <https://onlinelibrary.wiley.com/doi/abs/10.1002/pc.24236>
- [13] Klason C Kubát J, Boldizar A Rigdahl M. *Plaster: materialval och materialdata*. 5th edition. Stockholm: Teknikföretagen: 2006.
- [14] Scalenghe R. Resource or waste? A perspective of plastics degradation in soil with a focus on end-of-life options. *Heliyon* [internet]. 2018 December[Cited: May 27]; 4(12). Available from: <https://www.sciencedirect.com/science/article/pii/S2405844018301336>
- [15] European Committee for Standardization. *Plastics -Guide for vocabulary in the field of Degradable and Biodegradable Polymers and Plastic Items*, CEN/TR 15351:2006 report (2006). [Cited April: 3]. Available from: <http://esearch.cen.eu/>
- [16] Jones RG. Kahovec J. Stepto R. Wilks M et al. *Compendium of Polymer Terminology and Nomenclature, IUPAC Recommendations 2008* [e-book]. Cambridge: The Royal Society of Chemistry; 2009. [Cited: 8 April]. Available from: <https://www.iupac.org/cms/wp-content/uploads/2016/01/Compendium-of-Polymer-Terminology-and-Nomenclature-IUPAC-Recommendations-2008.pdf>
- [17] NOAA. What are microplastics?[internet]. National Ocean Service website. 2018[25 June; cited 28 May 2019]. Available from: <https://oceanservice.noaa.gov/facts/microplastics.html>
- [18] Bastioli C. *Handbook of biodegradable polymers*. 2nd edition. Shrewsbury: Smithers Rapra Technology Ltd; 2014.
- [19] Nampoothiri K M, Nair R N, Pappy John R. An overview of the recent developments in polylactide (PLA) research. *Bioresource Technology* [internet]. 2010 November[Cited: April 17];101(22):8493-8501. Available from: https://ac.els-cdn.com/S0960852410009508/1-s2.0-S0960852410009508-main.pdf?_tid=2df86dcf-f11d-4b82-bb35-3472950578a7&acdnat=1555490071_7947423edd1af3de170008a694e568a0
- [20] Muller R.J. Biodegradability of Polymers: Regulations and Methods for Testing. In *Biopolymer Online* [internet]. 2005 [Cited: April 17];365-374. Available from: https://application.wiley-vch.de/books/biopoly/pdf_v10/vol110_19.pdf

- [21] Qi X, Ren Y, Wang X. New advances in the biodegradation of Poly(lactic) acid. *International Biodegradation Biodegradation* [internet]. 2017 February [Cited: April 16];117:215-223. Available from: <https://www.sciencedirect.com/science/article/pii/S0964830517300100>
- [22] Urayama H, Kanamori T, Kimura Y. Properties and biodegradability of polymer blends of poly(L-lactide)s with different optical purity of the lactate units. *Macromolecular Materials and Engineering* [internet]. February 2002 [Cited: April 17]287(2):116-121. Available from: <https://onlinelibrary.wiley.com/doi/epdf/10.1002/1439-2054%2820020201%29287%3A2%3C116%3A%3AAID-MAME116%3E3.0.CO%3B2-Z>
- [23] Rojan P, Nampoothiri KM, Pandey A. Fermentative production of lactic acid from biomass: an overview on process developments and future perspectives. *Applied Microbiology and Biotechnology* [internet]. 2007 March [Cited: April 16];74(3):524-534. Available from: <https://link.springer.com/article/10.1007%2Fs00253-006-0779-6>
- [24] Castro-Aguirre A, Iñiguez-Franco F, Samsudin H, Fang X et al. Poly(lactic acid)-mass production, processing, industrial applications, and end of life. *Advanced Drug Delivery Reviews* [internet]. 2016 December [Cited: April 24];107(15):333-366. Available from: <https://www.sciencedirect.com/science/article/pii/S0169409X16300965>
- [25] Sin LT, Rahmat AR, Rahman WAWA. *Poly(lactic) Acid - PLA Biopolymer Technology and Applications* [e-book]. Oxford: Elsevier;2012 [Cited: April 23]. Available from: [https://app.knovel.com/hotlink/toc/id:kpPAPLABT1/poly\(lactic\)-acid-pla-biopolymer/poly\(lactic\)-acid-pla-biopolymer](https://app.knovel.com/hotlink/toc/id:kpPAPLABT1/poly(lactic)-acid-pla-biopolymer/poly(lactic)-acid-pla-biopolymer)
- [26] MH Hartmann. *High molecular weight Poly(lactic) Acid Polymers* [e-Book]. Springer, Berlin, Heidelberg;1998 [Cited: April 23]. Available from: https://link.springer.com/chapter/10.1007/978-3-662-03680-8_15
- [27] Hu Y, Daoud WA, Cheuk KKL, Lin CSK. Newly Developed Techniques on Polycondensation, Ring-Opening Polymerization and Polymer Modification: Focus on Poly(Lactic Acid). *Materials (Basel)*[internet]. 2016 February [cited May 16];9(3):133. Available from: <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5456738/>
- [28] Karamanlioglu M, Preziosi R, Robson GD. Abiotic and biotic environmental degradation of the bioplastic polymer poly(lactic acid): A review. *Polymer Degradation and Stability* [internet]. March 2017 [Cited: April 18] 137:122-130. Available from: <https://www.sciencedirect.com/science/article/pii/S0141391017300095>

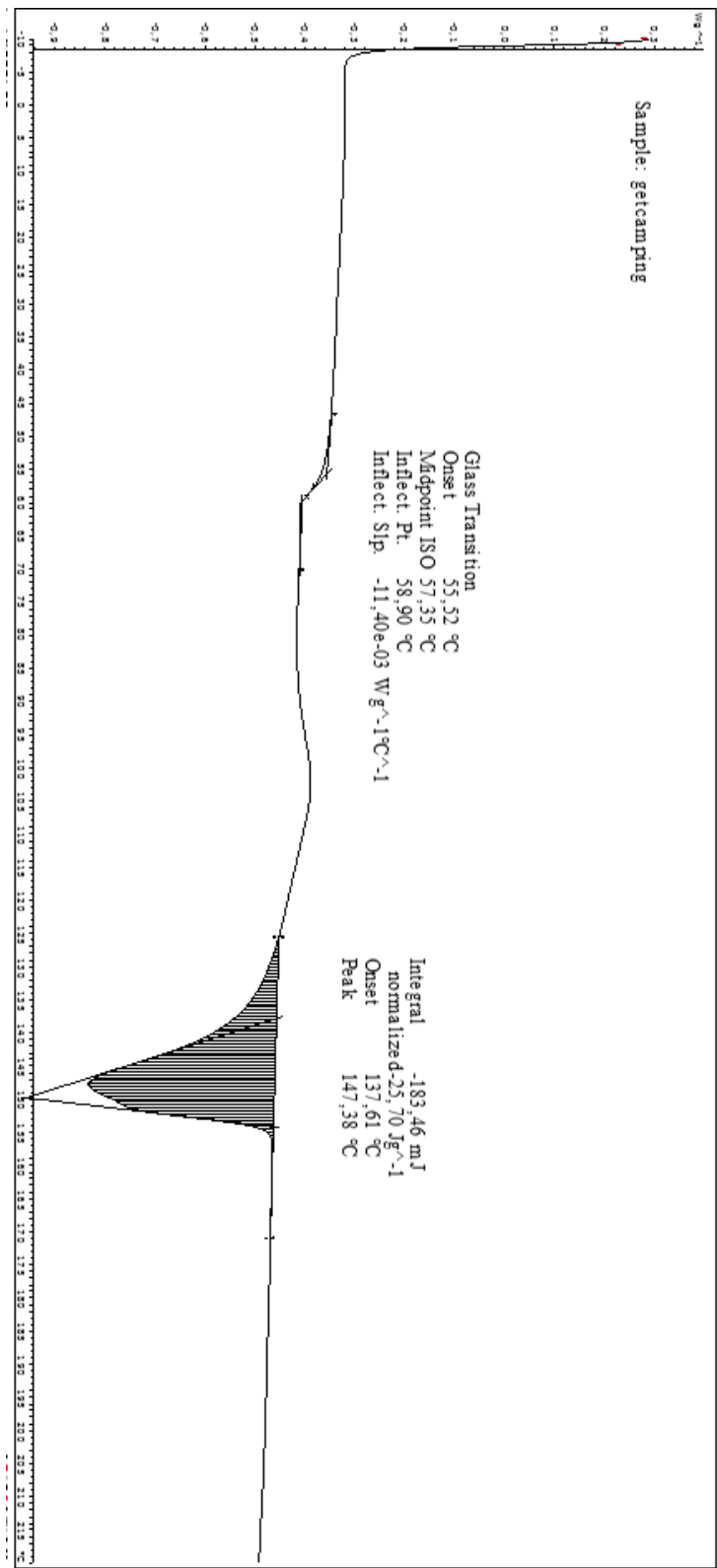
- [29] Siparsky GL, Voorhees KJ, Miao F. Hydrolysis of polylactic acid (PLA) and polycaprolactone (PCL) in aqueous acetonitril solutions: Autocatalysis. *Journal of Environmental Polymer Degradation* [internet]. January 1998 [Cited: April 23];6(1):31–41. Available from: <https://link.springer.com/article/10.1023/A:1022826528673>
- [30] Rudnik E, Briassoulis. Degradation behaviour of Poly(lactic acid) films and fibers in soil under Mediterrenean field conditions and laboratory simulations testing. *Industrial Crops and Products* [internet]. May 2011 [Cited: 16 April];33(3):648-658. Available from: https://ac.els-cdn.com/S0926669010003511/1-s2.0-S0926669010003511-main.pdf?_tid=1b257daf-0173-474f-b541-d74666cc3607&acdnat=1555504846_1dc930a6c7f60ff2889c56c9b8e3d865
- [31] Gallet G, Lempiäinen R, Karlsson S. Characterisation by soil phase microextraction-gas chromatography-mass spectrometry of matrix changes of poly(L-lactide) exposed to outdoor soil environment. *Polymer Degradation and Stability* [internet]. 2000 [cited April 17];71(1):147-151 Available from: <https://www.sciencedirect.com/science/article/pii/S0141391000001658>
- [32] Ho K-L G, Pometto III A L, Gadea-Rivas A, Briceño J A et. al. Degradation of Polylactic Acid (PLA) in Costa Rican Soil and Iowa State Unoversity Compost Rows. *Journal of environmental polymer degradation* [internet]. October 1999 [Cited: April 17]; 7(4):173–177 Avalaible from: <https://link.springer.com/article/10.1023/A:1022874530586>
- [33] Hoshino A, Sawada H, Yokota Masahisa, Tsuji M et. al. Influence of Weather Conditions and Soil Properties in Degradation of Biodegradable Plastics in Soil. *Soil Science and Plant Nutrition* [internet]. April 2000 [Cited: April 18]; 47(1):35-43. Available from: <https://www.tandfonline.com/doi/abs/10.1080/00380768.2001.10408366>
- [34] Karamanlioglu M, Robson GD. The influence of biotic and abiotic factors on the rate of degradation of poly(lactic) acid (PLA) coupons buried in compost and soil. *Polymer Degradation and Stability* [internet]. October 2013 [Cited: April 18];98(10):2063-2071. Avialable from: <https://www.sciencedirect.com/science/article/pii/S0141391013002085>
- [35] Prabhu TN, Prashantha K. A review on present status and future challenges of starch based polymer films and their composites in food packaging applications. *Polymer composites* [internet]. October 2016 [Cited: May 14]; 39(7):2499-2522. Available from: <https://onlinelibrary.wiley.com/doi/10.1002/pc.24236>

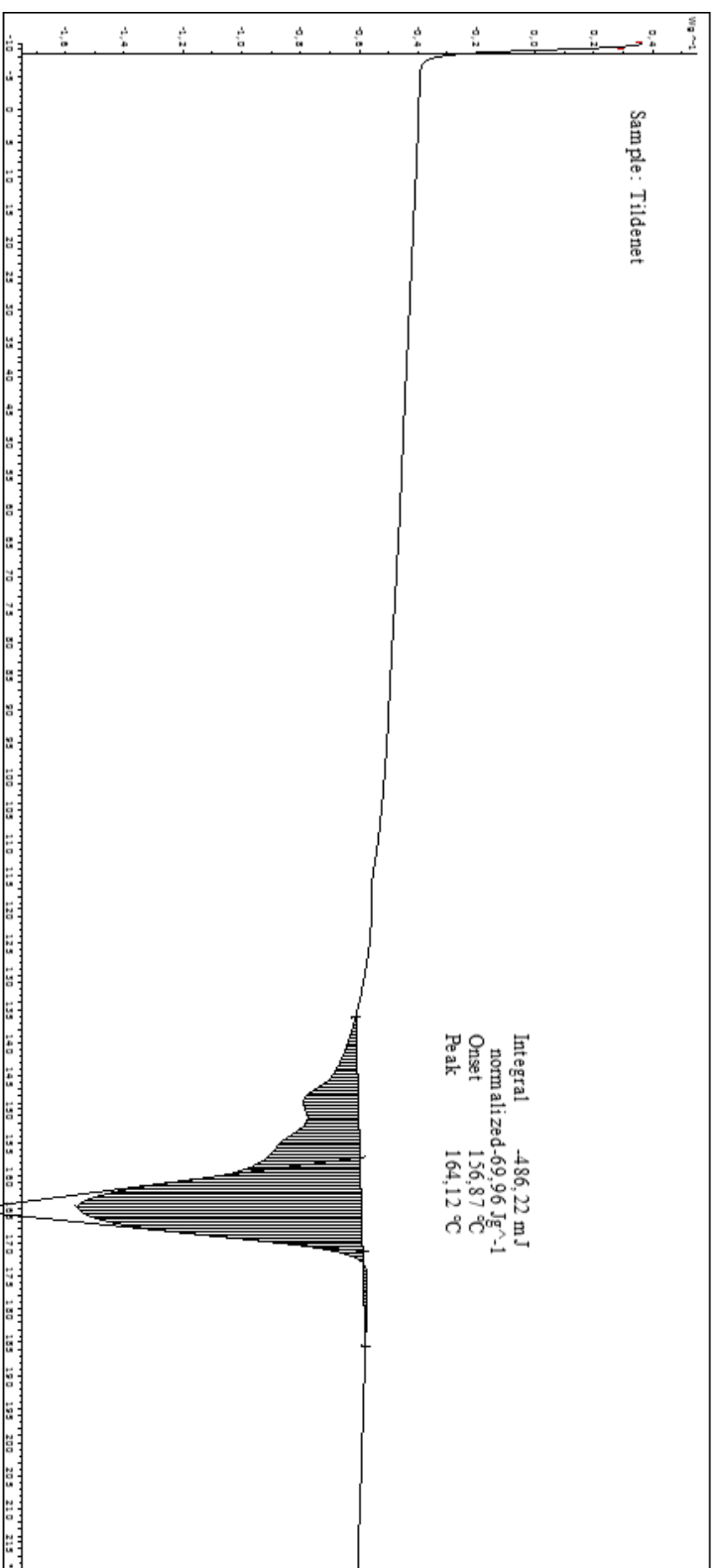
- [36] Kalia, Susheel. Biodegradable Green Composites [e-book]. New Jersey: John Wiley Sons; 2016 [Cited: May 2]. Available from: <https://app.knovel.com/hotlink/toc/id:kpBGC00003/biodegradable-green-composites/biodegradable-green-composites>
- [37] Kaseem M, Hamad K, Deri F. Thermoplastic Starch Blends: A Review of Recent Works. Polymer Science Series A [internet]. February 2012 [Cited: May 7];54(2):165–176. Available from: <https://link.springer.com/article/10.1134/S0965545X1202006X>
- [38] Nafchi AM, Moradpout M, Saeidi M, Alias AK. Thermoplastic starches: properties, challenges, and prospects. Starch [internet]. January 2013 [Cited: May 6];65(1-2):61-72. Available from: <https://onlinelibrary.wiley.com/doi/full/10.1002/star.201200201>
- [39] Shanks R, Kong I. Thermoplastic Starch. Thermoplastic Elastomers [e-book]. IntechOpen; 2012 [Cited: May 2]. Available from: https://www.researchgate.net/publication/224829333_Thermoplastic_Starch
- [40] Bootklad M, Kaewtatip K. Biodegradation of thermoplastic starch/eggshell powder composites. Carbohydrate Polymers [internet]. September 2013 [Cited: May 17];97(2):315-320. Available from: <https://www.sciencedirect.com/science/article/pii/S0144861713005055>
- [41] Janssen L, Moscicki L. Thermoplastic Starch: A Green Material for Various Industries. Germany; WILEY-VCH Verlag GmbH Co. KGaA, Weinheim: 2009.
- [42] Kalambur S, Rizvi S S H. An Overview Of Starch-Based Plastic Blends From Reactive Extrusion. Journal of Plastic Film Sheeting [internet]. January 2006 [Cited: May 14];22(1):39-58. Available from: <https://journals.sagepub.com/doi/abs/10.1177/8756087906062729>
- [43] Pang MM, Pun MY, Ishak Z A M. Degradation Studies During Water Absorption, Aerobic Biodegradation, and Soil Burial of Biobased Thermoplastic Starch from Agricultural Waste/Polypropylene Blends. Applied Polymer Science [internet]. March 2013 [Cited: May 7]; 129(6):3656-3664. Available from: <https://onlinelibrary.wiley.com/doi/full/10.1002/app.39123>
- [44] Schlemmer D, Sales M J A, Resck I S. Degradation of different polystyrene/thermoplastic starch blends buried in soil. Carbohydrate Polymers [internet]. January 2009 [cited: May 7]; 75(1):58-62. Available from: <https://www.sciencedirect.com/science/article/pii/S0144861708002877>
- [45] Plastics - Determination of the Ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved (ISO 17556:2012)

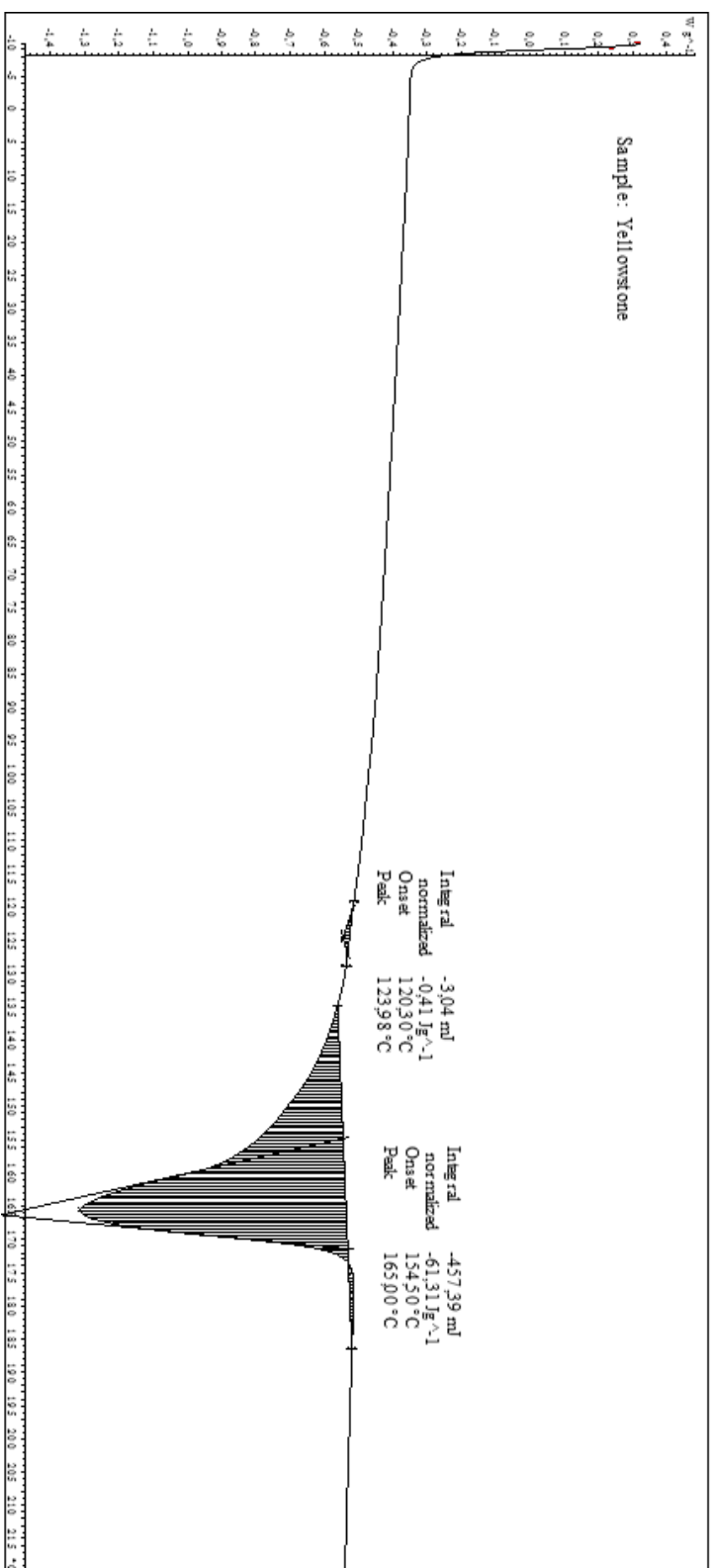
- [46] German standard methods for the examination of water, waste water and sludge; bio-assays (group L); surfactant biodegradation and elimination test for simulation of municipal waste water treatment plants (L 26) (DIN 38412:1994)

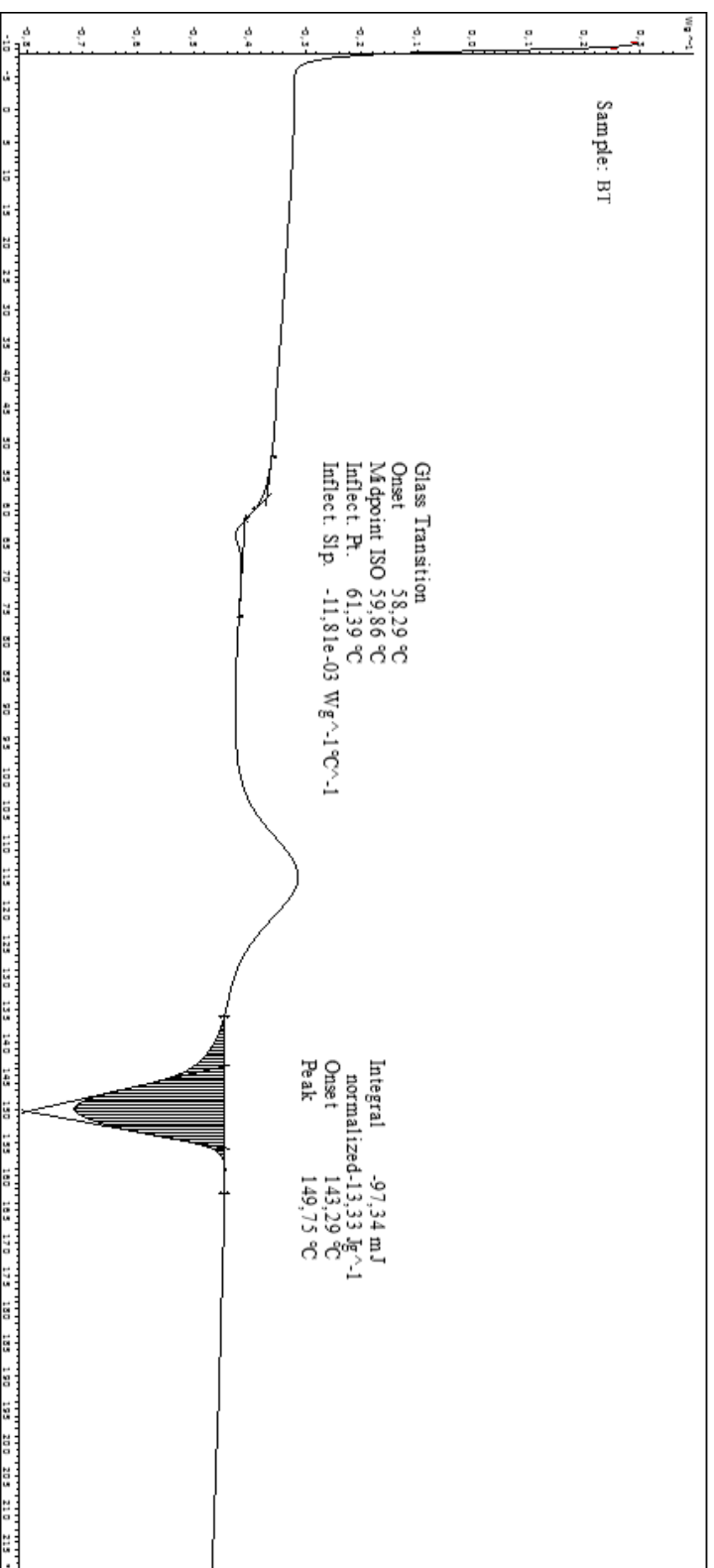
- [47] Packaging - Requirements for packaging recoverable through composting and biodegradation - Test scheme and evaluation criteria for the final acceptance of packaging (EN 13432:2000)

Appendix A DSC

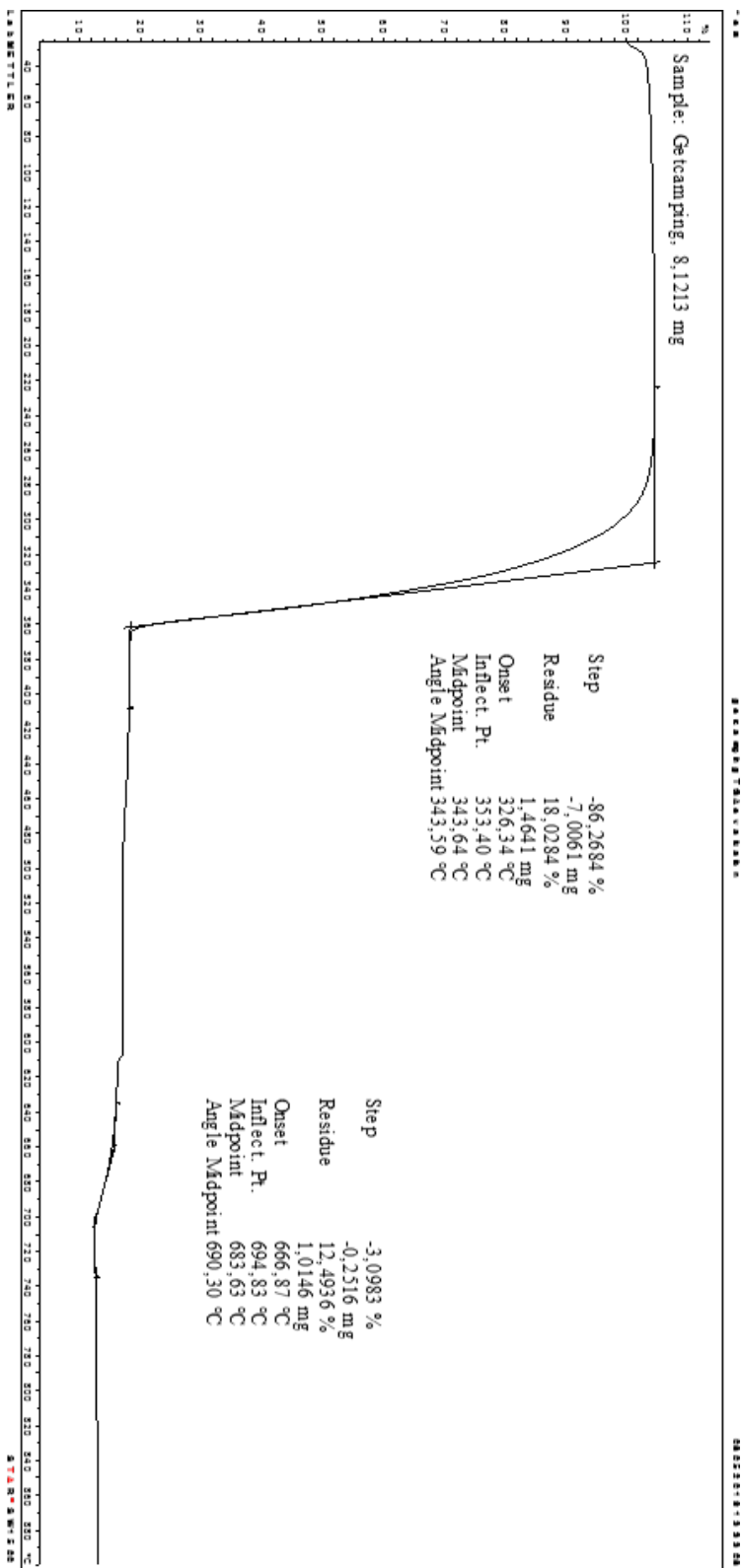


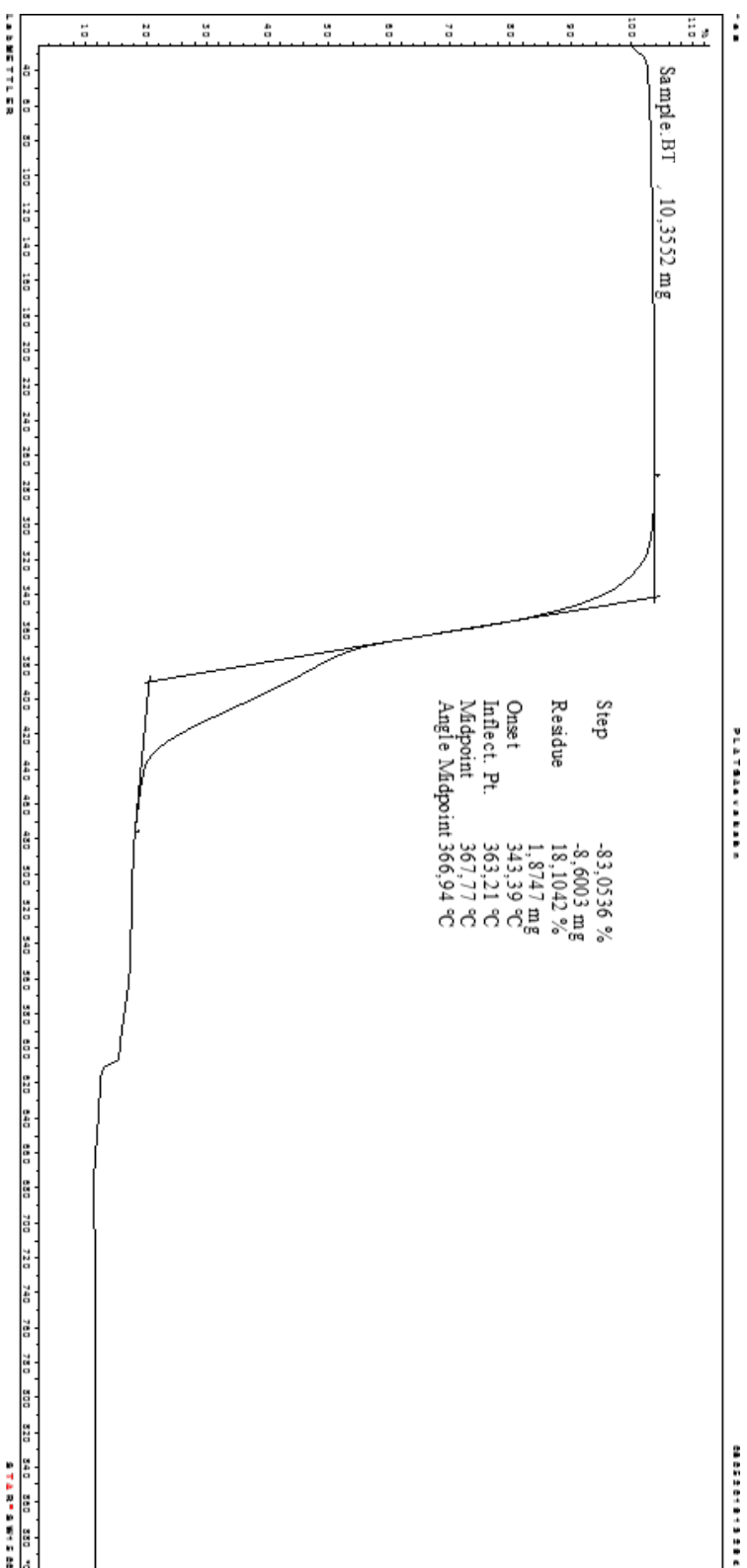


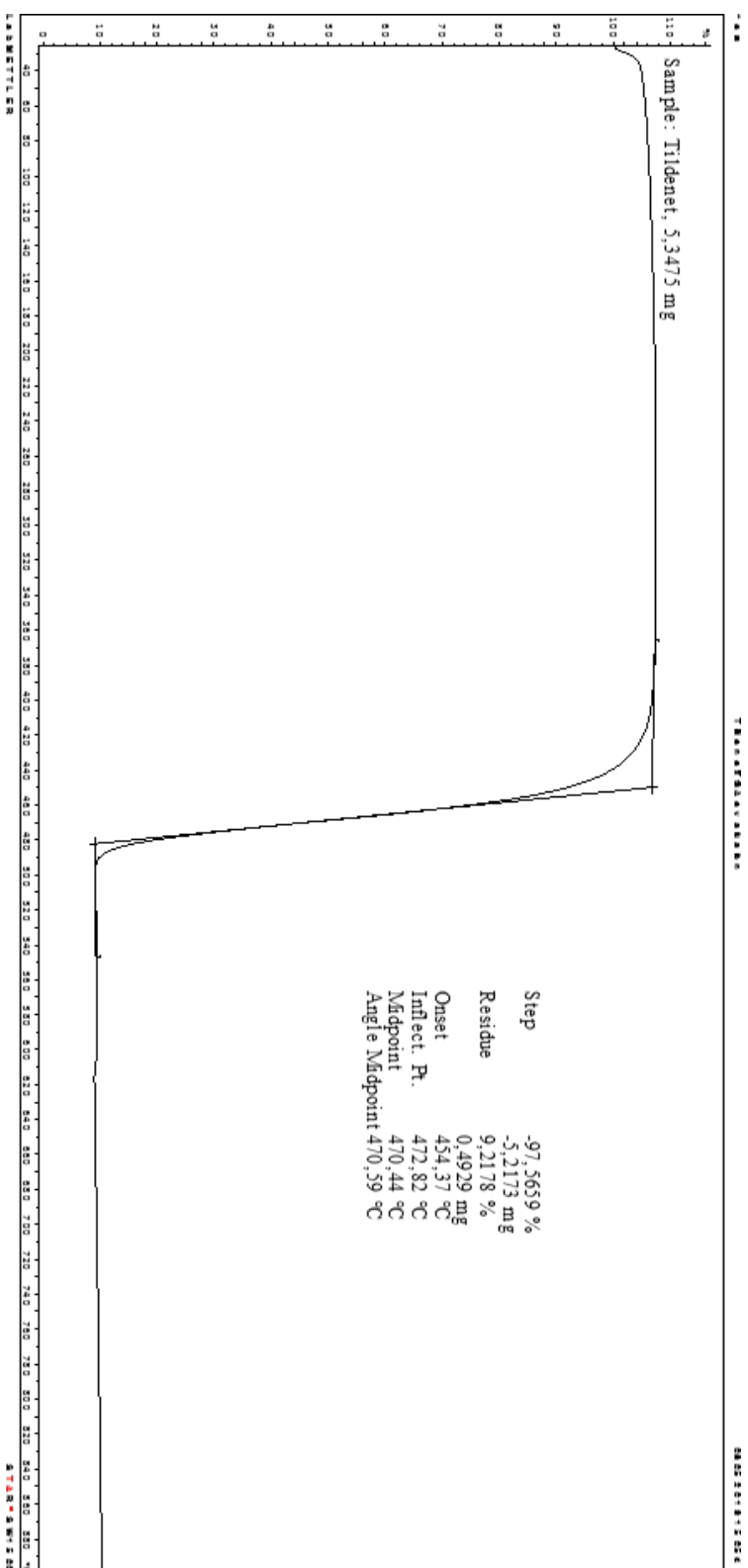




Appendix B TGA

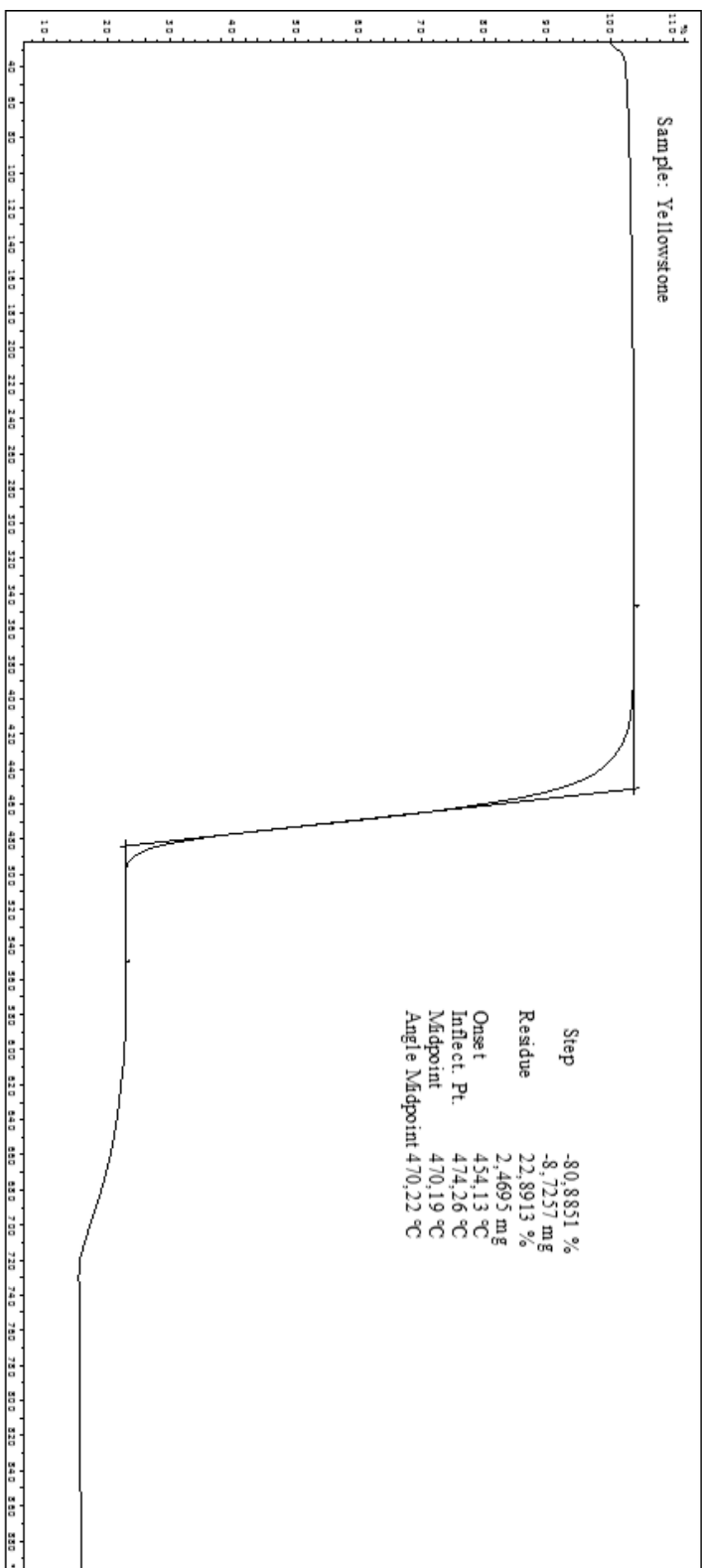






Sample: Yellowstone

Step	-80.8851 %
Residue	-8.7257 mg
	22.8913 %
Onset	2.4695 mg
Infect. Pt.	454.13 °C
Mfdpoint	474.26 °C
Angle Mfdpoint	470.19 °C
	470.22 °C



Appendix C FTIR

