Review
Comparison of the aerobic biodegradation of biopolymers and the corresponding bioplastics: A review

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HIGHLIGHTS
• The biodegradation of unmodified and modified biopolymers in soils is compared.
• Structural modification of a biopolymer hardly influences its biodegradation.
• Chemically modified biopolymers become subject to different biodegradation mechanisms.
• A model is proposed to apply knowledge on biopolymer degradation to bioplastics.

GRAPHICAL ABSTRACT

ABSTRACT
Biodegradable plastics made from biopolymers (made in nature) or from bio-based polymers (made in a factory) are becoming increasingly important in replacing the massive amounts of conventional, non-degradable fossil-based plastics that have been produced and disposed over the past decades. In this review we compare the biodegradation rates and mechanisms of the bioplastics thermoplastic starch, cellulose acetate and lignin based bioplastics with the biodegradation rates and mechanisms of starch, cellulose and lignin, which are the unmodified biopolymers from which these bioplastics are produced. With this comparison we aim to determine to what extent the extensive knowledge on unmodified biopolymer biodegradation can be applied to the biodegradation of bioplastics (modified biopolymers) in the terrestrial environment. This knowledge is important, since it can be of great help in giving direction to the future research and development of bioplastics and for the development of bioplastic waste assessments and policies. We found that the similarities and differences in biodegradation are dependent on the structural changes imposed on a biopolymer during the bioplastic production process. A change in higher level structure, as found in thermoplastic starch, only resulted in a limited number of differences in the biodegradation process. However, when the chemical structure of a polymer is changed, as for cellulose acetate, different microorganisms and enzymes are involved in the biodegradation. Based on the cellulose acetate biodegradation process, a conceptual model was proposed that can be used as a starting point in predicting biodegradation rates of other chemically modified biopolymers used as bioplastics. Future bioplastic biodegradation research should focus on conducting long-term field experiments, since most studies are conducted in a...
1. Introduction

Plastics are materials consisting of long polymer chains and are used on large scales because of their low cost and variety in mechanical characteristics and applications. However, plastics are traditionally produced from fossil oil and can only rarely be closed-loop recycled (World Economic Forum, Ellen MacArthur Foundation and McKinsey and Company, 2016) and are therefore not sustainable. Since large-scale plastic production started in the 1950s it has increased to 359 million tons (Mt) per year in 2018 (Plastics Europe, 2019). The total cumulative plastic production for the period 1950–2015 was estimated at 8300 Mt. In 2015, the cumulative amount of plastic waste generated was 6300 Mt, of which 79% ended up in either landfills or the natural environment (Geyer et al., 2017). This is problematic, since most of these fossil-based plastics are not or hardly biodegradable within a short timeframe and can cause harm to ecosystems (Chae and An, 2018). To overcome these issues, biodegradable plastics based on renewable resources are developed: the so-called bioplastics and bio-based plastics.

These terms are often not correctly used, which leads to a lot of confusion (Gruter, 2019). A bioplastic is obtained from a biopolymer, which is formed in a biological system such as PHA’s, starch, cellulose and lignin. The biopolymers are under most general conditions also biodegradable (see definition in paragraph 2). Bioplastics should be distinguished from synthetic (man-made) bio-based plastics that are made from monomers that originate from biological (once living) systems and bio-based polymers are not always biodegradable. Examples are PLA, PBS, bio-PE and many others. For some of these, the biodegradation in seawater and sediment was studied (Briassoulis et al., 2020). In the past years, the use of bioplastics and bio-based plastics has increased to 2.11 Mt per year in 2019 and is expected to increase to 2.4 Mt per year in 2024 (European Bioplastics, 2020). Bioplastics are produced from a range of natural resources, among which agricultural products such as corn, cassava, cotton linters, or flax fibres, and agricultural by-products such as rice straw (Maran et al., 2014; Mostafa et al., 2018; Bilo et al., 2018). Since these bioplastics consists of modified natural polymers, many of them chemically resemble the biopolymers they
are based on. This raises the question if these modified biopolymers also show behaviour similar to their corresponding unmodified biopolymers when they end up in the environment. An important process that could potentially be similar for both polymers is biodegradation.

The biodegradation of unmodified, naturally occurring biopolymers in soils has long been a research interest, since it is a crucial factor in nutrient cycling in ecosystems (Prescott, 2009). In addition, a considerable amount of research has gone into understanding the mechanisms that stabilise fractions of natural litter, since soils are large carbon reservoirs that could potentially weaken or strengthen climate change when their input and outputs change (Schmidt et al., 2011; Lehmann and Kleber, 2015). The biodegradation of modified biopolymers in soils has also been researched, but not as extensively as the degradation of unmodified biopolymers. Web of Knowledge yields about 100–300 hits when searching on bioplastic or biopolymer biodegradation or decomposition as keywords, where search words as “litter decomposition” and “organic litter biodegradation” result in thousands of papers.

It is essential to know if the biodegradation of unmodified and modified biopolymers resemble each other for the following two reasons: 1) already existing extensive knowledge on unmodified biopolymer degradation can be used to predict the biodegradation of bioplastics and make bioplastic biodegradation research less expensive, since the biodegradation mechanisms that need to be researched are already known. Consequently, these biodegradability predictions can be used in the development of new modified biopolymers, since biopolymers for bioplastic production can be selected based on their biodegradation properties. 2) An increased understanding of bioplastic degradability will help in assessing the environmental impact of plastic pollution in soils, which can be a starting point for better legislation and management policies. Therefore, the objective of this review is to give an overview of the literature on the biodegradation of a selection of naturally occurring, unmodified biopolymers and their modified bioplastic derivatives, and discussing the differences and similarities found.

This review will only concern naturally occurring unmodified biopolymers that have a modified bioplastic derivative. This excludes for example the commonly used polyactic acid (PLA), the polyester of lactic acid, which is produced from microbial fermentation of sugars (Tokiwa et al., 2009) and has no untreated natural biopolymer “precursor”. Although polyhydroxyalkanoates (PHAs), of which polyhydroxybutyrate (PHB) is most commonly used, are biopolymers they fall beyond the scope of this review as they can be used as bioplastic directly, without modification.

Three biopolymers that meet the criteria stated above are starch, cellulose and lignin and their modified variants thermoplastic starch (TPS), cellulose acetate (CA) and lignin-based polymers, respectively (Table 1). The main focus of this review will be on comparing the biodegradation of these polymers on the individual, molecular level. In addition to this, the biodegradation behaviour of TPS, CA and lignin-based plastics when incorporated in a polymer blend will also be discussed, since bioplastics often consist of multiple polymers that can influence each other’s degradation. Furthermore, the impact of environmental factors on both unmodified and modified natural polymers will be reviewed and discussed.

To enable a comparison between biodegradation of biopolymers, this review will first briefly introduce the main concepts of biodegradation. Thereafter it will summarise the most important findings from the available peer-reviewed literature on starch and TPS, cellulose and CA, and lignin and lignin-based plastics biodegradability and biodegradation mechanisms. When appropriate, the differences and similarities in biodegradability will be discussed in order to determine to what extent the knowledge on biopolymer biodegradation can be applied to modified biopolymer biodegradation.

2. Biodegradation

Biodegradation is defined as the mineralisation of organic material by microorganisms (e.g. fungi, archaea and bacteria), which eventually results in the final products carbon dioxide and water under aerobic circumstances. When mineralisation is not complete, biotransformation occurs, creating organic and inorganic metabolites or transformation products (Singh and Sharma, 2008). The most important biodegradation processes for biopolymers, such as the hydrolysis of ester bonds to liberate the monomers are executed by extracellular enzymes that are excreted by microorganisms (Singh and Sharma, 2008; Tokiwa et al., 2009). Biodegradation to small molecules needs to occur outside of the microorganism because the substrate (the biopolymer that needs to be degraded) is often too large to be taken up. The active site of the extracellular enzyme forms a complex with the substrate and cleaves a part of it off. This smaller, soluble part can be transported into the microorganism (Warren, 1996). Within the organisms compounds are further digested through endoenzymes. Most microorganisms use multiple enzymes to fully biodegrade a substrate, these enzymes are together called a system (Warren, 1996). These processes are the biotic side of the total decomposition of a compound. At the same time abiotic processes occur, which chemically and physically break down the material, e.g. photodegradation and chemical hydrolysis under high temperatures and/or acidic or basic conditions (Singh and Sharma, 2008). Biotic and abiotic degradation processes can also influence each other, mechanical degradation can for example lead to increased susceptibility of the polymer to enzymatic degradation, accelerating biodegradation (Haslam, 2004). Mechanical degradation can also occur through meso- and micro-faunal activities, such as earthworms which fragmentise litter and incorporate it in the mineral soil (Prescott, 2009). As a result, the total decomposition of organic material is determined by both biotic and abiotic processes.

3. Starch & thermoplastic starch

3.1. Starch

Starch is a commonly occurring polysaccharide that functions as an energy carrier in plants and is considered to be an easily accessible energy source for microorganisms. It consists of branched amylopectin and linear amyllose chains, which are both made up of glucose molecules. These glucose molecules are connected through relatively weak α-glycosidic bonds (Kögel-Knabner, 2002; Savada et al., 2009). On a higher structural level, starch has a granular shape, which is made up of alternating amorphous and semi crystalline layers (Haslam, 2004).

<table>
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<th>Unmodified biopolymer</th>
<th>Modified biopolymers</th>
<th>Main chemical difference</th>
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<tr>
<td>Starch</td>
<td>Thermoplastic starch (TPS)</td>
<td>Destructuration of crystalline and granular structures; addition of a plasticizer (Van Tuil et al., 2001; Nafchi et al., 2013), 1. Substitution of hydrogen by Acetate; addition of plasticizer (Haske-Cornelius et al., 2017), 2. Addition of lignocellulosic fibres to a biopolymer matrix (Garrison et al., 2016), 3. Plasticised lignin (e.g. arboform)</td>
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<td>Cellulose–acetate (CA)</td>
<td>1. Reinforcing cellulose fibres</td>
<td>1. Plasticisation of starch &amp; different types of chemical modification (Wang et al., 2016), 2. Addition of lignocellulosic fibres to a biopolymer matrix (Garrison et al., 2016; Ibrahim et al., 2018)</td>
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3.1.1. Degradation mechanisms

Starch is mainly degraded by glycoside hydrolases, a large group of enzymes that catalyse the hydrolysis of glycosidic bonds (Warren, 1996). The enzyme α-amylase performs the primary cleavage of long starch polymers, creating shorter fragments. These fragments are hydrolysed by a variety of enzymes such as β-amylase, glucosamylase and α-glucosidase, which are all specialised in hydrolysing α-glycosidic bonds (Warren, 1996; German et al., 2011). Enzymes capable of starch hydrolysis are reported to be present in many different soils (Haslam, 2004) and the fungus Aspergillus oryzae and bacteria Bacillus circulans, Klebsiella pneumonia and Bacillus stearo thermophilus produce a variety of starch degrading enzymes (Warren, 1996). Besides glyco-side hydrolases, lytic polysaccharide monooxygenases (LPMOs) are also capable of cleaving glucose linkages by catalysing oxidative cleavage. LPMOs are copper enzymes and mainly produced by bacteria and fungi (Johansen, 2016). In addition, starch can be made more susceptible to biodegradation by gelatinisation. Gelatinisation takes place when starch is dissolved in water at higher temperatures and is an irreversible process that breaks down intramolecular hydrogen bonds, which results in the starch loses its granular shape (Haslam, 2004). This causes the number of easier degradable, amorphous regions to increase (Tokiwa et al., 2009).

3.1.2. Degradation rate

In a review, Haslam (2004) concluded that starch degradation rate typically follow an asymptotic curve and that a large fraction of starch already degrades within 3 days after entering the soil. It can, however, take several weeks to a year to degrade the starch fraction virtually entirely (Lähesmäki and Piispanen, 1988; Kögel-Knabner, 2002). Besides starch degrading bacteria and fungi (Nafchi et al., 2013), the most common plasticizers are water and glycerol, which results in the starch loses its granular shape (Haslam, 2004). This causes the number of easier degradable, amorphous regions to increase (Tokiwa et al., 2009).

3.2. Thermoplastic starch

Starch is one of the most frequently used resources for bioplastic production, because of its abundance in nature (especially from agricultural products) and low costs (Nafchi et al., 2013). It is mainly used for plastic films, bags and agricultural mulching films (Tang and Alavi, 2011). During the TPS production process starch loses its natural granular shape and crystalline structure. This process of deconstruction is achieved by exposing starch grains to heat and shear in combination with the addition of a plasticizer. The plasticizer breaks and replaces the hydrogen bonds between the starch polymers, which enables the polymer chains to move more freely (Van Tuil et al., 2001; Nafchi et al., 2013). The most common plasticizers are water and glycerol, but amides, sugars, acids and lipids are used as well (Niranjana Prabhu and Prashanth, 2018). The properties of TPS are dependent on the type of natural starch, the type and amount of plasticizer and the temperature at which deconstruction takes place. Starch (both as raw material and as TPS) is often used in a blend with other bio- and bio-based polymers such as PLA, PHB and natural fibres in order to improve the mechanical characteristics of the plastic (Tang and Alavi, 2011; Nafchi et al., 2013).

3.2.1. Degradation mechanisms

Biodegradation of TPS in the soil has been researched in multiple studies. Accinelli et al. (2012) studied the biodegradation of Mater-Bi (a TPS) carrier bags in both a laboratory (soil and compost) and field (soil) setting. After a 3 month incubation period in the lab, the number of TPS degrading microbes increased at the TPS-soil/compost interface, while the amount of microbes at a 15 cm distance from the TPS films remained unchanged. In addition, the growth of fungi was higher than that of bacteria and the fungal community composition changed, indicating that fungi have a higher TPS biodegradation potential than bacteria. Under field conditions no increased microbe population was found at the TPS-soil interface and even a decrease was observed at 15 cm distance. This is in line with the field study by Adhikari et al. (2016), who did not find an increase in soil bacterial and fungal biomass or diversity two years after the burial of PBS-starch (containing 50% starch) films in the soil. In contrast with the study by Accinelli et al. (2012), Adhikari et al. (2016) found a positive relation between bacterial biomass and PBS-starch degradation, and concluded that biodegradation is mainly dependent on the bacterial biomass of the soil. Effective TPS degrading fungi species are Rhizopus Oryzae (Accinelli et al., 2012) and species of the genus Aspergillus and Penicillium (Accinelli et al., 2012; Maran et al., 2014). TPS degrading bacteria mentioned in literature are Pseudomonas sp., Streptococcus sp., Staphylococcus sp., Moraxella sp. and especially Bacillus sp. (Maran et al., 2014; Nevorolová et al., 2019) and Bacillus licheniformis (Jayasekara et al., 2005). The importance and involvement of glucosidases other than alpha-amylase or LPMOs in the biodegradation process was not reported in literature.

Li et al. (2015) reported that both molecular and crystalline structures have an effect on enzymatic degradation of TPS films by fungal derived α-amylase. A fast degradation mechanism acts on the regions with small, soluble starch molecules and in amorphous regions of the film surface. The latter is explained by the increased binding efficiency for α-amylase in amorphous regions. At the same time the retrogradation of small starch molecules occurs. Retrogradation is the process in which the TPS reorganises to its original, granular shape. This increases the crystallinity of the TPS and decreases the degradation rate. Because of these two interfering mechanisms, no correlation was found between the size of starch grains incorporated in films and enzymatic degradation rate (Li et al., 2015). In addition, Rosa et al. (2008) observed a positive relation between the content of the plasticizer glycerol and biodegradation rate by α-amylase in an acetate buffered solution. Higher glycerol content increase gelatinisation rates, and enhances the susceptibility of TPS to biodegradation. This relation was also found in a TPS composting experiment where higher glycerol contents increased water adsorption and enhanced microbial growth (Maran et al., 2014).

3.2.2. Degradation rate

A variety of TPS degradation rates is reported in the available literature. Cassava TPS foams and cassava TPS foams reinforced with grape stalks were completely degraded after 7 weeks of burial in vegetable compost soil in the lab. The degradation rate of the TPS foams reinforced with grape stalks increased in the 5th week, possibly due to increased enzyme-substrate contact area, caused by the more open structure created by the addition of the grape stalks (Engel et al., 2019). Palm fruit based TPS displayed a 84% mass loss after 18 weeks of soil burial under controlled laboratory conditions (Neto et al., 2018). In the 3 month lab experiment by Accinelli et al. (2012) a weight loss in Mater-Bi TPS of 43% and 37% was measured in compost and soil, respectively. In a 12 week composting lab experiment with Mater-Bi carrier bags a mass loss of 94–95% was observed, while after 12 months under home composting conditions the measured weight loss was only 7–14% (Adamcsová et al., 2019). The mass loss measured in the
field experiment of Accinelli et al. (2012) was 3% and thus considerably lower. The authors ascribe the low weight loss to low soil moisture conditions during the burial period and shallow burial depth of 5 cm. It is also mentioned that Briassoulis (2007) found a complete degradation of TPS films in 4–6 months, with higher moisture levels and burial at 20 cm deep. However, in another field experiment with Mater-Bi, no weight loss was measured after 100 days of burial (Bilo et al., 2018).

The addition of carboxylic acid functional groups decreased the weight loss of cassava based TPS after 30 days of soil burial in the lab significantly; unmodified TPS lost 72% of its weight, while 2% citric acid and 2% ascorbic acid TPS lost 61% and 65%, respectively. The carboxyl groups limit the amount of places where microbial attack can take place (Zain et al., 2018). In general, the biodegradability of a blend with TPS and another bio- or bio-based polymer decreases with decreasing starch content (Tokiwa et al., 2009; Tang and Alavi, 2011; Encalada et al., 2018). Blending with starch can also increase the biodegradability of a less bio-degradable polymer (Jayasekara et al., 2005; Singh and Sharma, 2008).

For example, the addition of 6–30% of TPS to a synthetic polymer increases the plastic’s overall biodegradability (Tang and Alavi, 2011). Gómez and Michel (2013) found a blend of corn starch and polypropylene to degrade by 31% after a 660 days soil incubation period. A pure polypropylene film degraded by only 1% during the same period. A similar result was obtained by Adhikari et al. (2016). A poly (butylene succinate)-starch (PBS-starch) blend film degraded by 7% in 28 days after burial, while the weight of a pure PBS bioplastic decreased with 1%. Bher et al. (2019) observed a priming effect in a PLA-TPS blend, and hypothesised that the easily degradable glycerol plasticizer could be the main cause of this effect.

4. Cellulose & cellulose acetate

4.1. Cellulose

Cellulose is, just as starch, a polysaccharide consisting of glucose monomers, but in cellulose these are mainly linked by stronger β-glycosidic linkages, making cellulose a more resistant material that is much harder to decompose. In nature, cellulose is found in high quantities, especially as the main structural component of plant cell walls (Savada et al., 2009). Cellulose normally occurs in crystalline form, with long and straight glucose chains connected through hydrogen bonds, and a small fraction of about 15% appears in amorphous form (Kögel-Knabner, 2002). Biodegradation of amorphous cellulose occurs faster than the biodegradation of crystalline cellulose (Pérez et al., 2002; Tokiwa et al., 2009).

4.1.1. Degradation mechanisms

Fungi and eubacteria form the largest share of the cellulolytic (cellulose-degrading) microorganisms (Pérez et al., 2002; Kögel-Knabner, 2002). These organisms can live in synergy with non-cellulolytic species and together cause complete cellulose decomposition (Pérez et al., 2002). The group of enzymes most responsible for extracellular cellulose degradation are cellulases, which just as α-glucosidase belong to the glycoside hydrolases (Warren, 1996). These cellulases are produced by the microorganism’s hydrolytic systems and capable of breaking the β–glycosidic links. Cellulases are distinguished in endoglucanases (EGs), which hydrolyse internal cellulose bonds in amorphous cellulose and thereby create new end groups, and cellobiohydrolases (CBHs) that only react on end groups. These end groups can be either created by EGs or already exist. CBHs were considered to be the only enzymes capable of degrading crystalline cellulose by Pérez et al. (2002), but according to Johansen (2016) LPMOs are more important in the first phase of cellulose biodegradation. The rate of enzymatic hydrolytic cleavage of cellulose was reported to increase during later phases of biodegradation (Navarro et al., 2014). Tokin et al. (2020) found the synergy between cellulases and LPMOs to be dependent on both the substrate and the combination of enzymes involved in the biodegradation. Both oxidative and hydrolytic cleavage of cellulose eventually produces cellobiose, the disaccharide of glucose. Cellobiose is finally cleaved into glucose molecules by the enzyme β-glucosidase (Fig. 1) (Pérez et al., 2002; Johansen, 2016). In general, the enzyme systems that perform cellulose degradation are considered to be more diverse than those that hydrolyse starch (Warren, 1996).

Two well-studied cellulose degrading fungi are Trichoderma reesei and Phanerochaete chrysosporium (Warren, 1996; Pérez et al., 2002). P. chrysosporium produces more β-glucosidases than T. reesei and their EGs and CBHs degrade best at acidic conditions. However, T. reesei does hardly produce LPMOs. The fungi Laetisaria arvalis is more effective in cellulose degradation since it produces both LPMOs and hydrolytic enzymes (Navarro et al., 2014). In addition, some thermophilic fungi are reported to be faster cellulose degraders than T. reesei (Pérez et al., 2002). The EGs of these fungi reach optimal activity in the domain of 55 and 80 °C and pH between 5 and 5.5, and the CBHs between 50 and 75 °C. The β-glucosidases produced have broader maximum activity ranges: between 35 and 71 °C and a pH of 4.1–8.1. Streptomyces, Pseudomonas and, Cellulomonas are, among others, bacteria reported to produce cellulose degrading enzymes (Warren, 1996; Pérez et al., 2002).

4.1.2. Degradation rate

Cellulose is considered to be a relatively fast biodegrading biopolymer (Gómez and Michel, 2013). In temperate and tropical forests soil a mean cellulose residence time of 81–495 days and 31–61 days, respectively, was reported (Hayakawa et al., 2014). Under standard composting methods in the lab, 97 ± 7% of cellulose was mineralised after 47 days of incubation (Degli-Innocenti et al., 1998). Cellulose is often used as a standard in polymer mineralisation experiments. Under standard methods (for example ASTM D 5338-92) this results in a cellulose mineralisation of over 70% (Jayasekara et al., 2005). Lähdesmäki and Piispanen (1988) observed increased cellulase activity in 1–2 years old spruce needle litter and a slight increase in aspen litter and humus, indicating that cellulose degradation is still active after several years. In contrast to starch, no positive relation between concentration, degradation rates and enzyme activity was observed for cellulose (German et al., 2011).

4.2. Cellulose acetate

Cellulose acetate (CA) is an organic polyester produced by the acetylation of cellulose fibres from different plant residues such as rye, rice straw, cotton, wheat or wood fibre. It is mainly used in plastic films, photographic films, textiles and cigarette filters (Puls et al., 2011). During the acetylation, a hydrogen atom in the cellulose is replaced with an acetyl group. The extent to which substitution takes place is called the degree of substitution (DS), which is the amount of acetyl groups per monomer (Haske-Cornelius et al., 2017). In addition, plasticizer can be added to the acetylated cellulose (Mostafa et al., 2018).

4.2.1. Degradation mechanisms

The biodegradation of CA by cellulases can be inhibited by the acetyl-groups that offer protection to microbial attack (Puls et al., 2011; Leppänén et al., 2020). CHB I and CHB II act only at the ends of the CA polymer chains (Fig. 1) and are stopped when they encounter an acetyl group. EGs are more capable of CA hydrolysis, since they work at random places along the cellulose chain. Biodegradation becomes more effective with a lower DS and becomes especially effective at a DS < 1.5–1.8. A synergy of EGs and CHBs can degrade CA with a DS < 0.9. Between a DS of 0.9 and 1.5 acetyl esterases remove acetyl groups, thereby lowering the DS. Acetyl esterases are enzymes produced by microorganisms that normally degrade acetyl groups containing biopolymers such as xylan and chitin (Puls et al., 2011). A more recent experimental study reported biodegradation to occur through the random oxidative cleavage by LPMOs in addition to hydrolysis by
cellulases and deacetylation by acetyl esterases. The synergy of cellulases, LPMOs and acetyl esterases degraded CA with a DS < 1.8 (Fig. 2) (Haske-Cornelius et al., 2017).

Both Puls et al. (2011) and Haske-Cornelius et al. (2017) mention the important role of acetyl xylan esterases (AXEs), a specific type of acetyl esterases, in the deacetylation process. Puls et al. (2011) report family 4 AXEs to be most efficient in deacetylation, while Haske-Cornelius et al. (2017) conclude that family 2 AXEs and glucomannan acetyl esterase (GAE) are more effective (Fig. 2). Furthermore, polymer chain length is negatively correlated to enzymatic deacetylation.

Cellulase producing bacteria reported to degrade CA are Pseudomonas strains (Puls et al., 2011), and two strains of Neisseria sicca and Alcaligenes xylosoxidans (Sakai et al., 1996). In addition, the N. sicca strains produce acetyl esterase. Furthermore, increased temperatures during decomposition in a CA composting experiment indicate that thermophilic microorganisms are important for CA degradation.

4.2.2. Degradation rate

In general, studies find CA to degrade relatively fast. A weight loss of 33% and 41% was measured for CA based on cotton linters and flax fibre, respectively. Samples were incubated for 14 days under standard composting conditions in a garden soil and cow manure mixture. The faster degradation of flax fibres was ascribed to minor chemical differences of the flax and cotton based CAs (Mostafa et al., 2018). Bilo et al. (2018) found complete degradation of a CA based on rice straw after 105 days of burial in soil. Mass loss increased after 90 days when the CA became powdery. As mentioned earlier, the degradation rate is also dependent on the DS of the material and the acetyl distribution during decomposition in a CA composting experiment indicate that thermophilic microorganisms are important for CA degradation.

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**Fig. 1.** The concept of cellulose biodegradation. First LPMOs (AA9) perform random oxidative cleavage creating more end sites both reducing (R) and non-reducing (NR) for exocellulases (in this figure CBH I and CBH II) to act on. At the same time endocellulases (EG I, II, III) are active, performing hydrolysis in the middle of amorphous cellulose chains. Finally, the cellobiose compounds created are broken into two glucose molecules by β-glycosidase (βG) (Johansen, 2016).


**Fig. 2.** Deacetylation by different esterases at varying degrees of substitution. At DS 1.8 deacetylation strongly decreases compared to DS 1.4 for all esterases. The difference between DS 0.9 and DS 1.4 is especially apparent for AXE 53, AXE 55 and GAE, which are also identified as the enzymes most capable of deacetylation due to the broad region selectivity and flexibility of their active site, that can adapt to different substrates present (from Haske-Cornelius et al., 2017).
along the cellulose chain; more non-substituted groups increase the effectiveness of cellulases (Puls et al., 2011). Sakai et al. (1996) observed 60% and 45% biodegradability in 20 days for CA with a DS of 1.8 and 2.3, respectively. During biodegradation, the DS of the residue CA remains unchanged, since the process of enzymatic hydrolysis occurs at a higher rate than deacetylation. The relation between the DS and degradation rate was found to be non-linear; an increase from DS 0.9–1.4 had less impact on degradation than from DS 1.4–1.8 (Puls et al., 2011; Haske-Cornelius et al., 2017). This is further supported by Leppänen et al. (2020), who observed a negative exponential relation between the DS and the enzymatic hydrolysis of cellulose-based films, among which CA.

5. Lignin & lignin-based bioplastics

5.1. Lignin

Lignin is, comparable to cellulose, insoluble, abundant in nature and present in cell walls, where it provides structural support. High lignin concentrations occur especially in wood, where it forms lignocellulose complexes with cellulose and hemicellulose (Savada et al., 2009). Lignin is an amorphous heteropolymer that mostly consists of the aromatic coniferyl, coumaryl and sinapyl alcohols, bound together by C–O–C or C–C–C linkages. About 50% of these are the β-O-4 aryl ether type (Datta et al., 2017). The ratio between the different alcohols differs per species and plant part (Kögel-Knabner, 2002). Lignin is considered to be a more decay resistant polymer than for example cellulose, due to its complex structure, and is therefore considered to be important in humus formation (Datta et al., 2017).

5.1.1. Degradation mechanisms

The complexity of lignin molecules is also reflected in the degradation process itself, in which many organisms and enzymes are involved. The most important lignolytic extracellular enzymes are laccase (Lac) and peroxidases (e.g. lignin peroxidase (LiP), versatile peroxidase (VP) and manganese peroxidase (MnP)) and the more recently discovered dye-decolorizing peroxidases (DyPs) (Pérez et al., 2002; Datta et al., 2017). LiPs have a higher redox potential than other peroxidases, making them very effective in directly degrading many compounds found in lignin. However, LiPs cannot enter plant cells because of their size, and are therefore only active at open regions of lumen, which is the hollow parts inside tubular lignin structures (Pérez et al., 2002). The other enzymes need a mediator to attack lignin molecules, which is a low-weight molecule used to transfer electrons from an enzyme to a substrate when the enzyme is too large to enter the substrate directly. VP possesses both the catalytic properties of LiP and MnP and is thus capable of degrading a large variety of chemical compounds. Lacs are reported to be not substrate-specific, while all peroxidases are (Datta et al., 2017). Zhang et al. (2020) found that a combination of enzymes leads to the most efficient biodegradation, especially when Lacs are included. Lacs and peroxidases can directly attack the lignin molecules by first causing oxidation of the commonly occurring β-O–4 linkage. Then, aromatic rings are cleaved, which in combination with the oxidation of β-O–4 linkages produces cyclic carbonate structures. Nevertheless, Datta et al. (2017) state that knowledge on lignin biodegradation in soils is still limited and that research in the coming years into newly discovered lignin degrading organisms will increase the understanding of lignin degrading mechanisms.

A large variety of lignolytic enzyme producing fungi and bacteria are reported in literature (Datta et al., 2017). Fungi, and especially white-rot fungi (e.g. Phanerochaete chrysosporium) are considered most efficient in lignin biodegradation (Pérez et al., 2002; Datta et al., 2017; Chio et al., 2019). The lignolytic enzymes discussed are sometimes all produced by one species, while other fungi species are only capable of producing a few or only one enzyme. Brown-rot fungi can also degrade lignin, though less effectively because it occurs through non-enzymatic oxidation reactions (Pérez et al., 2002; Datta et al., 2017). According to Kögel-Knabner (2002) these fungi are only capable of structurally changing the lignin, but not of completely mineralising it. Besides fungi, bacterial enzymes are also reported to catalyse lignin cleavage (Pérez et al., 2002; Datta et al., 2017; Chio et al., 2019). Some bacteria only act on the non-phenolic parts of the lignin molecule, for example Streptomyces viridosporus (Pérez et al., 2002; Datta et al., 2017).

5.1.2. Degradation rate

In an extensive review on the fate of lignin in soils Thevenot et al. (2010) found that in field litterbag degradation studies 48–87% of lignin was degraded after 5 years. The experiments discussed in the review were conducted in different climates and with different lignin litter types. In the same review 19–60% degradation was observed in experiments where lignin was incubated in the lab for 13 weeks to 2 years. Prescott (2009) also reported that lignin is able to degrade in years or decades. However, Thevenot et al. (2010) mention that besides high degradation rates, some studies also report stabilisation of lignin in the soil. This leads to considerable slower degradation rates and hence longer residence times. According to the authors lignin litter in soils can end up in different pools with different turnover rates, which are partly dependent on environmental controls. Klotzbücher et al. (2011) state that lignin degradation depends on the availability of easily degradable carbon sources, since this provides the microbial community with sufficient energy and nutrients for enzyme production. This process of co-metabolism causes biodegradation rates to be high during the first biodegradation stages, when carbon resources are abundant. In later degradation phases, the easily decomposable carbon gets depleted and biodegradation rates decline, leading to longer residence times of the lignin fraction that is left in the soil.

5.2. Lignin-based bioplastics

Lignin used for bioplastic production is often derived as a by-product from the pulp and paper industry. Lignin is separated from the natural lignocellulose complexes, which already causes chemical changes, such as the addition of sulphur (Wang et al., 2016). Lignin-based materials are naturally brittle and therefore need addition of plasticizer or other chemical modification to gain ductile properties. Another problematic characteristic of lignin is that internal condensation reactions can occur under high temperatures, which gives the material thermosetting properties. At the moment, a first generation of lignin-based thermoplastics is commercially available (e.g. Arboform and Xylomer) (Wang et al., 2016). Arboform consists of lignin, cellulose and natural additives (e.g. plasticizers and dyes) and is described to have both the properties of wood and of a thermoplastic (Naegele et al., 2002). Another application of lignin is the use of lignin containing fibres as strengthening compounds in other bioplastics (Garrison et al., 2016), for example TPS (Ibrahim et al., 2017) and protein based bioplastics (Bookklad et al., 2016). These fibres consist of lignocellulose complexes and hence also contain other compounds such as cellulose.

5.2.1. Degradation mechanisms

The degradation mechanisms acting on lignin-based bioplastics are not extensively described in literature. Ibrahim et al. (2018) found that in a TPS reinforced with 50% wt lignocellulosic fibres, flax fibres degraded significantly slower than those of palm, banana and bagasse (sugar cane residue). They ascribe this to the higher cellulose and lower hemicellulose content and small fibre diameter. The latter lowers the chance of the occurrence of matrix free zones during degradation, which decreases water penetration and therefore hydrolysis. This makes the substrate less susceptible to enzymatic degradation, compared to the other fibre-TPS composites and explains why the degradation rate for banana, palm and bagasse fibres increased after two weeks, while the rate of flax degradation remained constant. Naegele et al. (2002) state that the biodegradation of thermoplastic lignin-based
5.2.2. Degradation rate

Only one experimental result on lignin thermoplastic biodegradation was available during the writing of this review. In this experiment, conducted in an aqueous medium according to standard conditions (DIN ISO 14851: 2004) the bioplastic Arboform completely degraded in about 120 days, just as the reference cellulose sample (Plăvânescu, 2014). Neither soil or compost incubation, nor field burial biodegradation experimental results are available.

As mentioned above, the degradation rate of TPS reinforced by lignocellulosic fibres was dependent on the type of lignocellulosic fibre used. After 6 weeks of incubation in soil in the lab (30 °C, 30–40% moisture) 59, 47, 46 and 35% of the weight of flax, palm, banana and bagasse was left respectively. In addition, the TPS matrix degraded completely in about 4 weeks for all fibres (Ibrahim et al., 2018). Bootsland et al. (2016) observed decreasing biodegradation rates when lignocellulosic rubber wood sawdust was added to protein based plastics. Gómez and Michel (2013) hypothesize that the relatively slow degradation rate of coconut coir and rice hulls based materials (21 and 14%, respectively, in 660 days) is due to the relatively high lignin content of the fibres (46 and 21–40%, respectively).

6. Environmental controls

6.1. Environmental controls in biopolymer degradation

Besides the chemical composition and structure of the polymers themselves, biodegradation is controlled by environmental factors. This causes that some “easily degradable” sugars can stay in the SOM for centuries, while “recalcitrant” lignin turnover can be rather high (Schmidt et al., 2011). Climate is often considered to be important for determining degradation rate, but from a review of 70 published studies by Prescott (2009) it appeared that C:N ratio and total litter nutrient content had a larger effect on the rate of decomposition. According to Prescott (2009), many studies point out that the effect of climate shifts caused by global change on biodegradation are likely to be small, unless climate change causes a change in plants species. The reason for this is that the type of plant species is the most important factor in determining the litter type present (e.g. N-content) and therefore in determining litter decomposition. According to this theory, the chemical composition of the plant litter is more important than environmental conditions. However, Schmidt et al. (2011) state that physical, chemical and biological properties of the surrounding soil environment are the primary control in litter and soil organic matter degradation, while the molecular composition of the material is of secondary importance. Hayakawa et al. (2014) reported a positive relationship between cellulase activity and pH, leading to decreased cellulose degradation rates when the pH is low. Lehmann and Kleber (2015) state that while biopolymers become smaller and more soluble by biodegradation processes, the possibility of being chemically and physically protected either by adsorption to mineral surfaces or aggregate formation increases. Litter digestion by meso- and macrofauna can lead to increased aggregation too and thereby limit biodegradation rates, but it was also found that litter digestion can enhance the degradation of recalcitrant carbon. Earthworm activity increased when more broadleaf litter was present, which relates back to the finding that the litter type is important in determining the total degradation rate (Prescott, 2009). Hence, the relative importance of intrinsic chemical or environmental properties on biopolymer degradation are interrelated and complex and remain a matter of debate.

6.2. Environmental controls in modified biopolymer degradation

Literature reports temperature, moisture and photodegradation as influential environmental factors in modified biopolymer degradation. TPS was found to be sensitive to temperature and especially to moisture, since high temperatures and moisture can further increase the plasticization process, decreasing the mechanical properties of the material (Tang and Alavi, 2011). However, Briassoulis (2007) did not find an impact of temperature and moisture on the mechanical properties of TPS agricultural films, but he does report higher degradation rates under increased moisture and temperature. Garrison et al. (2016) mention that cellulose fibres are also vulnerable to heat, while lignin fibres are more susceptible to photo degradation.

When the DS of CA is too high, environmental influences such as photodegradation by UV light or chemical hydrolysis by high temperatures and high pH are needed to initiate biodegradation. These mechanisms can also increase the susceptibility of lower DS CA material to microbial attack (Puls et al., 2011). It was found that from a DS around 1.5–1.8 biodegradation processes start to dominate, but since most commercially used CA s have a DS of 2.5 this means that abiotic degrad-ation is first necessary before biotic degradation can occur (Puls et al., 2011; Haske-Cornelius et al., 2017). Yamashita and Endo (2005) described a decarboxylation mechanism, caused by the addition of polyphosphoric acid, phosphoric acid, or p-toluenesulfonic acid that make CA films more susceptible to chemical hydrolysis when in contact with soil water. The decrease in DS was accompanied by an increase in biodegradation rates. Photo-degradation was also reported to decrease the mechanical properties of TPS (Briassoulis, 2007), but was not mentioned to be of importance in biopolymer literature.

7. Discussion

7.1. Similarities and differences in biodegradation

7.1.1. Starch and thermoplastic starch

Table 2 summarises for each biopolymer and accompanying modified biopolymer (bioplastic) the similarities and differences in the biodegradation process. For starch and TPS, both the biodegradation mechanisms and rates are relatively similar. The main difference found is that besides alpha-amylases, other glucosidases and LPMOs are not reported to be of importance for TPS biodegradation. However, it is more likely that other enzymes in TPS degradation are not yet researched, than that they are not involved in the degradation process. This is further supported by the fact that biodegradation rates of starch and TPS are of the same order of magnitude. In addition, the fungus As- pergillus was reported to be important in both TPS and starch degradation. Hence, it is likely that the same enzymes are involved in biodegradation as well. A similar explanation can be given for the finding that fungi were not reported to be better starch degraders; it is more likely that this has not yet been a subject of research. Another explanation is that many experiments are conducted under composting conditions at a temperature range of 50–60 °C where fungi are not active and bacteria dominate (Nevoralová et al., 2019). The finding by Accinelli et al. (2012) that TPS carrier bags can be used as substrate for the fungus R. oryzae to produce fermentation products such as lactic acid (LA) further indicates that soil microbes use TPS and starch as similar substrates, since usually raw starch from crops or crop residues is used as substrate for LA-producing microbes.

The great extent to which starch and TPS degradation is similar could be explained by the production process of TPS. Starch is only altered on a higher structural level in order to produce TPS. Plasticisers are added, but these only occupy the space between the polymers and are not bound to them permanently. As described by Rosa et al. (2008) and Maran et al. (2014), plasticizers can even increase the biodegradation rate of TPS by increasing the gelatinisation rate. Thereby, the natural process of gelatinisation is comparable to the destructuration during TPS production. Both processes occur under high temperatures and make the starch or TPS more susceptible to biodegradation by increasing the amount of amorphous regions (Haslam, 2004; Li et al., 2015). TPS may in fact be more susceptible to
biodegradation, since its granular higher structure is already destroyed. However, research would be needed to verify this claim, since other processes such as retrogradation, as described by Li et al. (2015), are also involved.

7.1.2. Cellulose and cellulose acetate

While starch is only structurally altered in the TPS-making process, cellulose undergoes is chemically changed by replacing hydrogen atoms for acetyl groups. This leads to a large difference in cellulose and CA degradation, since deacetylation becomes part of the biodegradation process (Puls et al., 2011; Haske-Cornelius et al., 2017). The addition of acetyl groups makes the CA also corresponding to biopolymers in which acetyl groups naturally occur, such as acetylxylan and chitin. Consequently, the biodegradation of CA is the result of both deacetylation by acetylxylan esterases and the regular degradation of cellulose by cellulases and LPMOs. A generalised version of this theory is schematically visualised in Fig. 3, which can be used as a hypothesis or starting point in research on modified biopolymers. For further generalisation of this theory, more research should be conducted on modified biopolymers that gain correspondences of other biopolymers by undergoing chemical changes.

In this regard, a study by Nevoralová et al. (2019) on the biodegradation of acetylated TPS is striking, since the authors conclude that despite the decreasing carbon mineralisation rate with increasing DS, the biodegradation mechanisms for TPS and acetylated TPS are not fundamentally different. The increase in DS increases the hydrophobicity of the plastic, decreasing the degradation rate. This indicates that changes in degradation mechanisms could be biopolymer specific and/or that both structural and chemical changes might interfere.

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>Modified biopolymer</th>
<th>Biodegradability: similarities</th>
<th>Biodegradability: differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>Thermoplastic starch (TPS)</td>
<td>• Biodegradation by alpha-amylase</td>
<td>• Enzymes other than alpha-amylase not mentioned in literature (LPMOs and glucosidases)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Biodegradation by bacteria and fungi (Especially the genus Aspergillus and Bacillus)</td>
<td>• Fungi better TPS degraders than bacteria; no distinction made for starch.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Destructurised or gelatinised regions more susceptible to biodegradation</td>
<td></td>
</tr>
<tr>
<td>Cellulose</td>
<td>1. Cellulose-acetate (CA)</td>
<td>• Total biodegradation time in the order of months to years</td>
<td>• Deacetylation of CA (by AXEs &amp; GAEs)</td>
</tr>
<tr>
<td></td>
<td>2. Reinforcing cellulose fibres</td>
<td>• Biodegradation by bacteria (Especially the genus Pseudomonas)</td>
<td>• (White rot) fungi not mentioned to be important for CA degradation</td>
</tr>
<tr>
<td>Lignin</td>
<td>1. Plasticised lignin (e.g. arboform)</td>
<td>• Similar biodegradation rate</td>
<td>• Not enough experimental results to support claims</td>
</tr>
<tr>
<td></td>
<td>2. Reinforcing lignocellulose fibres</td>
<td>• Similar biodegradation properties as wood</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. The proposed conceptual model of the impact of changes of a biopolymer’s chemical structure, based on cellulose acetate. The modified biopolymer is created by the chemical change of biopolymer A, but due to this change, the modified biopolymer also shows correspondence to biopolymer B. The modified biopolymer is eventually degraded by the combined effect of biodegradation mechanisms A and B.
Decacylation is mentioned to be the rate-limiting step in the biodegradation process, but biodegradation rates and residence times are reported to be in the order of several months to a few years for CA and cellulose (Hayakawa et al., 2014; Bilo et al., 2018; Mostafa et al., 2018), although this is only the case when the DS of the CA is not too high to inhibit enzymatic decacylation, which is around DS 1.9. For CA with a DS > 1.9, this degradation mechanism is then necessary to bring down the DS and allow for biodegradation to occur (Puls et al., 2011; Haske-Cornelius et al., 2017).

The studies and reviews discussed in this review only mention bacteria as CA degraders while fungi (especially white-rot fungi) were reported to be more efficient cellulose degraders than bacteria. This could be due to the same reason that explains the difference in starch and TPS degrading microorganisms: the degradation of CA by fungi has simply not been researched, or most experiments are conducted under composting conditions unfavourable for fungi. Another explanation could be that bacteria are better in producing enzymes for decacylation. Nevertheless, the likeliness that fungi are involved in CA degradation is high, given that after decacylation biodegradation is similar to that of cellulose.

7.1.3. Lignin and lignin-based plastics

Despite the extensive number of studies on lignin biodegradation, little literature is available on the biodegradation of thermoplastic lignin-based bioplastics. The claim by Naegle et al. (2002) that Arboform is 100% biodegradable and that its degradation is comparable to that of wood and thus natural lignin, is not supported with experimental results. Based on the similarities and differences in starch-TPS and cellulose-CA degradation one could hypothesize that the biodegradation of lignin-based bioplastics largely depends on the chemical modifications it undergoes in the lignin isolation and in the plastic production process. When these modifications give the lignin characteristics that resemble other biopolymers, a combined degradation mechanism as described in Fig. 3 would be needed for biodegradation. When lignin is only structurally changed by separating it from the lignocellulose complex, its biodegradation is likely to be similar.

The biodegradation of lignocellulose fibres was found to be partly dependent on the relative concentrations of lignin, cellulose and hemicellulose. Higher lignin contents (Gómez and Michel, 2013) or high cellulose in combination with low hemicellulose contents (Ibrahim et al., 2018) resulted in slower degradation, compared to fibres with higher cellulose and hemicellulose contents, respectively. This is in line with the relative resistance of these polymers in natural litter (lignin > cellulose > hemicellulose).

Lignin-based polymer degradation could also be controlled by the availability of easily degradable carbon sources, as described for natural lignin by Klotzbücher et al. (2011). Blending lignin-based polymers and TPS could for example increase the overall biodegradation rate of the plastic, since TPS then forms the easily degradable carbon source. This is in line with the observations that blends of TPS with PLA, PHB and fossil-based polymers degrade faster than samples that are purely made of these polymers, though this theory is not used as explanation in literature. The priming effect of TPS might also be visible in the study by Ibrahim et al. (2018) where a slight decrease in weight loss rate occurs for banana, palm and bagasse fibre-TPS blends after the TPS matrix is fully degraded. However, this decrease was not significant. Bher et al. (2019) did observe a significant priming effect of TPS in a composting experiment, but hypothesized that this was mostly caught by the glycerol plasticizer. Thus, more lab incubation and long-term field burial experiments are necessary to produce solid proof for both the similar biodegradation mechanisms and rates of lignin-based plastics.

7.1.4. Environmental conditions

A deficiency of both moisture and temperature limit biodegradation of unmodified and modified biopolymers. However, studies as those by Lehmann and Kleber (2015) and Schmidt et al. (2011) suggest that chemical and physical protection mechanisms are of higher importance, but this matter was not discussed in literature on TPS, CA or lignin-based bioplastics. Given the similarities in biodegradation, it is likely that these stabilisation mechanisms are also at work on modified biopolymers in the soil, but no research was dedicated to this matter yet. Photodegradation was not mentioned as important degradation mechanism for soil litter, which is logical assuming that litter is accumulated and covered rather quickly, especially in a forest environment. For bioplastic litter the location and time of the year when it gets disposed in nature will be of importance for the extent of influence by UV degradation.

7.2. Predicting biodegradation rates of (newly developed) bioplastics

As discussed in Section 6.1, starch and TPS degrade according to similar mechanisms and at comparable rates. The biodegradation of CA is the result of two biopolymer degradation processes combined. This indicates that the knowledge on biopolymer degradation can be applied to the corresponding modified biopolymers to a considerable extent. There are however, some points of discussion that have to be taken into consideration when applying the results of this review to other modified biopolymers.

An important point of concern is the reproducibility of modified biopolymers biodegradation research. Garrison et al. (2016) state that there is a great lack of consistency in methodology between modified biopolymer biodegradation studies, which makes it hard to compare studies on both the same polymers with studies on different polymers. Thereby, the experiments described in this review are in general of three different types: biodegradation under standard composting conditions, incubation in a soil column in the lab, and soil burial in the field. Standard composting experiments enable for comparison between different polymers, since they occur under controlled and fixed conditions. However, composting experiments are conducted under high and constant temperatures (50–60 °C) and high moisture conditions. In addition, the microbial activity is usually higher in compost than in real soils, which could lead to an overestimation of a polymer’s biodegradation rate. This also applies to laboratory soil incubation experiments, which are often conducted at room temperature and at relatively high moisture conditions. These conditions rarely occur in soils at longer time scales, especially not in the topsoil where plastic litter is likely to end up. In addition, in both these experimental setup- environmental factors are excluded, such as photodegradation and soil formation processes (aggregate formation, SOM-metal ion complex formation), as well as macrofaunal activity. Studies have shown that degradation rates of the same bioplastic can differ significantly between indoor and outdoor conditions (e.g. Accinelli et al., 2012; Adamcová et al., 2019) or between different field burial experiments (Briassoulis, 2007; Bilo et al., 2018, Gómez and Michel, 2013). Therefore, the modified biopolymers have a different relative degradation rate order in compost and in soil. Lab incubating and composting experiments are therefore useful in assessing the biodegradation potential for a modified biopolymer, rather than giving a realistic biodegradation rate for the ambient environment. Besides this, lab experiments can also be valuable for determining and describing enzymatic biodegradation mechanisms and for identifying the microbes involved. The role of environmental conditions in field burial experiments makes these studies more representative, but also harder to compare with results from other studies. In order to overcome this issue, Briassoulis and Mistriotis (2018) found that the addition of 0.1 g nitrogen to natural soils as well as using a ratio of 1 g carbon per sample on 300 g of testing soil increases the reproducibility of the biodegradability research. These additions make the influence of the soil type in which the experiment takes place negligible, except for organic soils. Future research can use these results in order to perform comparable and reproducible degradation field studies of modified biopolymers.
Another issue is that many incubation and soil burial experiments only last several months and already end while the material is not fully degraded. This makes it hard to state whether a material is completely biodegradable or that a residue fraction remains in the soil for a long time, for example controlled by similar mechanisms that cause SOM stabilisation. Therefore, it is important to combine laboratory and long-term field research, in order to get full insight in the relation between environment, biodegradation mechanisms and biodegradation rates.

Furthermore, biodegradation rates can be measured in different ways. Mass loss was a measure used in many studies this review describes, but measuring mass loss becomes increasingly difficult when the degradation process proceeds. When incorporating the bioplastic as a powder, measuring mass loss becomes impossible. Biodegradation rates can also be based on CO₂ respiration measurements. The latter measures only the mineralisation of the plastic by microorganisms, while the first also takes into account biotransformation products. Interestingly, Grandy and Neff (2008) state that the majority of stable compounds in soil are secondary transformation products of soil (micro)organisms. Measuring only mineralisation could underestimate the actual biodegradation of a biopolymer. On the other hand, respired CO₂ can also originate from biodegradation of the organic material in the soil or compost the experiment takes place in (Maran et al., 2014) and thus should be subtracted from the total respired CO₂. This should be taken into account when comparing studies using different methodologies.

Another factor that should be taken into account when researching biodegradation rates is the morphology of the plastic. Large plastic fragments have a smaller specific surface area on which microorganisms and enzymes can act, which limits their biodegradation rate. Bilo et al. (2018) observed increasing degradation rates in rice straw-based plastics after the plastic became powdery due to earlier biodegradation. Pulß et al. (2011) mention that on a microscale different degradation rates create pits in the CA material, which increase the specific area and biodegradation rates. The PBS-starch blend researched by Adhikari et al. (2016) lost 7.2% of its weight after 28 days when it was incubated as a 2 mm thick film, while a weight reduction of 24.4% was measured when the blend was incubated as a 250 μm powder. In contrast to these findings, Gómez and Michel (2013) found that a film of a copolyester corn-based starch blend degraded by 55.1% after 660 days, while the ground sample degraded only by 39.7%. No explanation was given for this unexpected difference. The effect of morphology on degradation rates should be taken into account when researching the biodegradability of plastics.

This review only focussed on aerobic biodegradation, since this type of degradation is most common in soils. However, this excludes the biodegradation of (modified) biopolymers in anaerobic soil environments, such as peat areas and soils with stagnic properties leading to temporal water logging. Recently, new bacteria capable of anaerobic lignin degradation have been discovered that use new lignin biodegradation systems which can lead to a more fully understanding of lignin biodegradation (Datta et al., 2017). Pulß et al. (2011) mention that experiments show anaerobic degradation of CA and Gómez and Michel (2013) found similar degradation rates for cellulose paper under aerobic and anaerobic circumstances. Briassoulis (2007) reports that TPS degradation rates decreased after flooding of the field research area, which created anoxic soil conditions. Future research could expand the findings of this review to anaerobic terrestrial environments.

7.3. Bioplastic waste assessment & policy

Extended knowledge on modified biopolymer biodegradation is essential for policymakers to assess the environmental impacts of bioplastics waste streams and to create legislation in order to limit these impacts as much as possible. For example, most CA cigarette filters have a DS of 2.5, which is too high to immediately allow for enzymatic biodegradation (Pulß et al., 2011; Haske-Cornelius et al., 2017). Since cigarettes are likely to end up in the environment, legislation could only allow filters to be made of a CA with a DS < 1.9.

There is often a trade-off between the biodegradability and mechanically preferred properties of a bioplastic, since stronger mechanical characteristics often come at the cost of the plastic’s biodegradability (Leja and Lewandowicz, 2010). In these cases, legislation can be used to create the framework in which the industry can develop and apply modified biopolymers that possess the required mechanical properties and are biodegradable.

In addition, the concentration in which a modified biopolymer product is likely to end up in the environment could influence its biodegradation. Based on the decreased biodegradation rates of starch under low starch concentrations caused by decreased enzymatic activity (German et al., 2011), one could hypothesize that a bag of TPS could be degraded faster than regular starch, since it locally increases starch concentrations. On the other hand, most plastics in nature also physically degrade into micro- and nano-plastic particles. The investigations on the effects of bioplastic microplastics are still limited and largely unknown (Shruti and Kutralam-Muniasamy, 2019). When TPS litter would degrade to micro- or nanoparticles it could get stabilised in the soil, since concentrations are too low to make investing energy in enzyme production profitable for microorganisms. For conventional plastics this would be considered to be unfavourable, but when modified biopolymer micro- or nanofragments have no toxic properties, they can in theory be regarded as natural starch (or other biopolymer) material that becomes stabilised in the SOM. PBS-starch blends, rice based CA and lignin-based Arboform were all reported to contain toxic compounds by Adhikari et al. (2016), Bilo et al. (2018) and Naegle et al. (2002), respectively. This indicates that the stabilisation of small fragments of these modified biopolymers would not be harmful to the soil environment, but as stated by Shruti and Kutralam-Muniasamy (2019), experiments are necessary to determine the environmental impact of modified biopolymer micro- and nanoparticles.

7.4. Current gaps and future research directions

The very limited knowledge on biodegradation mechanisms and biodegradation rates of modified lignin materials emphasizes the need for more research into the biodegradation properties of these materials. Both lab and field experiments are necessary to get insight in the enzymes and microorganisms involved in the biodegradation as well as in the rates at which these processes take place. Starch and TPS, which are chemically very similar, were found to show similar biodegradation, while on the other hand the chemically modified CA requires the combined actions of cellulases and acetyl esterases for its biodegradation. This suggests that researching the enzymes reported to be lignin degraders (Lacs, LiPs, VPs, MnPs and DyPs) would be promising starting point to gain more insight into the biodegradation of lignin-based bioplastics.

Another opportunity lies in conducting more long term field burial experiments with modified biopolymers, since such studies were either scarce or absent for all modified biopolymers discussed. Besides the fact that laboratory studies do not capture all processes that are present in the field situation, bioplastic samples are rarely completely degraded at the end of the measuring period in a lab experiment. The last degradation phase of a material needs to be understood, since this knowledge is essential for determining the environmental impact of the material and thus for the assessment of the fate-in-nature and for subsequent policy making. Therefore, these field studies also need to research biodegradation under both aerobic and anaerobic circumstances and take into account the effect of the morphology and size of the modified biopolymers in order to get realistic and representative results for the real environmental situation.

8. Conclusion

From the results of this review, it can be concluded that knowledge on unmodified biopolymer degradation can be applied to predict the
biodegradation of the corresponding modified biopolymers to a considerable extent. Especially in TPS, where only a higher level structural change occurs during the bioplastic making process, biodegradation mechanisms and rates are virtually similar. Changes in the biodegradation process are caused by changes in the chemical structure of biopolymers, as occurs during the acetylation of cellulose to produce CA. The morphology are taken into account. This will provide understanding of biopolymers that possess characteristics of both the biopolymer they are containing unmodified biopolymers as chitin and xylan, and biodegradation occurs though a combination of cellulases and acetyl esterases.

The proposed conceptual model (Fig. 3) based on CA biodegradation can be used as a prediction when researching other modified biopolymers that possess characteristics of both the biopolymer they are based on and one or more other biopolymers. Future research should examine how lignin-based biopolymers degrade, using the lignolytic enzymes described in paragraph 5.1.1 as a starting point. The other main focus of future research should be on long-term field burial experiments in which (an) aerobic circumstances and biopolymer size and morphology are taken into account. This will provide understanding of the complete biodegradation and subsequent environmental impact of modified biopolymers, which can eventually be used for bioplastic policy making.

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