



A Review on The Effect of Chemical Engineering Design Considerations on The Biodegradability of Polysaccharide-Based Composite Polymers

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Executive summary

Being the major environmental pollutants, petroleum-based polymers consist of 99% of plastics produced for industrial and daily-life usage. Bioplastics are increasingly drawing more attention for being a promising solution to environmental issues. Among bioplastics, polysaccharide-incorporated plastics (PSIP) are of special interest for being renewable, sustainable and biodegradable. Polysaccharides are naturally existing polymers and have shown suitable properties if blended with synthetic polymers. In order to be transformed into an applicable plastic, they must go through processes which affects their inherent biodegradability. Research is significantly lacking on how these modifications including blending, grafting, functional group substitution, if and how their original sources, pretreatment, additives and process variables affect the final product biodegradability. This review paper aims to conduct an early attempted investigation into factors that impact PSIP biodegradability in order to help polymer reaction engineers with designing polysaccharide-based polymers in terms of biodegradability. Increasing crystallinity, substitution of functional groups, grafting, and crosslinking reduced biodegradability. Plasticizers and compatibilizers improved biodegradability with some exceptions. Also, biodegradation is greatly affected by environmental conditions that was discussed.

Contents

Executive summary	2
List of Tables.....	5
List of Figures.....	6
List of Abbreviations.....	7
Introduction	9
Biopolymers	11
Polysaccharides	11
Starch	12
Cellulose.....	12
Chitin and chitosan	12
Composites:	13
Biodegradability.....	13
Definitions	13
Mechanism.....	14
Degradation and biodegradation.....	15
Standards for biodegradability.....	15
Biodegradability testing conditions	16
Controlled and uncontrolled.....	16
Environmental medium	16
Undefined testing conditions.....	17
Methods of biodegradability measurements	17
Physical methods	17
Spectroscopic Methods.....	18
Respirometric Methods or Biogas Evolution	18
Meta-analysis.....	18
Thermal methods	19
Comparison.....	19
What affects biodegradability of polysaccharide-based polymers?.....	20
Source of polysaccharides	20
Chemical Structure	23

Functional group substitution	23
Starch modification	27
Grafting.....	28
Loading of polysaccharide	30
Minimum loading	35
Maximum loading	35
Optimal loading	37
Pre-treatment.....	39
Effect of other materials included in PSIP	40
Crosslinkers	40
Compatibilizers.....	41
Plasticizers.....	42
Environmental effect	44
Challenges.....	46
Of the field	46
Of the papers.....	47
Critiques on biodegradability researches.....	47
Temperature, moisture and PH	47
Testing conditions, duration, and biodegradability factor	48
Measurement methods.....	48
Conclusion and future work.....	56
Bibliography	57

List of Tables

Table 1. starch sources and their amylose content.....	21
Table 2. weight loss of PCL-starch blends during composting.....	33
Table 3. Composition of the different polyblend composites	34
Table 4. composition of LDPE and Starch.....	38
Table 5. Percentage weight loss of LDPE/Mnihad esculenta samples.....	39
Table 6. Percentage weight loss of LDPE/Zea Mays samples	39
Table 7. Percentage weight loss of LDPE/Ipomoea patatas samples.....	39
Table 8. papers.....	49
Table 9. Temperature, Moisture and PH of experiments	51
Table 10. test condition, duration and investigated biodegradability factor	52
Table 11. measurement methods and technique	54

List of Figures

Figure 1. structure of polysaccharide repeating unit.....	12
Figure 2. Standards for biodegradability measurement, astm d5988-18 and iso 17556:2019.....	16
Figure 3. Analyses methods of biodegradable polymers.....	19
Figure 4. degradation of starch with different amylose content	21
Figure 5. sources and types of polysaccharides.....	23
Figure 6. biodegradability of pure and modified thermoplastic starch.....	24
Figure 7. water absorption of pure and modified thermoplastic starch	25
Figure 8. hydrolysis of 12 substances over their degree of substitution	26
Figure 9. degradation of 12 substances in 2-12 weeks	26
Figure 10. chemical structure of CAB and PLL.....	27
Figure 11. Biodegradability of native and oxidized corn starch for 98 days.....	27
Figure 12. Three SEM figures	29
Figure 13. biodegradation of pure and modified polypropylene with cellulose fibers	31
Figure 14. weight loss of PMMA-CA blend with different compositions of CA.....	31
Figure 15. weight loss of PMMA-CAB blend with different compositions of CAB.....	32
Figure 16. weight loss of PLA-NR/LNR reinforced with cellulose	32
Figure 17. Biodegradation of 90/10 PLA/PCL modified with MCC	34
Figure 18. Biodegradation of 80/20 PLA/PCL modified with MCC	34
Figure 19. Weight loss of PCL/S modified with 5% and 15% SF	36
Figure 20. Mineralization of PBSA/Starch	37
Figure 21. Degradation rate and ratio of 20 CaS.....	38
Figure 22. Degradation rate and ratio of 40 CaS.....	38
Figure 23. Biodegradation of samples during 85 days of incubation	41
Figure 24. Weight loss of (a).PCL without plastisizers and (b). PCL with plastisizers	42
Figure 25. Weight loss curves after exposure of samples in the soil	43
Figure 26. CA films modified with acids	43
Figure 27. CA films modified with polyphosphoric acid	44
Figure 28. Weight loss of BPMKB on surface and underground	46

List of Abbreviations

ACNFs	Acetylated Cellulose Nanofibers
ASTM	American Society for Testing and Materials
BHC	Butylated Hemicellulose
BMP	Biochemical Methane Potential
BOD	Biochemical Oxygen Demand
CA	Cellulose Acetate
CA	Citric Acid
CAB	Cellulose Acetate Butyrate
CAP	Cellulose Acetate Phthalate
CaS	Cassava Starch
Cellulose IL	Cellulose Regenerated from Ionic Liquid
CFs	Cellulose Fibers
CMC	Carboxymethyl Cellulose
CNC	Cellulose Nanocrystals
CNFs	Cellulose Nanofibers
CS	Chitosan
DH	Degree Of Hydrolysis
DS	Degree Of Substitution
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EAA	Ethylene Acrylic Acid
EPSs	Exopolysaccharides
FTIR	Fourier-Transform Infrared
GA	Glutaraldehyde
GL	Glycerol
HACS	High-Amylose Cornstarch
ISO	International Organization for Standardization
LDPE	Low-Density Polyethylene
MA-DETA	Maleic anhydride-diethylenetriamine
MAM	Methacrylamide
MCC	Microcrystalline Cellulose

MCS	Waxy Mazie Cornstarch
MMA	Methyl Methacrylate
NAOH	Sodium Hydroxide
NR	Natural Rubber
PA	Polyacrylate
PAAc	Polyacrylic Acid
PBAT	Polybutylene Adipate Terephthalate
PBS	Polybutylene Succinate
PBSA	Polybutylene Succinate Adipate
PCL	Polycaprolactone
PE	Polyethylene
PEG	Polyethylene Glycol
PGA	Polyglycolic Acid
PGD	PCL-Grafted Dextran Copolymers
PHAS	Polyhydroxyalkanoates
PHB	Polyhydroxy Butyrate
PLA	Pylactic Acid
PLL	Poly(L-Lactide)
PMMA	Polymethyl Methacrylate
PP	Polypropylene
PS	Polystyrene
PSIP	Polysaccharide-Incorporated Polymer
PVA	Polyvinyl Alcohol
S	Starch
SEM	Scanning Electron Microscopy
SF	Sisal Fibers
SRKC	Semi-Refined Kappa Carrageenan
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TPAS	Thermoplastic Acetylated Starch
TPS	Thermoplastic Starch
XRD	X-Rays Diffraction
XRF	X-Ray Fluorescence

Introduction

Petrol-based plastic and synthetic polymers are produced at a rate of 450 Mt per year worldwide[1]. These substances cause important environmental problems, including treatment challenges of wastewater that contaminates groundwater and surface water, shortage of the organic compounds due to declining oil and gas resources, increasing oil and gas prices, contaminations in disposal and recycling, degradation issues, global warming, uneconomical costs and consumer toxicity risks. [2] while synthetic polymers are important in many industries for their durability and resistance to various forms of degradation, including photodegradation (the effect of sunlight) and that of microbial agents, they are "recognized as major solid waste environmental pollutants" [3]. These non-degradable polymers are now a source of pollution and pose a threat to the environment. Thus, there is a tendency to substitute such polymers with polymers that undergo biodegradable processes. Although recycling is an attractive solution, only a small percentage of polymers are actually recyclable and most polymer made articles end up in landfill. Biodegradation is the most acceptable means of solving these problems, as it is cost effective and eco-friendly. In many specific fields such as agriculture and biomedical use, biodegradation is the only means of degrading used polymers. Biodegradable polymers are therefore the only solution to the problem of landfill.

Biodegradation (i.e. Biotic degradation) is a chemical degradation of materials (i.e. Polymers) provoked by the action of microorganisms among which bacteria, fungi and algae are the most important. Biodegradable polymers decompose into carbon dioxide, methane, water, inorganic compounds or biomass by the actions of microorganisms. The term green chemistry was first used in 1990 and the basic concept is to eliminate or minimize the use of substances that are hazardous to the environment and people's health. In 1998, Paul Anastas and John Warner published the first manual of Green Chemistry, in which they proposed 12 principles. One principle concerns the development of chemicals which decompose and degrade into harmless materials in the environment after their useful life. Another is to use renewable materials whenever economically and technically possible.[4] in the case of polymers, biopolymers have been growing increasingly tending to replace conventional plastics in order to make polymer production much greener. Up until now there is not an exact definition of the term "biopolymer" and since some definitions given by researches were found contradictory, types and categories will be discussed instead of a singular definition in this paper. Biopolymers are classified based on different grounds. One is by biodegradability and based on that, biopolymers are either biodegradable or non-biodegradable. Another is by the source of the raw material being either fossil fuel-based or bio-based. Bio-based polymers can be produced from plants, animals and by microorganisms. With the categories above combined, biopolymers are three types [5]:

1. Biodegradable bio-based biopolymers
2. Non-biodegradable bio-based biopolymers
3. Biodegradable fossil fuel-made biopolymers

Polysaccharides, commonly known as carbohydrates, are natural long-chain polymers made of monosaccharide units joined together with glycosidic bonds. They are the most abundant

macromolecules in the biosphere and have various sources; they are found in fungi, algae, in plants as the main structural element or the key energy source and in the exoskeleton of animals.[6] polysaccharides are inherently biocompatible, biodegradable, non-toxic and diverse in structure and in property. Having an advantage over alternative natural substances for these characteristics, these biomolecules are especially interesting in the manufacturing of commercial polymers in order to produce a biodegradable bio-based biopolymer. Which is the greenest of biopolymers discussed above for having a renewable and sustainable source and being environmentally-friendly. However, their inherent biodegradability does not determine if and to what extent the final product is biodegradable. Biodegradability of polysaccharide-included polymers which is the major topic of this paper is dependent on different factors. Understanding how these process variables work and affect these biopolymers will help chemical engineers choose the best technical and a greener approach to producing polysaccharide-based plastics. These factors will be the principal discussion:

- Pre-treatment of polysaccharides
- Amount and method of inclusion
- Type of polymerization
- Type of the final product
- Choice of reaction agents, methods and conditions
- types of biodegradation test procedures
- Techniques of biodegradability measurements

Polysaccharides that exist in nature are raw materials and in order to make it useable in manufacturing processes, it should be modified by going through chemical reactions which change their structure to improve their properties. Also, non-biodegradable polymers with desirable end-use properties are mixed with polysaccharides to impart their biodegradability to the final product. These polysaccharide-included plastics are often in form of composites. Composites are materials that consist of two components: reinforcement and the matrix. The role of matrix is to support the reinforcing material and to evenly distribute the applied load to the product and the reinforcing element is the stronger component that reinforces the matrix. A petroleum-based polymer as the matrix can be reinforced with a modified polysaccharide filler often as nanofiller since nanocomposites have shown novel characteristics for the nanometric size effect. PSIP are sometimes in form of blends. When two or more polymers are physically mixed together, the resulting blend comes as a new polymer with new and different properties that the single polymer components.

A lot of work has been done on PSIP like starch filled composites but research on the actual environmental biodegradability of these products is very limited.[7] The aim of this work is to conduct an early attempted review on the effect of various engineering considerations on the biodegradability of polysaccharide-based polymer products. A lot of This review will provide polymer reaction engineers a resource in their efforts for green polymerization using polysaccharides, which is by either replacing unsustainable feedstocks with polysaccharide materials or including them within the process to impart their biodegradability to the final product.

Biopolymers

Biopolymers are growing to replace conventional plastics since they can have similar capacities and applications, but are non-toxic and environmentally sustainable for being bio-based and/or biodegradable. However, they cost 2 to 5 times more than conventional plastics. They were first manufactured in the 1950s[8], but only started being produced in industrial scale in 2000s. [9]. According to American Society for Testing and Materials (ASTM), bio-based plastic is described as "a plastic containing organic carbon of renewable origin such as agricultural, plant, animal, fungi, microorganisms, marine, or forestry materials living in a natural environment in equilibrium with the atmosphere"[8]. Based on this and explanations by [4], [10], the term "bioplastics" also describes plastics that can either be biodegradable or bio-based or both. Bio-based" means the raw materials are from renewable sources such as polysaccharides and. Not all bio-based plastics are biodegradable which is why PSIP, though being bio-based polymers, must be investigated for their biodegradability. As can be seen further in this paper, some polysaccharide-derived polymers are unexpectedly not biodegradable. Based on this, bioplastics are three groups. Biodegradable bio-based biopolymers, non-biodegradable bio-based biopolymers, and biodegradable fossil fuel-made biopolymers. [5] [9] They account for less than 1 percent of all plastics produced per year and 55% of this amount is biodegradable. The production of bioplastics was 2.11 million tons out of 360 million tons of plastics in 2019 and is expected to reach 2.43 in 2024.[9] some applications include bags, dishes, coffee stirrers, glasses, cutlery, mulching film, dust sheets, bottles, and packaging items [9]

Commercially available biodegradable polymers generally consist of polyesters and polysaccharides with hydrolysable ester and ether bonds, respectively. [11] Starch plastics and cellulose esters are among the most produced PSIP. [12] Biodegradable polymers can be categorized by their origins: produced by bacteria, produced from natural substances and produced by chemical synthesis. Among polymers produced by bacteria are polyesters like PHAS and PHB and two edible polysaccharides, Gellan gum and curdlan. Examples of naturally produced polymers are cellulose acetate and blended or grafted chitin. Synthetic biodegradable polymers are majorly aliphatic polymers. polyglycolic acid (PGA), polylactic acid (PLA), polycaprolactone (PCL) and poly butylene succinate (PBS) are synthetic biodegradable polymers. [11]. PLA, also produced from natural products like sugarcane-based saccharides as well, has attracted so much attention for industrial applications as a biopolymer. PLA blends with other polysaccharides, starch in particular, was one of the most seen PSIP during research for this literature review.

Polysaccharides

Polysaccharides also known as carbohydrates are the most abundant macromolecular polymers with repeating monosaccharide units that are joined together with glycosidic bonds (see Figure 1). Their structures are often linear, but may contain various degrees of branching. Polysaccharides have a general formula of $C_x(H_2O)_y$ where x is usually a large number between 200 and 2500. Considering that the repeating units in the polymer backbone are often six-carbon monosaccharides, the general formula can also be represented as $(C_6H_{10}O_5)_n$ where $40 \leq n \leq 3000$ [6]. Polysaccharides come from four major sources: plant, animal, microbes and algae [13]. Most popular

polysaccharides come from plant as first and animal as second. Starch and cellulose extracted from plants and chitin from animals are the most interesting in bioplastic industry to produce PSIP. Other polysaccharides such as pullulan, dextran and glycogen are rarely seen in bioplastics and have other applications such as in pharmaceutical industry. Cellulose-based biopolymers are mainly used to produce engineering plastics and sheets for electronic applications. Starch-based biopolymers are mainly used to produce rigid materials with high heat resistance such as plates and cutlery, and fungicides and insecticides in film-coatings. Polysaccharide immediately extracted from nature is called native. Native polysaccharides are not suitable for commercial applications for having poor mechanical properties and often go through physical and chemical processes called modification to be usable in producing biodegradable polymers. [6], [14] [9]

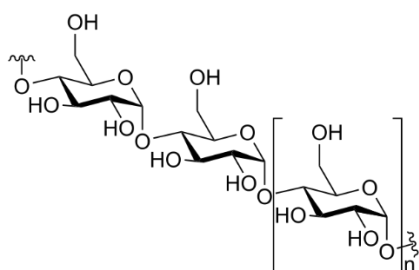


Figure 1. structure of polysaccharide repeating unit

Starch

Starch is a natural, renewable, and biodegradable polymer produced by many plants as a source of stored energy. It is the second most abundant natural material found in plant roots, stalks, crop seeds, and staple crops such as rice, corn, wheat, tapioca, and potato. The main sources are maize (82%), wheat (8%), potatoes (5%), and cassava (5%). Starch is made up of two types of polymers: amylose and amylopectin. Amylose is a linear homopolymer and may have a low level of branching. Amylopectin is the highly branched form of amylose. In most common types of starch, the weight percentages of amylose range between 72 and 82%, and that of amylopectin from 18 to 28%. Native starch is a flour-like white powder insoluble in cold water called granular starch. Modification of starch can be done through wet grinding, sieving, and drying. One very famous modified starch is thermoplastic starch that is very economic [9] [6].

Cellulose

Cellulose is the most abundant organic compound in nature with the formula $(C_6H_{10}O_5)_n$, consisting of a linear chain of several hundred to over ten thousand glucose units. It is the structural component of the cell wall of green plants and many forms of algae and seaweeds [6] native cellulose is not pure because the sources include other materials and polysaccharides like hemicellulose and lignin that lower its biodegradability. Cellulose modification is to clear impurities and is often done in two steps: alkaline treatment and bleaching treatment (such as hydrogen peroxide or sodium chlorite) to clear impurities like hemicellulose and lignin. The bleaching treatment of durian cellulose fibers were done in two steps with hydrogen peroxide or sodium chlorite for high purity of 94% cellulose. [15]

Chitin and chitosan

Chitin is the second most abundant natural polysaccharide after cellulose that is found in many parts of the world. This long-chain polymer derivative of glucose is the main component of the

cell walls of fungi, the exoskeletons of insects and crustaceans such crabs, lobsters and shrimps and is also found in squid and octopuses. It is often grafted or blended with other synthetic polymers like polyvinyl alcohol. Chitosan is a linear polysaccharide produced commercially by deacetylation of chitin [6] [16] [11].

Composites:

Composites are materials made of two types of components: the matrix whose role is to support and protect the filler materials and transmit and distribute the applied load to them and the mentioned fillers, which are the stronger and stiffer components reinforcing the matrix. Nanocomposites are composites reinforced with nanofillers that show unique properties, because of the nanometric size effect, compared to conventional composites even at low filler content. [14] cellulose fibers as a reinforcement for polymeric matrices has attracted significant attention owing to their low cost, good mechanical properties, good biodegradability, and promising renewability. From a technical viewpoint, biocomposites based on cellulose would be expected to exhibit an enhanced mechanical strength, a reduction in the material weight, lower production costs, and an improvement in the biodegradability of the final products [17]. Since blending of polymers with polysaccharides gives a material with one being dispersed into another, PSIP may also be referred to as composites throughout this review paper.

Biodegradability

Definitions

Degradation is the process of decomposition of a material to smaller particles by the effect of heat, moisture, sunlight, with or without enzymatic action that results in weakening polymer chains and creating more persistent particles. Biodegradation is a different term having a few definitions like "A process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals", "transformation of a substance into new compounds by the action of microorganisms, " a biologically catalyzed reduction in complexity of a chemical".[18]. In this literature, biodegradation is defined as a chemical degradation of polymers where the material is converted into carbon dioxide, water, inorganic compounds and biomass by the enzymatic action of microorganisms like bacteria, fungi and algae under appropriate environmental conditions. [3] [9] and Biodegradability is the ability of a material to go through the biodegradation process. Biodegradation leads to recycle of carbon, mineralization of organic matters and producing of new biomass. Mineralization is a process where biodegradable materials are converted into gases like CO₂, CH₄, and H₂, nitrogen compounds, water, salts, minerals and is only complete when all the material is consumed and all carbon is converted into carbon dioxide. Biodegradation can be divided into aerobic and anaerobic. Aerobic biodegradation or oxygen respiration is degradation of organic matters when oxygen is present. Microorganisms use O₂ to oxidize carbon into carbon dioxide. Oxygen is reduced which produces water. Thus, the major products of an aerobic biodegradation are carbon dioxide and water. Anaerobic biodegradation is the process of biodegradation in the absence of oxygen. Microorganisms either use other inorganic matters such as, nitrate and sulfate instead of oxygen as the electron acceptor (oxidizing agent) or undergo enzymatic hydrolysis which is often the case. [9] Methane and carbon dioxide are majorly produced in anaerobic biodegradation. [18]

Aerobic biodegradation reaction:

Bioplastic + O₂ + Nutrients → CO₂ + H₂O + New Biomass + stabilized Organic Matter + Mineral compounds + heat

Anaerobic biodegradation reaction:

Organic matter + H₂O + Nutrients → Digestate + CH₄ + CO₂ + minerals + Heat

Mechanism

Degradation

Although biodegradation is a biotic degradation and can occur without the effect of natural factors, [9] materials are disposed in natural environments where abiotic parameters such as light, weather, etc. exist which is why they should not be neglected. Materials can go through mechanical, light, thermal, and chemical transformation, all of which has a specific impact on biodegradability. Mechanical degradation occurs by many conditions like snow pressure, raining and bird damages. It often favors biodegradation insignificantly. Light degradation is when energy transfer of photons to material molecules makes them unstable. Photodegradation is the most efficient degradation. UV can break down polymer chains on the surface and produce free radical molecules that react with oxygen known as photo-oxidative degradation [9]. Thermal degradation which is a function of temperature, happens at melting temperature of thermoplastic polymers or at glass transition temperature of semi-crystalline polymers like cellulose. Structural changes with mobility and volume can help more accessibility of microbes. Thermal stability is the highest temperature a polymer can stand before undergoing thermal degradation. During chemical degradation, chemicals existing in the environment can react with polymer molecules and change their properties. Oxygen (O₂ or O₃) is the most powerful and depending on the chemical structure, it attacks covalent bonds and creates free radicals. Oxidative degradation is an important factor in biodegradation analysis. Another important chemical degradation is hydrolysis. Water can split hydrolysable covalent bonds as in groups ester, ether, etc. Cellulose, starch and some polyesters are hydro-biodegradable. In a material. Hydrolysis depends on water activity, temperature, PH and time. Crystalline parts of polymers prevent water and oxygen diffusion, thus oxidative and hydrolytic degradation are easier to happen for amorphous parts. [19] [12] [9] [11] [16]

Biodegradation

Biodegradation itself has three stages: bio-deterioration, Bio-fragmentation and dissimilation. During bio-deterioration, microorganisms grow on the material surface and the polymer undergoes mechanical, physical and chemical degradation as a result of microbial activity. Porosity is very influential and biofilm is formed in this stage. In the next stage, microbes break down the polymer into oligomers and monomers. Depolymerization happens by intracellular (endo-) and extracellular (exo-) enzymes released by microorganisms. Endoenzymes break down the polymer into smaller chains and exoenzymes act at the end of polymer chains to break monomers sequentially. Thermal, light, mechanical, chemical degradation may help chain scission (cleavage). Assimilation, the third stage, is a unique event in which fragments are finally converted into biodegradation products. Microorganisms integrate atoms from bio-fragments and use them as nutrients to build microbial cell structures. [19] [9]

There are six requirements for biodegradation. in simple, they are:[18]

1. The presence of microorganisms,
2. An energy source for microorganisms to use to grow,
3. A carbon source,
4. An electron acceptor such as O_2 , NO_3^- , SO_4^{2-} , CO_2 (oxygen in case of aerobic biodegradation)
5. Nutrients such as nitrogen, phosphorus and calcium
6. Right environmental conditions like temperature and PH

More than 90 types of microorganisms are responsible for biodegradation in different environments. Bacteria and fungi are the most common in biopolymer biodegradation. [9] Temperature directly controls biodegradation by controlling microbial enzyme reaction. Half of biodegradation rate is reduced by $10^\circ C$ decrease in temperature. Maximum T is $65^\circ C$. Microbial activity itself increases soil temperature making biodegradation different season by season. [18]

Therefore, based on these requirements and other degradations involved, biodegradation is dependent on climate, UV radiation, soil/water characteristics (moisture, temperature, ph, oxygen, nutrients and organic matters) and types and population of microorganisms as environmental parameters as well as time and material properties including physical properties of the material(i.e. Shape, thickness, surface area), porosity, chemical composition, chemical structure, molecular weight, molecular weight distribution, surface characteristics (hydrophobicity), crystallinity, melting or glass transition temperature are the most important. [19] [11][12] [9]

Degradation and biodegradation

Degradation stops at the second stage when the material is disintegrated into smaller particles. The process is biodegradation only If the process continues to the third stage of dissimilation where the biotic factor (microorganisms) comes to play. Therefore, degradation and biodegradation are different terms and should not be used interchangeably. However, degradation is often used for biodegradation within the context of biodegradation where it is not mistaken. Since this paper only aims to discuss biodegradability, degradation is used for simplicity and any research on degradation was already neglected during the searching phase.

Standards for biodegradability

According to International Organization for ISO 17556-2019, a material is considered to be completely biodegradable if it fully biodegrades in less than 24 months. The same definition is given by European Committee for Standardization, European standard EN 17033:2018. As a matter of fact, it is not possible to simulate the real biodegradation environment [20] since there is a huge diversity in disposal location of materials and environmental parameters have a great impact on biodegradation process. However, the most actual standard methodologies for biodegradation of plastics in soil are ASTM D5988-18 and ISO 17556:2019 which determine standard testing conditions for aerobic soil degradation(see Figure 2). Since most biodegradability tests are performed in soil and not aquatic systems, a PSIP for this literature is considered biodegradable if it biodegrades more than 60 wt.%.

Specifications	ASTM D5988-18	ISO 17556:2019
Type	The soil should be natural and fertile, preferably "sandy loam" collected from fields and forests not exposed to pollutants. The soil used should be a mixture of natural and fertile soils collected from the surface layers of at least 3 diverse locations.	Natural soil from fields and/or forests may be used as an inoculum to simulate biodegradation in a specific natural environment.
Particle size	Less than 2 mm	Less than 5 mm
Room Temperature	20 – 28 ± 2 °C	20 – 28 ± 2 °C but in preference 25 °C
pH	6–8	6–8
Moisture holding Capacity (MHC)	80–100%	40–60%
Running Time	Should not exceed 6 months	Should not exceed 6 months but may be extended up to 24 months
Reference Material	Cellulose or starch	Microcrystalline cellulose powder, ashless cellulose filters or poly(3-hydroxybutyrate)
Validation Criteria	The test is considered valid if after 6 months more than 70% biodegradation is achieved for the reference material and if the amount of CO ₂ evolved from the control reactors is within 20% of the mean at the plateau phase or at the end of the test.	The test is considered valid if the degree of biodegradation of the reference material is more than 60% at the plateau phase or at the end of the test and if the BOD (biological oxygen demand) values of or the amount of CO ₂ evolved from the controls are within 20% of the mean at the plateau phase or at the end of the test.

Figure 2. Standards for biodegradability measurement, *astm d5988-18* and *iso 17556:2019*

Biodegradability testing conditions

Controlled and uncontrolled

Biodegradation is a complex process that is affected by a large number of parameters, as explained in the previous section, and it is nearly impossible to predict the exact biodegradability behavior of a product in the real disposal conditions. [19] in order to obtain biodegradability results that is closest to actuality, materials should be tested in both controlled and natural biodegradation conditions (in vitro and in vivo). Soil, seas, rivers, anaerobic sludge, activated sludge, and aerobic or anaerobic compost are examples of natural systems.[11] abiotic factors such as temperature and humidity, PH, light, etc. As well as biotic factors (i.e., Types and amount of microorganisms) are not controlled but impact the process and other degradations work along and affect biodegradation. For instance, soil burial test can both provide a realistic environment or be designed in accordance with ASTM, EN, and ISO which determine qualities of the compost in the test, by giving parameters such as moisture and temperature a certain range. [21] [22]

Environmental medium

Biodegradation of materials is tested in different environments that is compost, soil and aquatic environments [8]. Most common biodegradability tests are carried out in compost. [9] Composting is an aerobic process in which the organic matter is converted to CO₂ and humus (a dark soil-like material) by the activity of microorganisms. Complete composting leaves no visually detectable or toxic residues. All compostable materials are biodegradable. [18] [12]. Home and industrial composting can have significantly different results because of different conditions. Industrial composting often meets specific conditions such as temperature, moisture and PH that is required more efficiently than home composting. Soil environments have the most potential in biodegradation for containing the most diverse groups of microorganisms. Bioplastic wastes are more likely to become pollutants in marine and other aquatic ecosystems. The researchers suggest that in order to

understand the biodegradation of bioplastics in marine systems, the material should be tested in various sea habitats because conditions are not the same in different marine regions. [12]

Undefined testing conditions

Some tests to quickly measure biodegradability (from 3 days to 15 days) are immersion in activated sludge, enzymatic and hydrolytic degradation in acidic, alkaline and buffer solution and water absorption test. Enzymatic degradation is often used for rapid evaluation of biodegradability but it does not give the actual degradation results in natural conditions. A particular enzyme is placed in the solution and the sample is immersed in it. In buffer solutions, hydrolysis may occur before enzymatic action. Water absorption test is performed because degradation begins with water in many polymers. Water permeability and solubility make such polymers susceptible to hydrolysis. In fact, water absorption test shows how much a polymer is likely to undergo hydrolysis degradation. The samples are immersed in water for a short time (hours to a few days) and taken out to be measured. [23] although these tests are not standardized and the results cannot be referenced, there are sometimes used by researchers as seen later.

Nonetheless, every biodegradability test should include the following. Chemical properties such as PH, total dry solid, volatile solid, moisture content, and C/N ratio (mass of carbon to mass of nitrogen) of the inoculums, temperature and Moisturization intervals, whether the samples are buried or placed on the surface of the soil, size and shape of the samples, the amount of soil used and depth of sample burial should all be determined and reported.

Methods of biodegradability measurements

There are qualitative and quantitative methods to analyze polymeric properties: physical methods, thermal methods respirometric, chromatographic, and spectroscopic, and meta-analysis.[11] some of these methods were exclusively designed to investigate biodegradation while some others measure other properties as an impact of biodegradation which can then be correlated with biodegradability.

Physical methods

Physical methods are observation of physical changes by visual or instrumental means. Some visually detectable changes are discoloration, fragmentation, surface erosion and changes in strength properties which are indicators of biodegradability. Strength characteristics can also be measured. An extensometer is a tool to measure these properties. For instance, tensile strength which is the highest stress a polymer can bear while being stretched before breaking decreases with biodegradation progress. More practical methods are evaluation of micromorphology and weight reduction. Micromorphology is observation of holes, cracks and porosity by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM is the study of surface morphology and TEM is observation of a very thin cross section of the sample sheet. Human vision cannot detect such microscopic changes that start at the beginning of a degradation process. [11] [9] Weight loss is the simplest and most widely used method that quantitatively measures weight loss in soil burial tests [11]. it is calculated as:

Equation 1.

$$D = \frac{w_0 - w_1}{w_0} \times 100\%$$

where: D = Degradation Ratio (%)

w_0 = initial weight (g)

w_1 = current weight (g)

Degradation rate and ratio are different for mass loss evaluation [24]. Ratio indicates what percentage of the initial weight is lost each day. The rate is given by ratio of a day divided by the number of the day. If the ratio of a sample is 2% in day 8 and 4% in day 9, the 2wt. % of the initial weight is consumed between day 8 and 9 and the degradation rate is 0.25 % for day 8.

Spectroscopic Methods

this method uses electromagnetic radiations like light to measure different properties of polymeric materials. It is a quantitative method based on radiation generated or absorbed by atoms and chemical bonds in a molecular or atomic structure. There are three techniques. Fourier-transform infrared (FTIR) spectroscopy studies the vibration of molecules. Infrared light alters the dipole moments of molecules creating a vibrational energy that is unique for each bond, hence for each functional group. These absorption bands are used to identify molecules and compositions of a polymer. [11] it is also employed to detect the change in bond intensity, which is caused by microbial degradation.[12] X-rays diffraction (XRD) uses X-rays, short-wavelength electromagnetic radiation created when decelerated high-energy electrons move into atoms' inner orbitals. They are used to analyze solid-state polymeric structures to determine degree of crystallinity. X-ray fluorescence (XRF) Is For the analysis of trace elements (minerals in living tissues) in polymers. It can determine the presence of stabilizers, plasticizers, additives, etc. in polymers. [11]

Respirometric Methods or Biogas Evolution

It can indirectly measure respiration metabolism rates of living creatures like microorganisms, cells and plants. During biodegradation, gases such as oxygen is consumed and biogas like carbon dioxide and methane is released as a result of microbial activity. Both can be measured and correlated with biodegradation progress. When polymers begin to degrade under aerobic conditions, oxygen is consumed and carbon dioxide is released. Therefore, both BOD (biochemical oxygen demand) and CO₂ evolution can be applied. In anaerobic biodegradation, the carbon in the material is mineralized into CO₂ and CH₄ and Biochemical methane potential (BMP) can be used. [25]The amount is measured using a sensor with computerized controlling program and the unit is milligram O₂ or biogas per day. [11] [9]

Meta-analysis

It is a statistical technique where data is collected from multiple analyzing methods and various researches on biodegradation and then analyzed. [11] research results, although to an acceptable level, are not free of errors and Meta-analysis helps to realize and minimize these errors to determine the most precise biodegradability results.

Thermal methods

Polymer characteristics are measured with the change in temperature. They are often used for polymer fingerprinting. Differential scanning calorimetry (DSC) is when a linear heating or cooling is applied to the material followed by measuring temperature and enthalpy which is the result of thermal processes such as melting, glass transition and crystallization. Heat capacity, glass transition temperature, crystallization temperature, thermal degradation temperature, and melting point are data that can be obtained. Differential thermal analysis (DTA) applies the same technique as DSC but the temperature difference between the sample and a reference material is monitored against time or temperature. It is often combined with Thermogravimetric Analysis for analysis. TGA is used to depict weight changes over time and temperature. Figure 3 shows all biodegradability measurement methods for biodegradable polymers . [11]

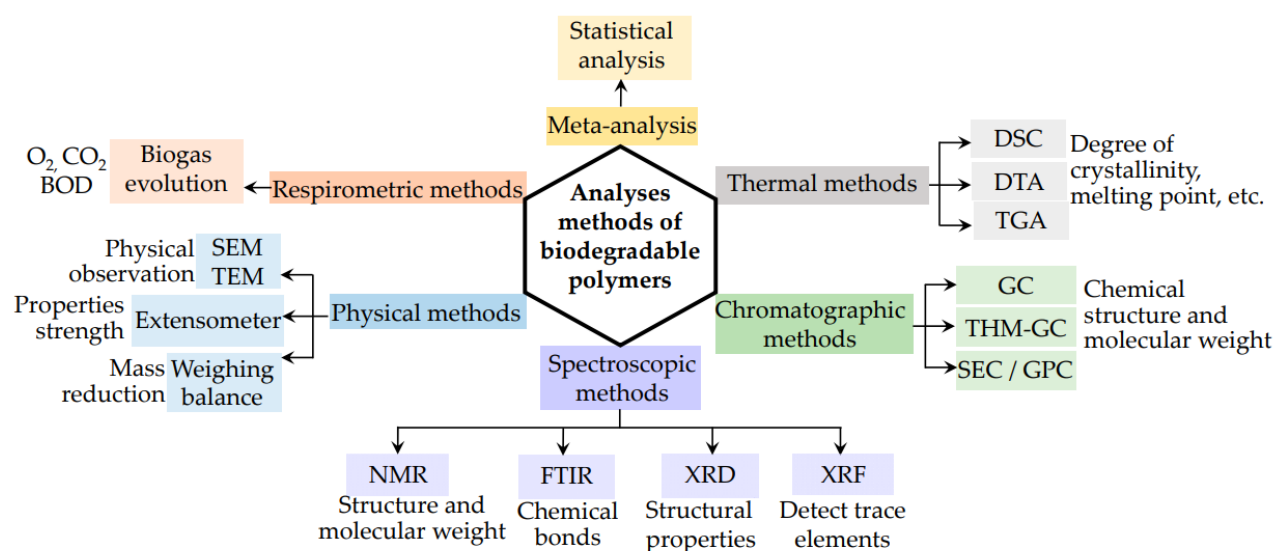


Figure 3. Analyses methods of biodegradable polymers

Comparison

According to [11], Method selection is mainly dependent on availability of instruments and tools to the examiners in institutions. In full availability, the method is determined by testing conditions. In a test by [26], TEM was more efficient but because the films were too brittle and cross-section could not be examined, SEM was applied. In testing the biodegradability of a nanocomposite with a 4 wt.% filler by [27], SEM and FTIR could not observe changes because of the low content. However, weight loss test showed visual differences, though not significant, of the composite with and without the filler.

Among all methods, physical is the most common with weight loss and SEM as the most popular. Visual observation of physical changes can be qualitatively correlated with how much biodegradation proceeded. Otherwise, they are either not applied to measure biodegradation statistically [11] in important experiments or used along with other methods. Human error come easily with this method as man cannot distinguish differences at certain sizes, making it difficult to compare results within one or from multiple experiments. As discussed before, biodegradation has three stages and degradation

stops at bio-fragmentation. In weight loss evaluation, low molecular weight fragments (the second stage) can be mistaken for fully degraded particles. Therefore, it does not imply that assimilation(mineralization) of the material, thus biodegradation has occurred. Measurement of biogas production (CO₂ and/or CH₄ evolution) or O₂ consumption (BOD) has an advantage over the conventional weight reduction because it only studies the byproducts of microbial action implying that mineralization is happening [9], even though it is not as popular as weight loss method. Mass reduction is used very commonly for simplicity but comes with other disadvantages. The residual soil that remains on the material even after washing away reduces measurement accuracy. [28]. In fact, it becomes nearly impossible to separate the sample from soil without damaging it specially in later stages [29]. According to (Hoshino et al., 2007) weight loss cannot measure biodegradations over 70% accurately for the reasons explained. This was the challenge in the cases of [30] and [31] with this method. Weight losses of samples were not estimated exactly because all films were disintegrated into very small pieces, with soil adhered to them making them difficult to collect without damaging. On the other hand, BOD is only for aerobic biodegradation and BMP is for testes under anaerobic conditions [25] while CO₂ evolution and mass loss can be used for both aerobic and anaerobic conditions. [9] CO₂ release is more suitable for when the only carbon source is the material. For biodegradation conditions where there are other organic matters as carbon source in the environment, it is not suitable because carbon dioxide may come from the material, the environment or both [19]. In soil burial technique, the soil must be free of carbon to be able to apply CO₂ evolution method. Thermal methods are used a lot for analysis of other properties of PSIP, but rarely for biodegradation. On rare occasions, TGA is applied along with physical methods in biodegradability tests. FTIR is the only spectroscopic method that is used along with physical methods, especially weight loss and SEM. It is not as popular as physical methods but more used than thermal analysis. Table 11 provides a realistic comparison of how common these methods are applied.

What affects biodegradability of polysaccharide-based polymers?

Raw polysaccharides are biodegradable when exposed to in situ soil degradation and is dependent on the number of hydrophilic polar function groups in their polymer chains. However, this inherent characteristic is modified when incorporated in composites whether as fillers or the matrix and is influenced by the chemical structure, the nature of components, cross-linking density, and environmental conditions [20]. According to [9] the biodegradability of bio-polymers is affected by the chemical and physical structure of the materials and not by the origin of their resources or their production process. The longer the polymer chain, the more crystalline and the more complex the polymer is, the more difficult biodegradation becomes. [9]

Source of polysaccharides

There are many origins one singular type of polysaccharide comes from. For example, starch can be obtained from fruits, tubers, grasses, crops such as rice, corn, wheat, tapioca, and potato and can be found in the pulps, seeds or culms [32]. However, there is a certain number of starch sources to use in PSIP production. Each starch type is known to consist of an average amylose content which will be discussed.

There exists a very small number of experiments designed to investigate the effect of polysaccharide source on final biodegradability. No results on sources of cellulose effect on biodegradability was found but there is little data on starch type. Results of a six-month test by [22] to see the effect of amylose content from different starch sources on biodegradability of PVA/starch blend films (Table 1, Figure 4) indicate that higher amylose content lowers biodegradation rate because crystallinity increases and it is harder for microorganisms to penetrate crystalline parts.

Table 1. starch sources and their amylose content

Starch Source	Abbr.	Amylose (wt. %)
High Amylose Starch	Ham	73
Potato Starch	PS	35
Corn Starch	CS	21

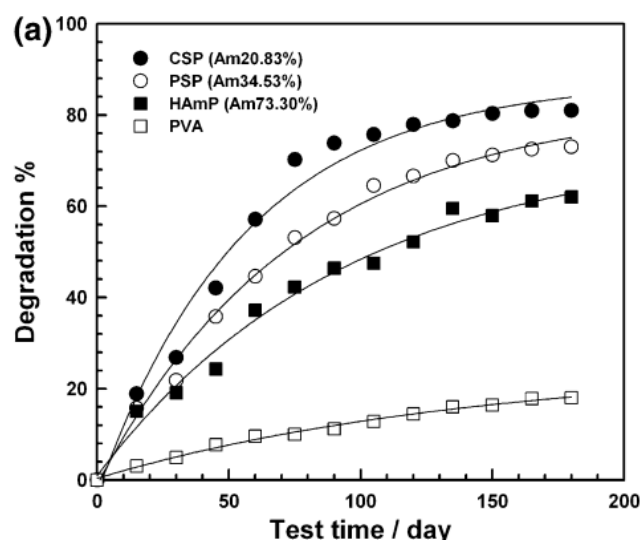


Figure 4. degradation of starch with different amylose content

Between granular starch, high-amylose cornstarch (HACS) and waxy maize cornstarch (MCS) with amylose/amylopectin weight ratios 30/70 70/30, 0/100 tested in compost by [33], the highest weight loss belonged to MCS with no amylose content but the weight loss results were very close (by 1%). Another similar experiment was done. A two-month biodegradability test on corn, cassava and wheat starch were performed in compost by [34] but no statistical data on neither amylose content nor weight loss was reported. Based on visual examinations like change in tonality and integrity there were not noteworthy differences between the three sources and all starch types showed almost the same rate of degradation in vegetal compost. There are a few considerations that justify the slightly different results. One explanation is that while pure starch was tested in [22], the starch in [33] consisted of only 40% of the blend and the amylose content effect could not be individually observed because weight loss is calculated for the blend not starch. [22] and [34] where pure starch was tested, three samples in [22] had very different amylose content which is responsible for the distinct weight loss results while in [34], the average amylose percentage is nearly the same for corn, cassava, wheat. Therefore, [34], [22] and [33] do not contradict each other and more amylose content in starch decreases biodegradability.

A few experiments to compare different types of polysaccharides and their derivatives were found. Biodegradation investigation of binary blend of cellulose–LDPE the ternary blend of cellulose–

LDPE–chitin or chitosan with indicated that while addition of both chitosan and chitin to the blend increases biodegradability, chitin included blend has faster degradation than chitosan. [35]. [36] tested blend of cassava starch and Semi-refined kappa carrageenan (SRKC) with polyacrylic acid (PAAc) to produce super water absorbents and Starch-included blend had higher biodegradation than pure PAAc and cellulose (used as control), highest biodegradability in fact. In another test by [37], polylactide was blended with random natural polysaccharides and the results in order of faster degradation were starch, chitosan, ethyl cellulose. In the blend of gelatin with the same content of carboxymethyl cellulose (CMC) and chitosan, chitosan showed higher biodegradation [38]. [39] tested pure starch and cellulose and the time to reach 100% degradation was 30 and 105 days. This shows that type of polysaccharide incorporated influences biodegradation and starch has shown the highest biodegradability. So, the four majorly used polysaccharides in PSIP, the order of faster biodegradability is starch, cellulose, chitin and chitosan. The effect of various types on biodegradation can be sometimes attributed to polysaccharide structure. Exopolysaccharides (EPSs) produced by different lactic acid bacteria had different structures and different biodegradation test results. The repeating units of the EPSs that degraded were simple, with only one single residue as a side chain, Whereas the non-degradable EPSs had double substitution on the backbone which reduced accessibility of enzymes to the material. [40]

Even though polysaccharides can be grouped into four general groups, they are very diverse in where they come from (see Figure 5), thus have many types [13]. Besides, PSIP are new to researchers and is becoming increasingly popular with more attention given to them in near future, to look into how other and each type of polysaccharides affects biodegradability. Moreover, cellulose and starch and a few others such as chitin are the most abundant of all. They are inexpensive and have proven their good properties when blended with other polymers. This might explain why there is not much biodegradability investigation on various polysaccharide sources and their plastic biodegradability.

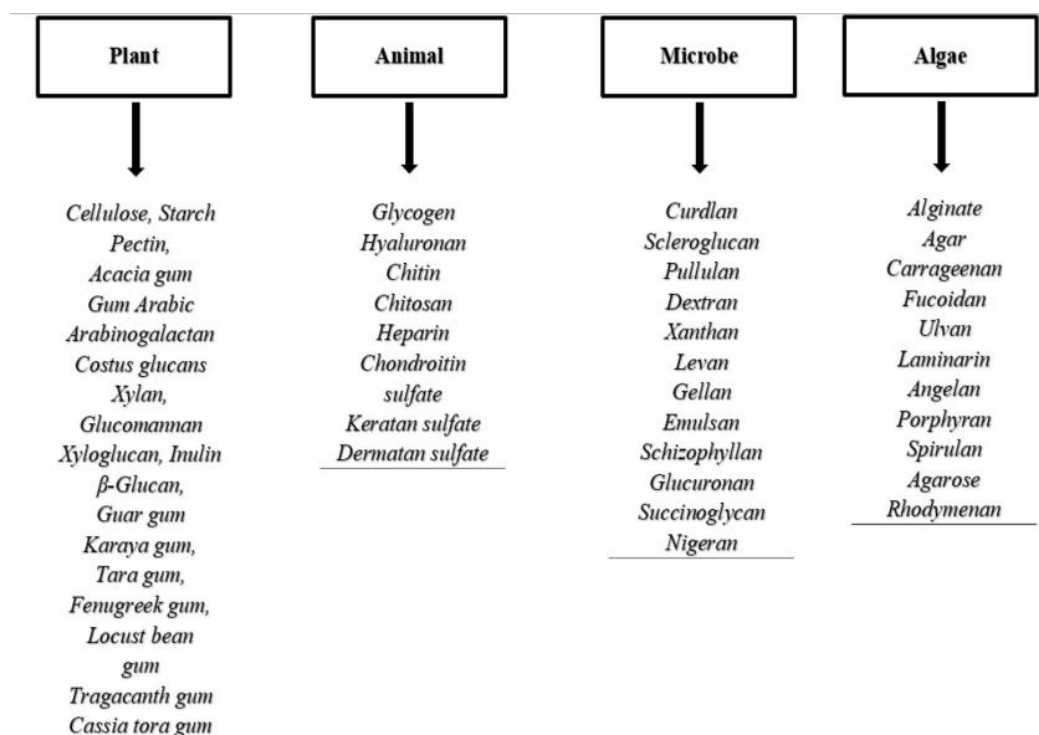


Figure 5. sources and types of polysaccharides

Chemical Structure

Modification of polysaccharide are done to achieve the desired properties for their end use. Modification of polysaccharides mostly includes modification of their chemical structure such as in grafting, functional group substitution, and crosslinking. Starch grafting with other polyesters and synthetic polymers and modification of cellulose by substitution of its hydroxyl group with acetyl, carboxyl and ester is very common. The impact of these modification methods on biodegradability is explained.

Functional group substitution

Functional group substitution of polysaccharides is stated as degree of substitution (DS). Biodegradability has a negative correlation with DS. Etherified HACS tested with different degrees of substitution showed that the biodegradability of etherified HACS decreased with increasing DS. [41] Research on cellulose acetate (CA) by both [42] and [43] shows that CA biodegradation rate depends on the degree of acetyl group substitution and biodegradation rate decreases when degree of substitution increases, to the point that when DS is around 2.5, biodegradation is very reduced but not stopped by the high number of functional groups. In [43], with DS above 2.4, the degradation was delayed until reinoculation. Among Non-acetylated (TPS) and acetylated thermoplastic starch (TPAS) with high and low degrees of substitution that was tested under composting condition by [44], non-acetylated starch had the highest biodegradation rate, TPAS with DS 1.5 being next and TPAS with DS about 2.5 being the slowest to degrade.

Polysaccharides are hydrophilic. They absorb water which increases microbial growth but causes swelling. One application of acid modification is to reduce swelling. The acidic functional group forms H-bonds with the host polymer, improving moisture resistance. In a case by [45] Carboxylic

group substitution(esterification) of starch decreased biodegradability. TPS was modified with 1-4% citric acid and ascorbic acids separately. The degree of substitution was 0.027 to 0.054 which is a low DS. Biodegradation of TPS, 2% citric acid modified TPS and 2% ascorbic acid modified TPS are shown over 30 days (see Figure 6). Citric acid forms stronger hydrogen bonds with starch and resists water more than ascorbic acid which is why Citric modified TPS has lower degradation. The behavior of water absorption and biodegradation rate of the three samples, as seen in Figure 6 and Figure 7, are similar which is in agreement of the explanation above. In another case of acid modification, Low density polyethylene (LDPE) and TPS blend was reinforced with cellulose nanofibers (CNFs) and acetylated Cellulose nanofibers (ACNFs). Acetylation of fibers was done for the purpose of better dispersion in the matrix, because it reduces hydrophilicity and polarity of CNFs which makes them more suitable in nonpolar polymer matrixes. During 30 days of testing, increasing nanofibers content increased biodegradability, but the biodegradability of ACNFs reinforced blends was lower compared with the CNFs. As mentioned, Hydroxyl groups substitution with acetyl groups enhances the compatibility of ACNFs with the blend. This formation reduces cracks and holes, the main driving force for water diffusion and microbial growth[46]. According to [39] modification like acetylation of all polysaccharides increases hydrophobicity and reduces enzyme accessibility, thus lowers biodegradability.

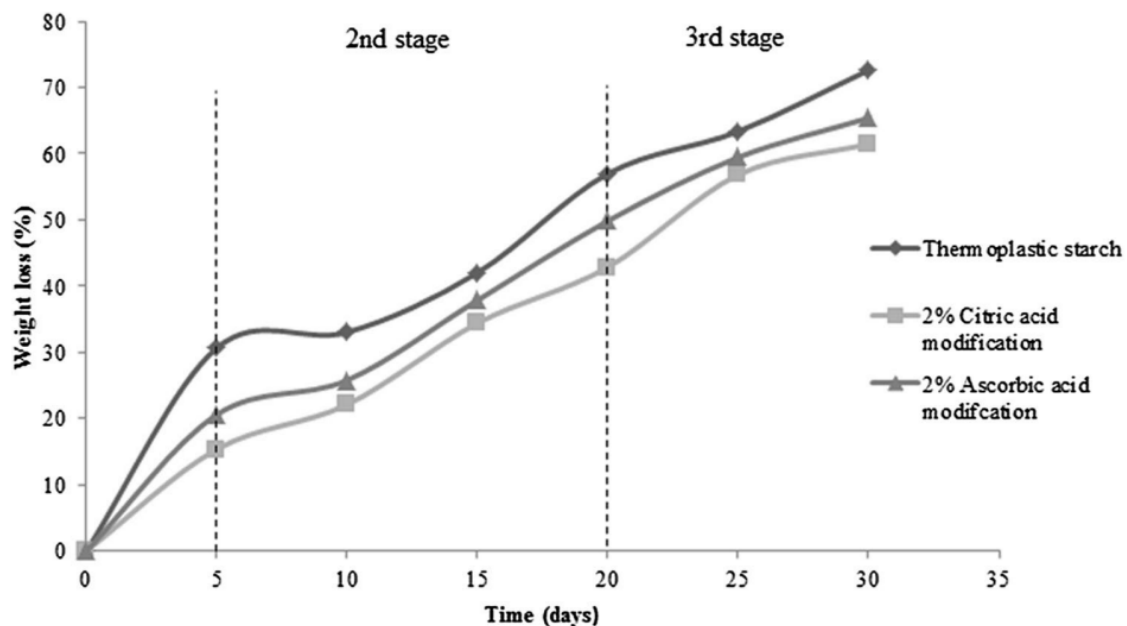


Figure 6. biodegradability of pure and modified thermoplastic starch with citric acid and ascorbic acid

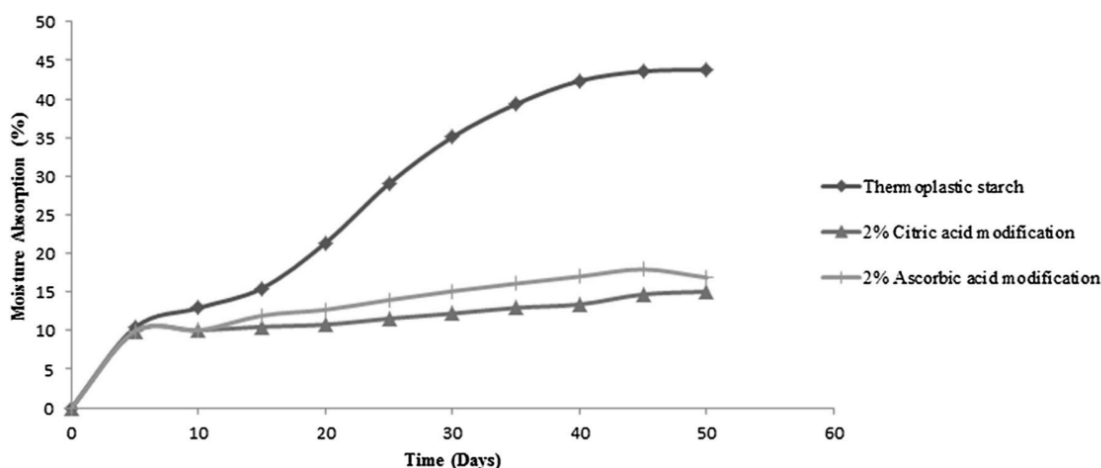


Figure 7. water absorption of pure and modified thermoplastic starch with citric acid and ascorbic acid

However, the relationship is not always easily predictable. 14 cellulose-based materials were investigated (see Figure 8, Figure 9). Two materials, CMC crosslinked by Al-salt and butylated hemicellulose (BHC DS: 1) degraded rapidly and reached 100 % degradation after 2 weeks of composting. The fast rate can be attributed to their water solubility which enhances biodegradability in high moisture conditions. Cellulose IL (regenerated from ionic liquid), cellophane and cellulose carbamate reached full degradation after 4 weeks. Acetylated celluloses; cellulose acetate, cellulose palmitate and cellulose octanoate did not degrade at all in the experiment. Although cellulose palmitate has the same DS as BHC which was fully degraded, cellulose palmitate has long fatty acid substituents on the backbone. Same is with cellulose octanoate. These substituents prevent microbes from attaching to the backbone. The first figure shows degree of hydrolysis over degree of substitution and the second figure is the composting results. Observing data for enzymatic hydrolysis, there is a negative relation between DS and DH (degree of hydrolysis) which is glucose content/initial cellulose content. The same relation is expected for composting experiment to some extent but the compost experiment is not in complete agreement with the hydrolysis experiment. No relation can be assumed between DS and biodegradation rate as both molecular structure of the functional group and water solubility play a factor. Methyl cellulose has a higher DS than cellulose IL ($1.7 > 0.0$) but degrades faster because of its water solubility. Cellulose palmitate has a lower DS than methyl cellulose but does not degrade at all for having long-chained substituents. However, it can be concluded that the degree of substitution as well as the length of the substituent are much more important factors that hinder biodegradation [47]. Tested by [48], degree of fungal biodegradation is dependent on the structure and content of the cellulose derivative (hydroxyethyl and hydroxypropyl cellulose) included in the polyurethane composite matrix. Small variations in cellulose structure produce large changes in biodegradability behavior

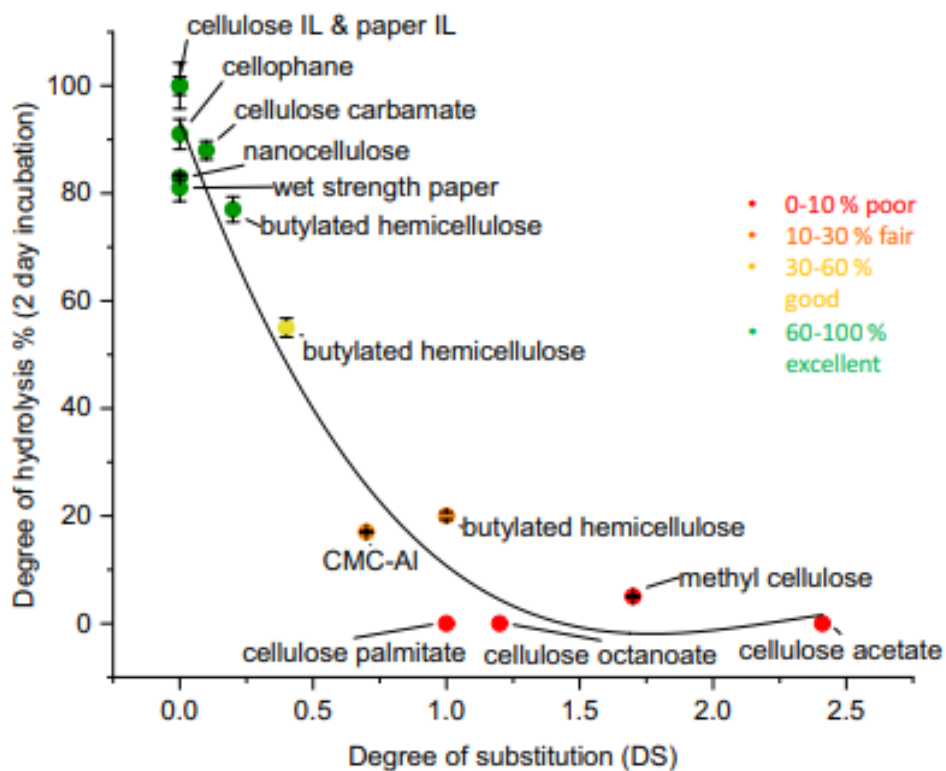


Figure 8. hydrolysis of 12 substances over their degree of substitution

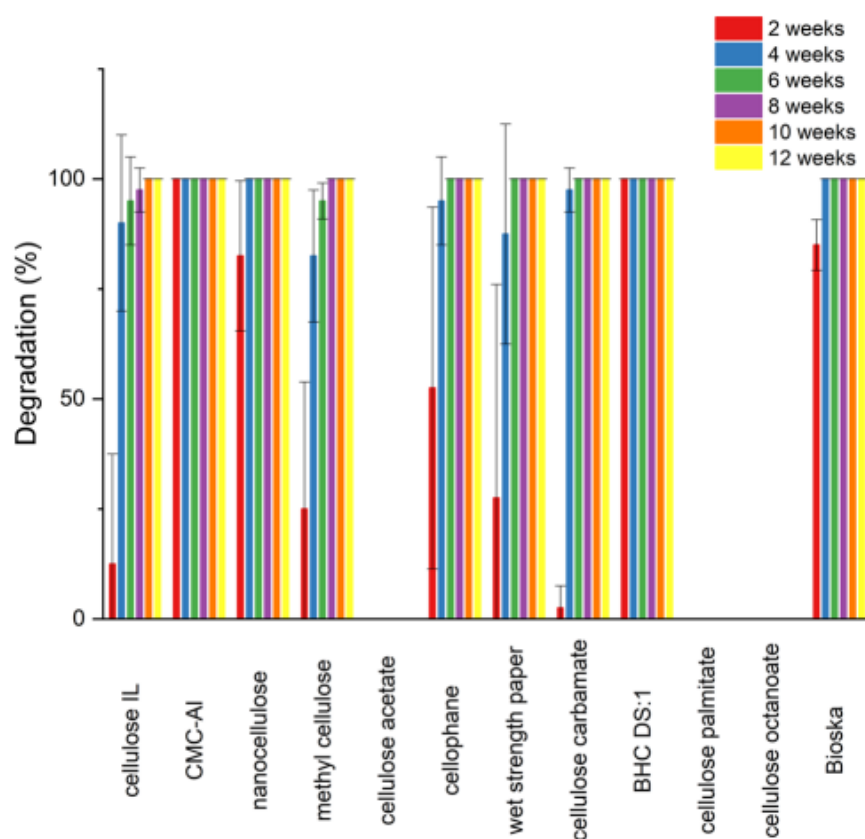


Figure 9. degradation of 12 substances in 2-12 weeks

In fact, the longer and more complex the substituents, the slower the biodegradation process. The concept is also confirmed by [9] that discuss biodegradability of bioplastics in general. Mater-Bi is a starch-based biopolymer (starch, additives and polybutylene adipate terephthalate (PBAT)). PBAT and starch are both biodegradable, but in the biodegradation test, additives and starch were first to consume and PBAT degraded in later stages because PBAT has a more complex structure than starch.[21] As another example [49] tested biodegradability of pure poly(L-lactide) (PLL) and cellulose acetate butyrate (CAB) (see Figure 10) . While PLL fully degraded in 30 days, CAB did not degrade in 90 days. Although cellulose is fully biodegradable, bigger DS and more complex structure of CAB with different functional groups hinders hydrolysis and microorganisms' penetration.

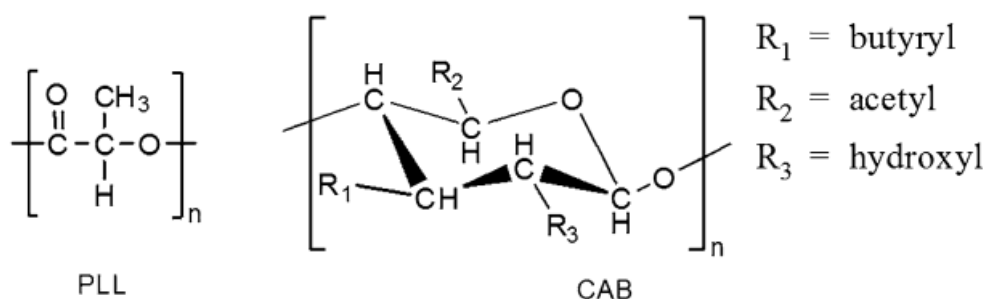


Figure 10. chemical structure of CAB and PLL

In another experiment, despite the fact that propionyl and acetyl groups are chemically quite similar, Propionated and acetylated thermoplastic starch showed very different behaviors [44]. The very fast biodegradation of propionated TPS at a rate similar to non-acetylated TPS could be for the parts of the sample that were not accessible [or permitted by propionyls] during modification. In another test by [7] between acetylated starch and thermoplastic acetylated starch in PLA blends, PLA/TPAS showed higher mass loss. This means that besides degree of substitution, it is also a matter of both the type of functional group and polysaccharide that is being modified.

Starch modification

Biodegradability of native and oxidized corn starch (with hydrogen peroxide) was tested for 98 days. Oxidization is a popular starch modification that is done by substituting starch hydroxyl groups with aldehyde or carboxyl groups. As seen in Figure 11, the weight loss in all stages, despite being insignificant, is consistent with the results from other functional group substitution [27].

Sample	WL (%)		
	1st stage	2nd stage	3rd stage
TPS	29.0 ± 0.8 ^b	92.9 ± 2.5 ^a	99.9 ± 0.06 ^b
TPS-Ox	26.9 ± 0.2 ^a	86.9 ± 15.7 ^a	98.0 ± 0.9 ^a

Figure 11. Biodegradability of native and oxidized corn starch for 98 days

Native starch had better biodegradability in another test. Raw starch before any type of modification is granular. In PCL/Starch blends, granular starch enhanced biodegradation compared to PCL/waxy-starch blend. The same was with hydrolysis. Granular starch undergoes higher weight loss than TPS. It may be due to granular starch having more surface area and thus being better exposed to microbes to consume. Therefore, destructuring of starch reduces biodegradability. [29]. Looking at Table 2, It can also be seen that between granular cornstarch and two other modified starch, HACS and MCS, granular starch had the highest weight loss [33].

In conclusion, polysaccharide modifications may result in both lower and higher biodegradability depending in the nature of both modifiers and polysaccharides and we cannot make the same conclusion for all polysaccharides as claimed by [39], declaring that polysaccharide modification slows down biodegradation.

Grafting

Grafting polysaccharides is another approach to modification. There is a linear relation between percentage grafting and biodegradability. With higher degrees of grafting, biodegradability rate decreases. Grafting of PCL onto starch for the purpose of more rigidity decreased degradation because PCL chains reduce starch availability to microorganisms. [33] Pure starch and polystyrene-graft-starch copolymers with different degrees of grafting were tested in three different types of soil for 6 months. Starch degraded 55 to 93 %, while the copolymer did 37 to 77 % in different soil systems. It was determined that there is a significant linear correlation between percentage of mass loss and percentage of grafting. A possible explanation is that portions of starch is protected by PS grafting which limits microorganisms' accessibility to starch. During 6 months, only starch degraded and not any PS. Therefore, biodegradation was dependent on how much starch was accessible to microorganisms. [50]. Figure 12 clearly show higher PS grafting covers more starch.

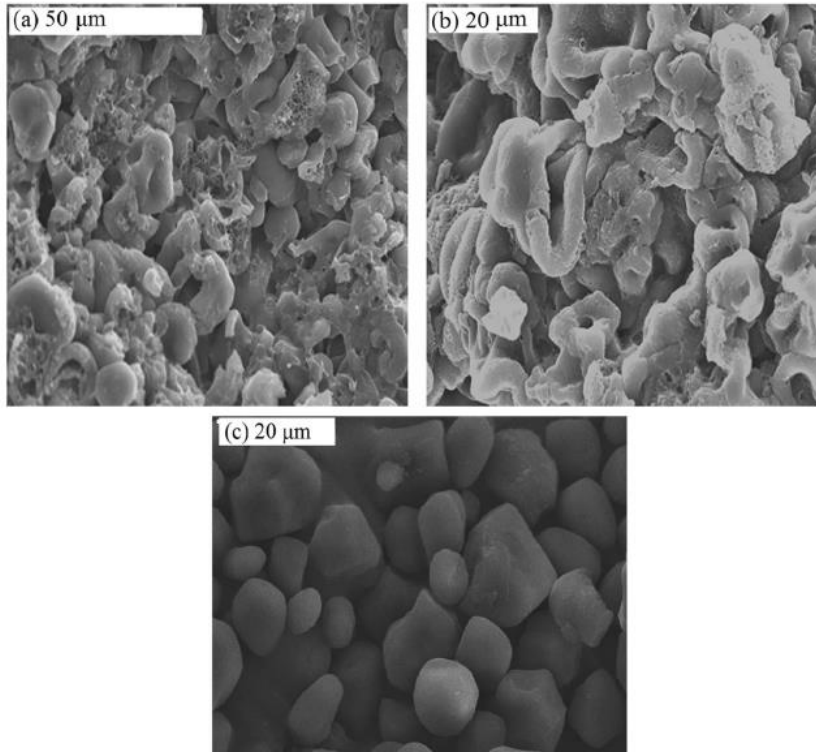


Figure 12. Three SEM figures of (c) pure starch, (b) PS-graft-starch copolymers with $G=16.24\%$ and (a) PS-graft-starch copolymers with $G=25.27\%$

Equation 2

$$G(\%) = (\text{weight of grafted PS} / \text{weight of PS-graft-starch}) \times 100$$

When degrees of grafting are the same, biodegradability comes down to hydrophilicity of the grafting agents. In [51], TPS was grafted with vinyl monomers such as methyl methacrylate (MMA) and methacrylamide (MAM). The films grafted with MAM degraded slower than films grafted with MAA Due to less water absorption by MAM. Unlike degree of substitution, high degrees of grafting can turn a biodegradable PSIP into a nonbiodegradable one. A grafting degree is determined when PSIC biodegradation does not occur. For polystyrene-graft-starch copolymers in [50] the maximum $G\%$ was very different in different soils: 43 % in soil sample 1, 77 % in soil sample 2, and 37 % in soil sample 3. The three soils had almost the same PH and moisture level tested under the same temperature, so it was claimed by the author that microbial nature was responsible for the difference. Maximum percentage is dependent on polymer components as well. Maximum $G\%$ for starch grafted with MA-DETA was 29%. Therefore, deciding the maximum grafting for all grafted copolymers is nearly impossible.

Loading of polysaccharide

The discussion in this section is to see the effect of amount on biodegradability and why there is a maximum loading as well as a minimum weight percentage at which biodegradation starts and on what basis the best polysaccharide content in PSIP is decided.

Generally, incorporation of polysaccharides in polymers increases PSIP biodegradation because of their inherent biodegradability and with increased content of polysaccharide included, the biodegradation increases as well. However, depending on the type of both polysaccharide and other components in the composite, biodegradation behavior is not a simple and predictable linear function of polysaccharide content.

Incorporation of Yerba mate extract with different concentrations (0, 5 and 20 wt.%) into cassava starch-glycerol films increased biodegradation in all compositions for allowing more microorganisms attack during 12 days of testing and 20wt.% blend obviously degraded faster. [28]. Similarly, PE/TPS (25% TPS) was filled with Nanofibers and acetylated nanofibers by 1, 3, and 5 wt.% in a test by [46]. Increasing the content, increased biodegradability and maximum weight loss was observed for 5 wt.%. [52] investigated the effect of CNFs, extracted from wheat straws, on PE/S blend biodegradability for 30 days. The blend was reinforced by different amounts of CNFs (6–14 wt.%). Due to the weak interaction of CNFs and the polymer, mechanical properties were undesirable but the biodegradability was enhanced due to the hydrophilicity of both TPS and CNFs. In another experiment, increased contents (0, 5, 10, 15, 20 wt.%) of microcrystalline cellulose (MCC) as filler were tested on TPS matrix for 3 weeks. As the result, higher MCC content had more effective enzymatic degradation. Hydrophilicity of the sample was dependent on MCC content and despite the fact that moisture content decreased with MCC increase because of more crystallinity, heavy microbe growth was observed for more MCC amounts. It is attributed to more carbon source in samples after MCC addition which triggers microorganisms activity [53].

The same result was obtained by [54] in which cellulose fibers (CFs) extracted from rice straw was added to propylene (PP) as a filler by amounts of 10, 20, 30, 40 and 50 wt.%. As seen in Figure 13, all composites constantly degraded over time and degradation rate increased with increasing CFs contents. Pure PP did not degrade at all and the remaining weight percentage of PP/CFs composites with 90/10, 80/20, 70/30, 60/40, and 50/50 wt.% was 96.98, 92.28, 88.82, 83.00, and 76.89 wt.%, respectively.

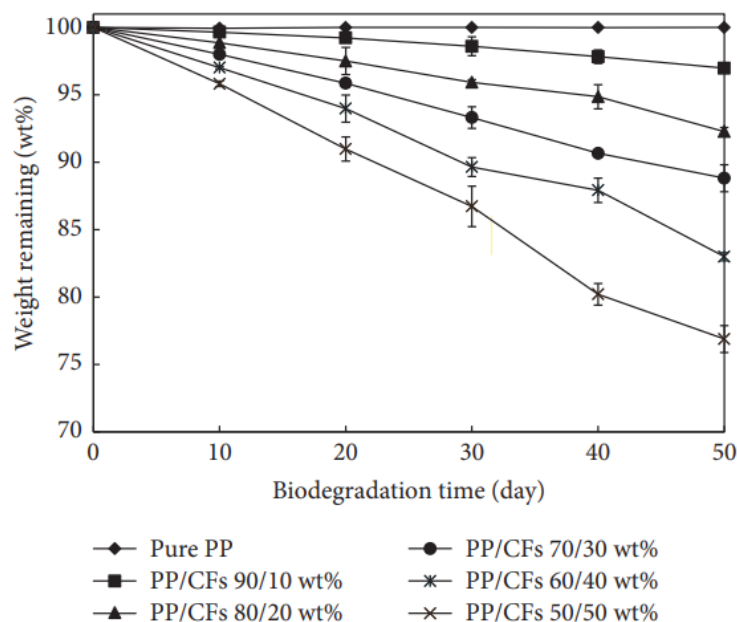


Figure 13. biodegradation of pure and modified polypropylene with cellulose fibers

This statistically linear relation was observed for starch addition. Starch is a highly hydrophilic macromolecule. It is often used as the degradable additive in the preparation of biodegradable polyethylene film [3]. [33] incorporated Granular cornstarch by different composition. Higher starch content increased blend biodegradation steadily during 250 days. (see Table 2)

[23] prepared Blends of Polymethyl methacrylate (PMMA) with CA and Cellulose acetate phthalate (CAP) in order to measure biodegradability using soil burial, enzymatic degradation in phosphate buffer, hydrolytic degradation, activated sludge degradation and water absorption test. All tests were in agreement; Biodegradability increased with the increase in CA and CAP content in the compositions. Weight loss in soil for different content of CA and CAP in Figure 14 and Figure 15 is the same for other tests.

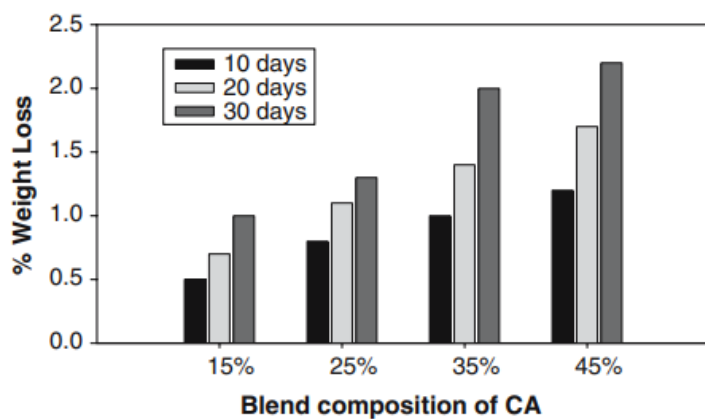


Figure 14. weight loss of PMMA-CA blend with different compositions of CA

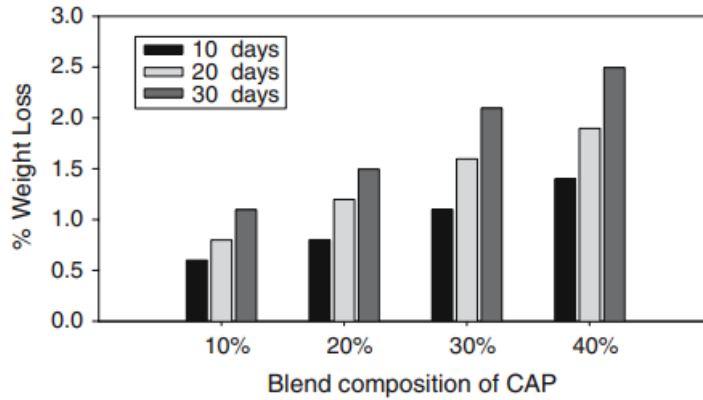


Figure 15. weight loss of PMMA-CAB blend with different compositions of CAB

Water absorption test was in agreement with biodegradation ratio in another experiment by [17] in which Agave Angustifolia Cellulose fibers was used as reinforcement with 2.5 wt.% to 10 wt.% in PLA/Natural Rubber blend. Water absorption test indicated that lower water resistance increases degradation rate. Cellulose is hydrophilic and increases water absorption of the biocomposite which increases biodegradability. From 2.5% to 10% of cellulose in the composition, 10% showed the highest biodegradability (Figure 16). Therefore, the reason for biodegradability increase with polysaccharide content increase is the hydrophilicity. More water intake provides a better pathway for microbial growth and thus a faster biodegradation. Also, polysaccharide consumption by microorganisms at first creates cracks and holes giving more access for microbes to attack the other polymers' chains.

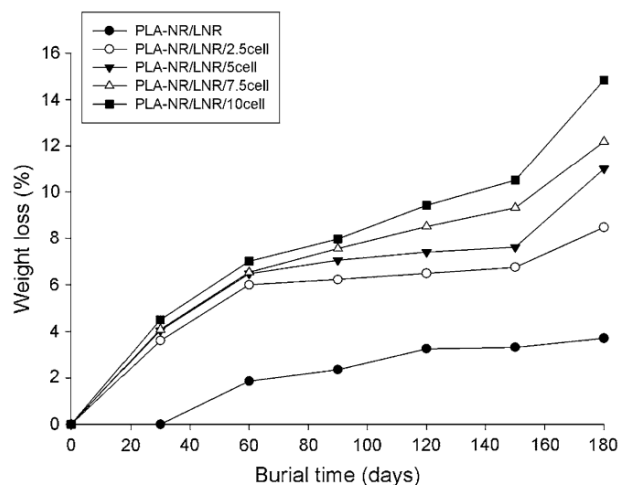


Figure 16. weight loss of PLA-NR/LNR reinforced with cellulose

Testing PLA/PHB blends with cellulose interlayers showed that addition of a cellulose paper interlayer to PLA/PHB blend accelerates biodegradation because it increased the rate of PLA hydrolysis [55].

The last explanation clarifies why more increasing starch or cellulose inclusion often increases biodegradability in a steady process. In the addition of various content of MCC to a blend during 140

days, most cellulose was consumed by day 37 while the biodegradation of the blends continued for the full duration. [56] in the mentioned test by [33], It can be seen that the blend weight loss is actually an indication of only the host polymer (PCL) and not both PCL and starch. Starch is consumed by all the same amount (almost fully) in each composition and depending on how much starch is consumed and in result water absorption and porosity, the other components biodegrade (Table 2).

Table 2. weight loss of PCL-starch blends during composting

Entry	Composition (PCL–starch blend)	Weight loss (%)			Weight loss of extracted fractions after 250 days composting (%)	
		90 days	120 days	250 days	PCL	Starch
1	100/0	0.8	1.1	45.6	–	–
2	90/10	1.6	2.2	56.5	51.9	98.3
3	80/20	1.8	2.3	61.4	52.3	97.9
4	70/30	2.8	3.5	66.1	52.4	97.9
5	60/40	11.1	11.3	70.5	52.8	96.9
6	50/50	11.7	13.3	75.8	53.7	97.9
7	60/40 HCS	2.8	5.6	72.0	54.9	97.6
8	60/40 MCS	3.2	6.3	72.9	55.6	98.8

Weight loss after 250 days composting was determined as follows: $100 \times (\text{Initial weight of component} - \text{Final weight (recovered weight) of component}) / \text{Initial weight of component}$.

There was one experiment with totally different results unlike the others. Bio-nanocomposite of Alginate and crude seaweed extracts were prepared and cellulose nanocrystals (CNC) were added as filler. Alginate was extracted from two types of brown seaweed. CNC was isolated from Dried kombu and sargassum which are brown seaweeds as well. The weight loss test after indoor soil burial and lake immersion for 35 days showed the addition of CNC in both 5 and 25 wt.% to the films slowed the degradation rate. This is because the high crystallinity of CNC (98.1 and 87.3% for CNC from kombu and sargassum) along with its nano-size effect creates strong molecular bonds with the matrix. [31] these strong interactions of polysaccharides that overpower their biodegradability is further discussed later in this section.

It is not always only the polysaccharide content that determines biodegradability. Biodegradation of PLA/ PCL/ MCC polyblends in different compositions were tested by international protocols (see Table 3). Addition of MCC as a biofiller increased biodegradation rate in blend of PLA/PCL (blue line) in both compositions (80/20 and 90/10) by a high number of MCC hydrophilic OH groups as chain ends. Nonetheless, while more content of MCC in PLA/PCL 90/10 blend increased degradation, it decreased the rate in PLA/PCL 80/20 (see Figure 17, Figure 18). [56] it is concluded that blend composition plays a crucial role in determining biodegradability as well as filler concentration.

Table 3. Composition of the different polyblend composites

Sample Designation	PLA (g)	PCL (g)	MCC (g)
nPLA	10	0	0
nPCL	0	10	0
PLA/PCL: 80/20	8	2	0
PLA/PCL: 90/10	9	1	0
PLA/PCL/MCC: 80/20/1	7.92	1.98	0.1
PLA/PCL/MCC: 80/20/3	7.76	1.94	0.3
PLA/PCL/MCC: 90/10/1	9	0.9	0.1
PLA/PCL/MCC: 90/10/3	8.40	1.3	0.3

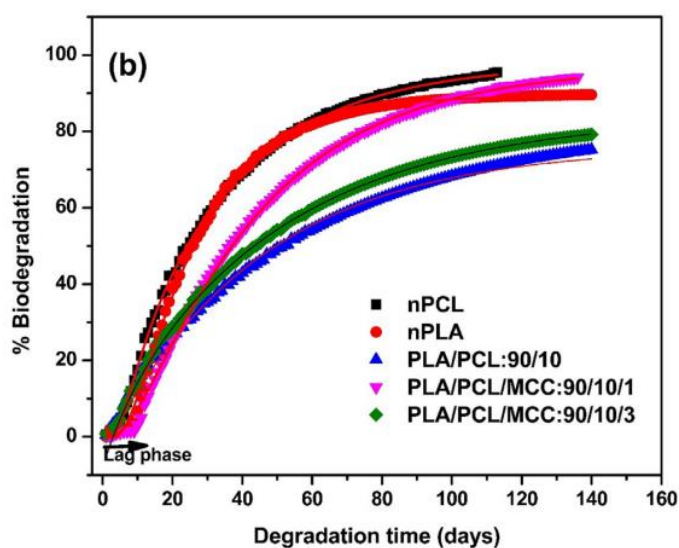


Figure 17. Biodegradation of 90/10 PLA/PCL modified with MCC

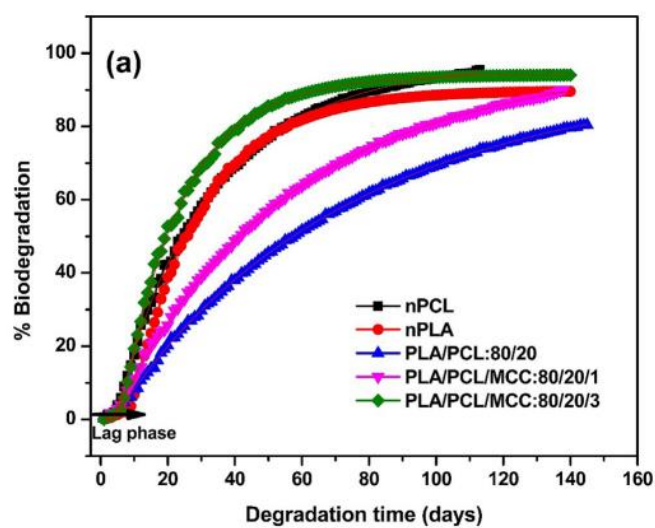


Figure 18. Biodegradation of 80/20 PLA/PCL modified with MCC

Minimum loading

When including polysaccharides into composites, biodegradability is not always improved by any amount to have the desired biodegradability. There is a minimum content that must be included to start seeing the effect on final biodegradation of the product, Depending on the polysaccharide type and biodegradability of other polymers. For instance, since polyethylene is not biodegradable, for blends containing up to 10 wt.% plasticized starch, the amount of starch consumption is insignificant since the weight loss is very small, even after 8 weeks of exposure. Only in blends with 20 and especially 30 wt.% starch there is a higher weight loss.[57]. In a year-long experiment by [58], there was no significant weight loss for 4 and 8 wt. % of starch inclusion but for 10 wt. % and higher this idea can be perceived in another way in [27]. Bentonite nanoclay was modified with chitosan to use as filler in starch nanocomposite by 4 wt.%. CS-Bent fillers give antimicrobial activity to the films but they are immersed in a starch matrix, which acts as nutrient for microorganisms. However, the amount is too low to affect biodegradation results significantly. Although this is not about the minimum polysaccharide loading but to further emphasize that depending on the polysaccharide type, the biodegradability effect is very different. [14] observed that while 2.5 wt.% addition of starch nanocrystals produces big changes on water permeability, up to 30 wt.% of starch nanoparticles did not have any significant effect. The difference might be for the disparity of the two. Similarly, inclusion of a small amount of cellulose derivatives (5 to 10 wt. %) in castor oil-based polyurethanes by [48] resulted in big changes on biodegradability. Based on the many experiments [29], [33], [57], [53], [17], [31] where the smallest incorporation for starch and cellulose is 10-30 wt. % and 0.5-5 wt. % respectively, we can conclude that average minimum loading weight percentage for starch and cellulose is 15 wt.% and 2.5 wt. %, in order.

Maximum loading

On the other hand, incorporation of big amounts of polysaccharides may have unexpected negative results on biodegradability in some cases. And that is why there is a maximum loading. Sial fibers(SF) extracted from Agave Sisalana-a hardy Mexican plant- were chosen as filler to PCL/S blends. [29] The results of the indoor soil burial test for 14 months were interesting (see Figure 19). While 5% SF blend showed a higher and steady weight loss than non-filled blend, Increasing SFs to 15% made the blend less biodegradable than non-filled PCL/S. There was even a lag phase for about the first 6 months. The reason is that fiber-fiber interactions and fiber-starch interactions in 15% SF blend was so strong that it reduced microbial access to the polymer. Although after 6 months, the fiber and starch acted as support for microbial attack, the amount of weight loss did not exceed the pure blend as biodegradation proceeded.

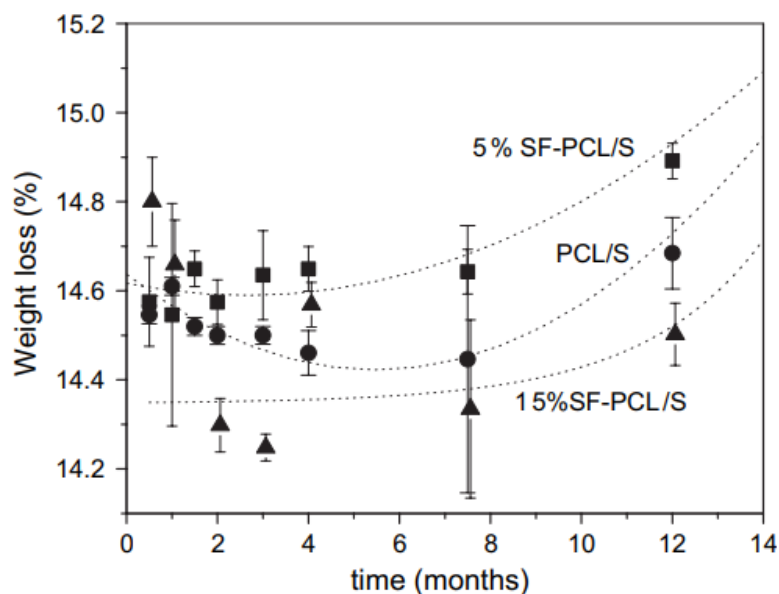


Figure 19. Weight loss of PCL/S modified with 5% and 15% SF

This is why the nature of components because of how they interact with each other is an important factor as well as their compositions. Blends of PLL and CAB were prepared with plasticizers and the biodegradability of pure PLL, pure CAB and blends was tested under real aerobic composting conditions. PLL fully degraded in 30 days and CAB did not degrade in 90 days (see Figure 10). 80/20 PLL/CAB film degraded completely within 9 days but 50/50 PLL/CAB did not in 90 days. The reason is when the amount of CAB is little, it reduces the crystallinity of PLL matrix which helps biodegradation. In 50wt. % of Cab, the non-biodegradability of it becomes dominant and makes the entire blend nondegradable. The best formulations were found to be PLL ≥ 70 , CAB ≤ 30 with 20wt. % plasticizer. All PLL/CAB/plasticizer blends with 80/20/20 degraded in 90 days. [49] sometimes, an amount is chosen as maximum because increasing the content either does not change biodegradation or shows a lower degradation rate than smaller amounts. In polybutylene succinate adipate/starch composites, starch content of 20 % by weight passed biodegradability test and increasing it to 25% and 30% showed no significantly enhanced biodegradation than 20% as seen in Figure 20. So, PBSA/S 80/20 was selected.[7]

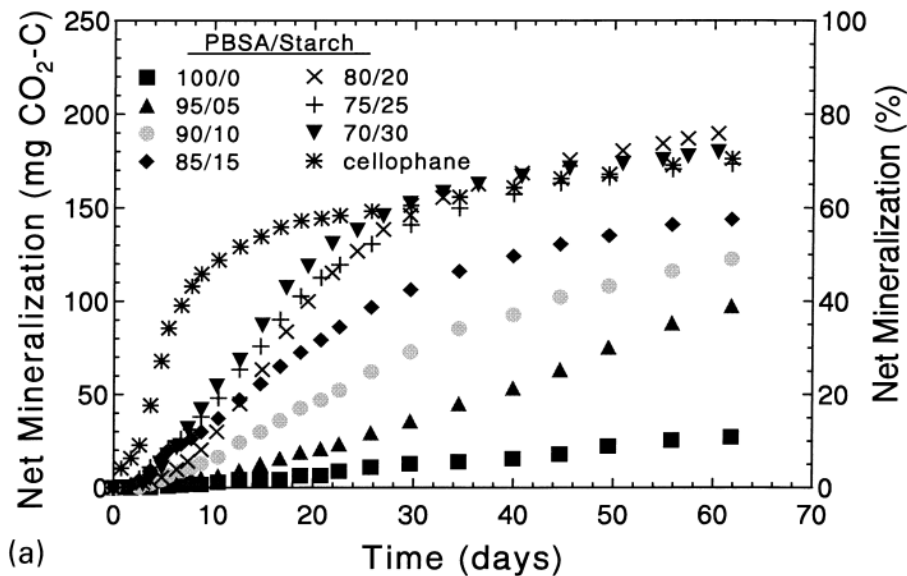


Figure 20. Mineralization of PBSA/Starch

[59] showed that incorporation of 1 wt.% and 1.5 wt.% of cellulose nanocrystals into PLA increased biodegradation more than higher amounts of 2.5 and 4 wt.%

Optimal loading

In addition, the maximum weight loaded into PSIP may be not be for the negative effect but a choice by designers to avoid unwanted properties. For instance, preparation of PCL and granular starch was done by maximum 50wt. % of starch, because higher amount would make the blend brittle and highly difficult to melt. [33] Agricultural and desert soil burial of PP/CMC blends during 6 months by [60] with 5, 10, 15, 20 wt.% CMC showed that increasing CMC content increases biodegradability, but the best CMC load was 15wt. % for showing desired mechanical properties for the end product. Along with desired characteristics, A good polysaccharide loading is also determined by how stable the biodegradation process is for that amount. A product with a steady biodegradation rate in testing is more trustable to show predicted biodegradation behavior in the real environment. In an effort to make low-density polyethylene partially biodegradable by [24], it was blended with cassava starch with different compositions, 5,10,15,20,40,50 wt.% starch in the blend and tested for 28 days (Table 4). The ratio for the blends is 2.74%, 2.50%, 9.78%, 18.66%, 78.05%, 45.85 in order of starch increasing. Higher amount of S increased biodegradability except for 50 CaS that was lower than 40 CaS (the reason is not discussed in the paper). However, looking at Figure 21, degradation rate of all compositions during four weeks were inconsistent except for 20 CaS. For 40 CaS, Figure 22, The degradation rate during the first, second, third and fourth week for was 2.68%, 9.90%, 0.87%, 0.91%, respectively. There was a high increase in the second week followed by a big drop on third week. For 20 CaS, the rate was 0.59%, 0.58%, 0.76% and 0.93% from first to fourth week which is very stable. Therefore, despite 40 CaS being the most biodegradable, 80/20 LDPE/Starch blend is more suitable for applications.

Table 4. composition of LDPE and Starch

Sample name	LDPE (wt.%)	<i>Manihot esculenta</i> Starch (wt.%)
5 CaS	95	5
10 CaS	90	10
15 CaS	85	15
20 CaS	80	20
40 CaS	60	40
50 CaS	50	50

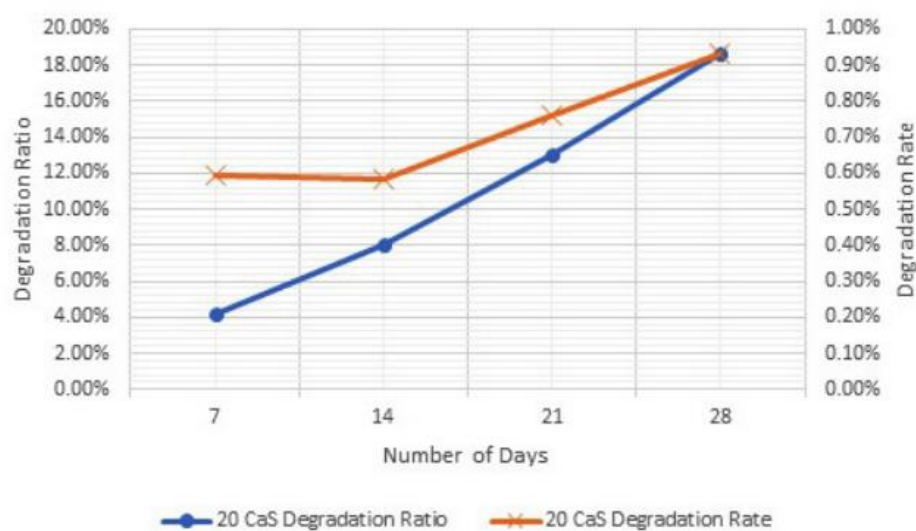


Figure 21. Degradation rate and ratio of 20 CaS

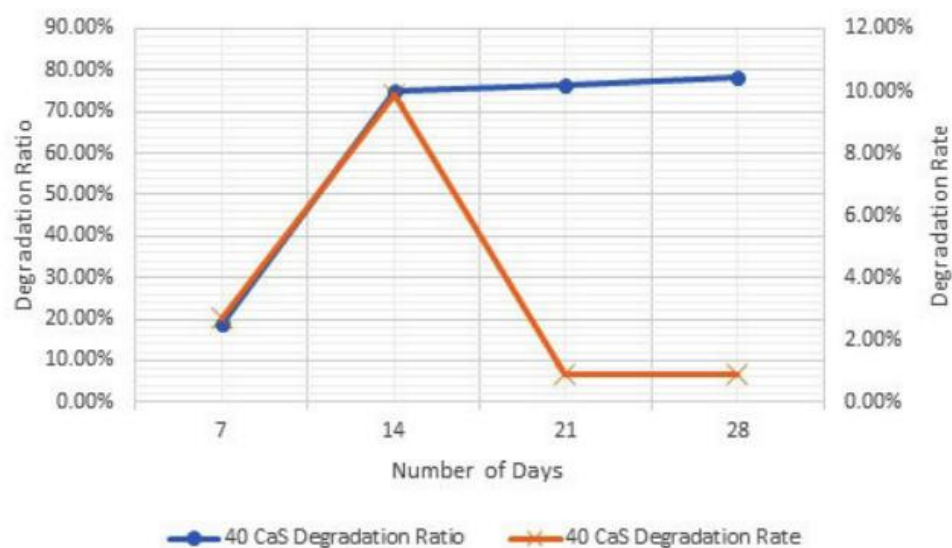


Figure 22. Degradation rate and ratio of 40 CaS

The same test was conducted on other sources of starch: Zea mays (corn starch), Ipomoea batatas (potato starch), and Manihot esculenta (cassava starch). Same as cassava, 80/20 LDPE/S was the most steadily biodegraded composition for all (Table 5, Table 6, Table 7). Incorporation of 1 wt.% and 1.5 wt.% of CNCs into PLA increased biodegradation more than higher amounts of 2.5 and 4 wt. %

Table 5. Percentage weight loss of LDPE/Manihot esculenta samples

Period	LDPE (wt.%)					
	95	90	85	80	60	50
Percentage Weight Loss (%)						
Week 1	1.35	1.42	5.66	4.15	18.73	27.00
Week 2	2.01	1.53	7.56	8.07	75.05	45.53
Week 3	2.34	1.61	7.83	12.98	76.57	45.79
Week 4	2.74	2.50	9.78	18.66	78.05	45.85

Table 6. Percentage weight loss of LDPE/Zea Mays samples

Period	LDPE (wt.%)					
	95	90	85	80	60	50
Percentage Weight Loss (%)						
Week 1	10.73	8.91	6.54	4.27	29.15	13.77
Week 2	17.94	22.12	9.27	5.76	50.97	23.23
Week 3	23.03	43.87	12.91	6.83	68.08	32.64
Week 4	27.08	43.94	16.07	7.47	75.41	40.89

Table 7. Percentage weight loss of LDPE/Ipomoea patatas samples

Period	LDPE (wt.%)					
	95	90	85	80	60	50
Percentage Weight Loss (%)						
Week 1	1.03	0.71	28.07	2.58	17.96	36.86
Week 2	1.19	0.95	29.42	6.87	32.01	59.58
Week 3	1.33	2.32	30.59	8.38	46.88	71.03
Week 4	1.37	2.68	31.57	9.20	49.34	76.20

Pre-treatment

According to [9] biodegradability of bioplastics is not affected by their production process. However, some experiments were found on this matter that may or may not prove this wrong because the data is very little.

The only experiment designed solely to investigate pre-treatment effect was by [38] about drying temperatures. Drying temperature is an important process in production of edible blend films and films are often dried at ambient temperature. Both room and oven temperature (25 °C and 45 °C) were tested for gelatin/carboxymethyl cellulose/chitosan blend with five different compositions. Most and not all oven dried films showed a lower percentage weight loss compared to room dried films. [38] no other specific research concerning this was found other than small pieces of information. [36] blended SRKC with PAAc and the blend showed lower degradation rate than pure PAAc due to acidification of the compost by release of sulfate after biodegradation of SRKC. Sulfate was used in preparation. Purity of cellulose when extracting impacts biodegradability. Cellulose extraction is often done in two steps: alkaline treatment and bleaching treatment (such as hydrogen peroxide or sodium chlorite) to clear impurities like hemicellulose and lignin. [15] In the testing of cellulose fibers as filler to polypropylene, fibers were extracted from rice straws. Cellulose sources (rice, wheat, etc.) contain other components such as lignin and hemicellulose and many researchers have reported that alkaline treatment removes all other components on cellulose surface resulting in pure extracted cellulose fibers. But in this case, after NaOH treatment, lignin was still present (by yellow color of the extracts) and it was washed with H₂O₂. The resulting CFs showed lower water absorption than CFs without H₂O₂ washing. The test was carried out only with H₂O₂-washed CFs because CFs with impurities could reduce PP and CFs adhesion. So, it is not determined if H₂O₂ washing in the pre-treatment would affect final biodegradability. [54]

Effect of other materials included in PSIP

In order to achieve desired properties as well as the desired biodegradability for a PSIP, additives, plasticizers, crosslinkers and compatibilizers are also added in the preparation process. As discussed in the previous sections, biodegradability is partly dependent on the nature of components. For instance comparison of fiber/starch, fiber/PVA, fiber/polyacrylate (PA) and PE films made of 16% polymer (PA, starch, or PVA) and 84% waste fibers (ramie and cotton fibers) by both the field and laboratory tests is a simple demonstration of the effect of nature of other polymers: Fiber/starch 1–2 months, fiber/PVA 2-3 months and fiber/PA 3-4 months. [61] since there is a big variety of polymers to blend with polysaccharides, this section only discusses additives and if and how they have an effect on biodegradability.

Crosslinkers

Separate Polymeric chains of polysaccharides are joined together by other materials as called crosslinking agents in order to improve mechanical strength. Crosslinking density is another influential factor on biodegradability. [9]

A comparison of some films with and without a crosslinker was done. [62] The period to complete 90% degradation were:

- Starch-PVA-glycerol-antimicrobial Film crosslinked by GA (28 day)
- Starch–glycerol film crosslinked by citric acid (30 days) ,
- Soy protein film crosslinked by genipin (33 days),
- Cassava starch film (12 days)
- Starch–PVA–urea film reinforced with jute fiber (16 days)

Since soy protein has the same degradation trend as starch-PVA and antimicrobials proved to not interfere with biodegradation, it was included that lower time requirement for the last two cases were probably due to absence of a crosslinker agent. [62]. So crosslinking starch decreases degradation rate. [20] states that corn starch filled PVA films showed 50% mass loss while corn starch filled PVA/lignocellulosic fiber films lost 40% of initial weight because PVA/lignocellulosic is crosslinked which reduces microbial accessibility to polymeric chains. [36] made an effort to produce super water absorbents by blending cassava starch and SRKC with PAAc. Although Starch-included blend had higher biodegradation, they both showed an initial biodegradation curve at 3 weeks which could be attributed to polysaccharides trapped within the crosslinked network (Figure 23). Hence, crosslinking lowers biodegradability of PSIP.

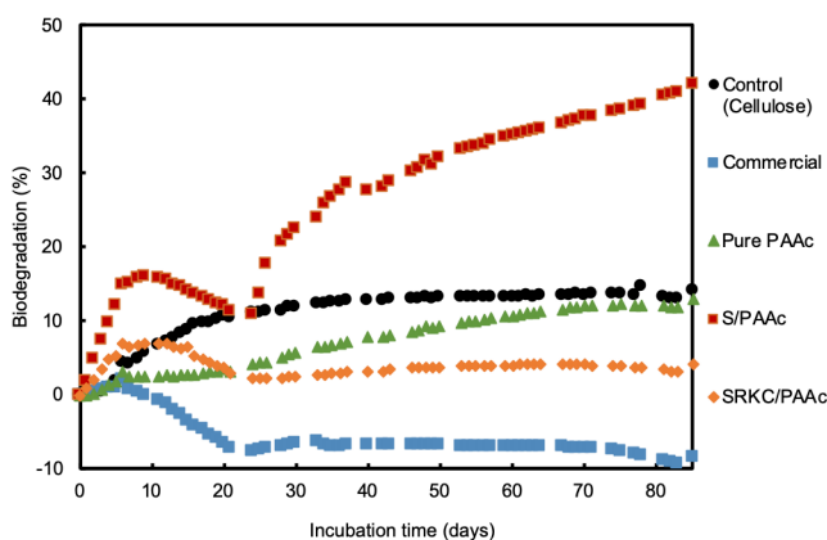


Figure 23. Biodegradation of samples during 85 days of incubation

Compatibilizers

Compatibilizers are included as polysaccharide composites for the purpose of better interaction and dispersion between the polysaccharide and other polymers in the composite. According to [33] compatibilization and/or homogeneity of the two separated phases are in favor of the degradation of the host polymer. Research for PCL/S blends claims that including a compatibilizing agent in the blend improves biodegradability. The 8 wt.% addition of additives including the compatibilizer in PCL/S/CNFs 45/25/21 wt. % helped with biodegradation as they were the first to decompose which creates cracks and holes in the blend structure, making water diffusion and microbial accessibility easier and biodegradation faster [29]. [33] tested blending of Starch which is hydrophilic and PCL which is a hydrophobic polyester. When blended, they do not efficiently interact. Adding PCL-grafted dextran copolymers (PGD) as compatibilizer to PCL/starch blends increased biodegradability. In fact, better diffusion of starch into PCL matrix by PGD gives microorganisms growing on starch surface a faster pathway to PCL. This means that if starch is under the minimum wt.%, and not very well dispersed in or interacted with the host polymer to transfer microbial growth,

addition of a hydrophilic compatibilizer may not only help, but also form H-bonds with starch leading to lowering biodegradability. This could be the reason uncompatibilized PCL/starch blends were tested with 30 wt.% starch and blends with compatibilizer were tested with 40 wt.% starch in order to make sure starch and PCL are better connected and for the compatibilizer to work efficiently. In a test by [57], use of Ethylene acrylic acid copolymer (EAA) as a compatibilizer on LDPE/plasticized starch blend during treatment in activated sludge has a negative effect on the biodegradation rate. Starch minimum loading for this blend is 32 wt.% and all compositions are below this number. So, the negative effect of the compatibilizer is probably because of the strong complexes it forms with the hydroxyl groups of starch.

Plasticizers

Plasticizers are used to help with the mechanical properties of PSIP. Regardless of their mechanism, plasticizers increase biodegradation (Figure 24). They often act on their own characteristics to affect biodegradability. The major property of plasticizers to increase biodegradation is hydrophilicity. Blends of PLL and CAB were prepared with Both polyethylene glycol (PEG) and a polyester adipate (Paraplex G40) as plasticizers and between the two, the blend with paraplex G40 took longer to degrade probably due to its heat and humidity resistance [49]. PEG is a very popular plasticizer with the common composition of 20 wt.% in many PSIPs and often accelerates biodegradation (Figure 25). In another test, the addition of sorbitol as plasticizer to cellulose-based bioplastics reduced the degree of crystallinity in cellulose. This decreases the biopolymer density which in turn accelerates the process of biodegradation. Also, sorbitol is a hydrophilic material. Water is a growing medium for most bacteria and microbes, so the higher water content helps biodegradation. [63]

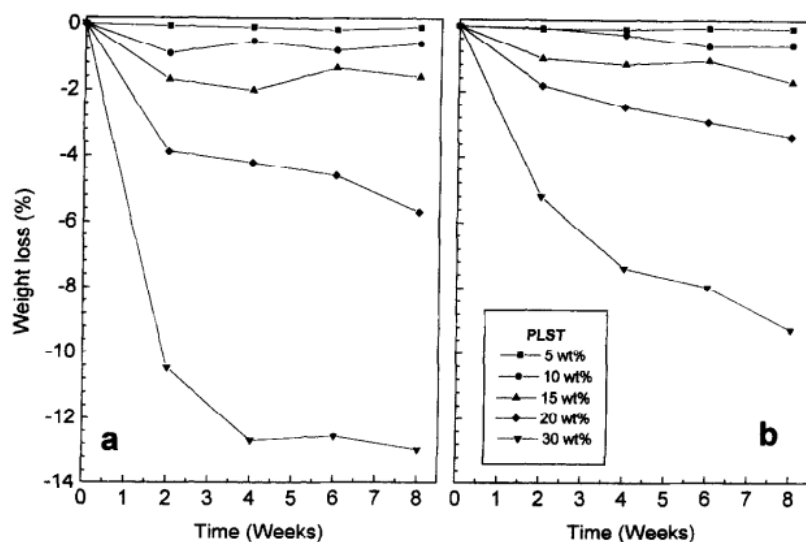


Figure 24. Weight loss of (a).PCL without plasticizers and (b). PCL with plasticizers

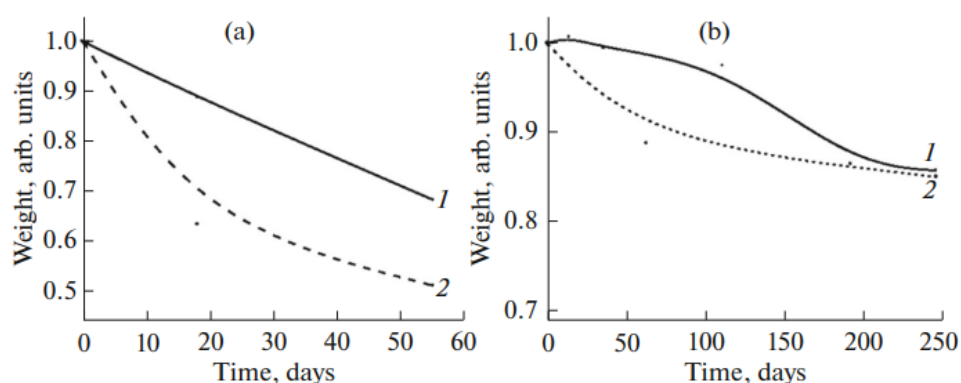


Figure 25. Weight loss curves after exposure of samples in the soil: a: (1) PLA-Starch (60 : 40. Wt%), (2) PLA-Starch-PEG (60 : 20 : 20. Wt %) : b: (1) PLA-chitosan (70 : 30, wt %), (2) PLA-chitosan-PEG (60 : 20 : 20, wt %)

In order to compare glycerol-based and acidic-based plasticizers, biodegradation of starch/PVA films when glycerol (GL) and citric acid (CA) were used as additives was tested by [22]. CA-added films demonstrated faster biodegradation than GL because CA served as a "nutritive element" for microorganisms in the soil. In order to realize how these acid additives affect biodegradability, [42] tested acid-containing Cellulose acetate (CA) films with various acids. As Figure 26 illustrates, biodegradation rate of acid-containing CA films increased compared to that of the nonadditive CA film. All types of acids in this experiment raised biodegradation rate and more acid concentration increased degradation (see Figure 27). Adding acids makes cellulose acetate more prone to hydrolysis and CA is deacetylated when contacted with water in the environment and is converted into a lower degree of acetylation. Thus, CA with lower DS has a higher biodegradability. As can be seen, the mechanism for acidic additives is the same as glycerol and other plasticizers mentioned. It comes to hydrophilicity. The more hydrophilic, the faster the material biodegrades.

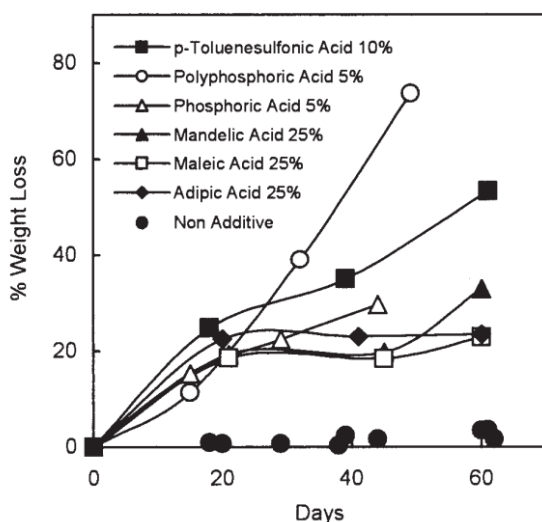


Figure 26. CA films modified with acids

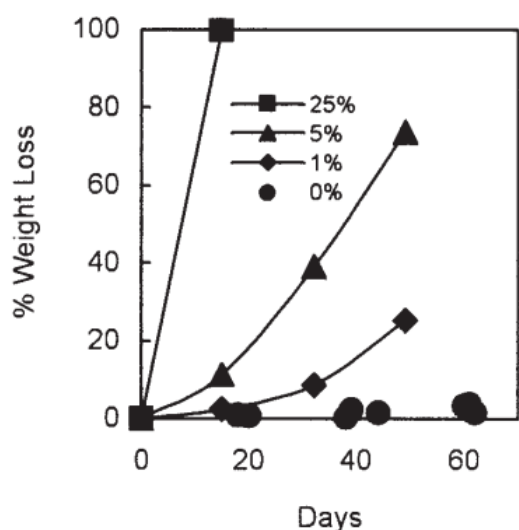


Figure 27. CA films modified with polyphosphoric acid

[44] plasticized TPAS with triacetin and triethyl-citrate that had the same degree of acetylation ($DS=2.5$). Triethyl-citrate-plasticized TPAS had higher carbon mineralization (higher degradation) which is related to more hydrophilicity it produced to starch.

Like the polysaccharide, plasticizers must include a min and max amount to avoid unwanted properties. In addition of triacetin and diacetin (a type of glycerol) to Cellulose acetate as plasticizers, content of plasticizer should range between 20 and 30 %wt. Lower content exceeds melting point and higher content lowers mechanical properties.[43]. Based on [43], [35], [37], [22], [44], [49], the amount of plasticizer can range from 10 wt. % to 40.wt.% depending on the plasticizer and polysaccharide with 20 wt.% being the optimal and most popular. Apart from plasticizers, materials that help microorganisms to grow will help biodegradation of PSIP and vice versa. An instance is addition of 5 wt.% crude kaolin to a starch-based bioplastic as the reinforcing element which improved biodegradation for increasing microbial activity regardless of the environment [64]. In [65] since Lignin has a complex structure, it reduced starch biodegradation in urea-crosslinked starch under anaerobic soil conditions because it protects the starch oxidation by its highly complex chemical structure.

Environmental effect

One of the most crucial factors to consider in biodegradation of PSIP is the environment. An important question is where and under what conditions the PSIP biodegrades. Parameters such as temperature, soil water content, relative humidity and PH and types of microorganisms greatly impact biodegradability [66] to the point of significant differences in biodegradation results in different testing systems. Results about some of these parameters was collected from this research.

Biodegradable characteristics differ significantly in aerobic and anaerobic experimental conditions. As in [25] PLA/Starch was biodegradable by testing according to ISO 14851 but did not pass the test under anaerobic conditions.

The conditional parameters to affect biodegradation of polymers in general are temperature, humidity, and PH[67]. Temperature directly controls biodegradation by controlling microbial enzyme reaction. Half of biodegradation rate is reduced by 10°C decrease in temperature and maximum T is 65°C [18] and the optimal for PSIP is room temperature[8]. Moisture is another most influential parameter. Soil moisture proved to affect biodegradability of starch-reinforced Acamprosates because it increases water solubility of the composite constituents.[30] in a similar test by [21] with more interesting results, Mater-Bi (starch, additives and PBAT) was tested in conditions with different Temperature and moisture. Data indicated that the biodegradation of starch and additives aren't influenced by the decrease of temperature and moisture during the degradation process (maturation phase of composting), but the biodegradation of PBAT was strongly affected. In fact, moisture is most influential parameter that determines microbial activity and prevents biopolymers from transforming into a stable organic matter[21]. [43] observed the implicit role of PH in biodegradation. The first step in the degradation of Cellulose acetate is the deacetylation. Deacetylation is established partly by heat and high PH.

Pure starch and polystyrene-grafted-starch copolymer were tested in three different soils in the same condition for 6 months: soil rich in humus (sample 1), soil for cactus growing (sample 2), and soil for orchid growing (sample 3). PH and water content were almost the same. Pure starch degraded 55%, 93%, 80% in soil samples 1, 2, 3, respectively. The difference in results for the copolymer was obvious as well [50]. It means different soils have completely different capabilities of degrading the same material. In [40], EPSs produced by different types of lactic acid bacteria were tested in two environments. Four EPSs degraded in soil cultures, whereas only three of these EPSs were degraded in the fecal slurry. The initial rate of degradation of the EPSs that were degraded both by the fecal slurry and the soil inocula was faster in the fecal slurry. This can be attributed to the specific types of microorganisms in soil that was not present in fecal slurry and vice versa.

An experiment by [29] showed that biodegradation in liquid media was much lower than in soil. [23] had different results. In order to reach similar weight loss for a composite reinforced with 45 wt.% cellulose acetate, the time requirement for biodegradation was 30 days in soil burial, 10 days in buffer solution and 5 days in activated sludge. The fastest biodegradation in sludge could be by the big microbe population. But unlike [29], not all liquid media demonstrates lower biodegradation than soil. Buffer solution had faster rate in another experiment as well. Liquid PHB/CAB was tested by [68] in buffer solutions with PH 1.0 and 13.0 and natural lake water. Blending of CAB with PHB increased the degradation rates in both media. However, in an acidic medium, increasing the CAB content accelerates the degradation, whereas in an alkaline medium, the degradation rate decreases with the CAB content increasing. The degradation of PHB/CAB blend in natural lake water was slower than pure PHB since CAB reduces possibility of PHB contact with water just like in soil[68].

According to [29], A mixture of microbial population (bacteria, fungi,...) that work together in the degradation will have the most efficient biodegradation. Among various types of soil, garden soil is the best for biodegradation[58]. [50] is consistent with this as starch had the fastest biodegradation in soil for orchid growing than soil for cactus and humus.

Whether the material is buried or placed on the surface also matters. In- and on-soil biodegradation test of Cassava starch-based bioplastics reinforced with metakaolin (BPMKB) had different results. Biodegradation is faster by 20 wt. % when material is buried than when it is on the ground because of better microbes contact (Figure 28). [64] such information can help with better choices in disposal of PSIP. Shape and dimensions of the material should be considered as well. [58] tested thickness of starch containing blends on scale of micrometers and showed that thickness has a negative effect on biodegradability. Overall, the bigger the material dimensions, the more time it takes to biodegrade.

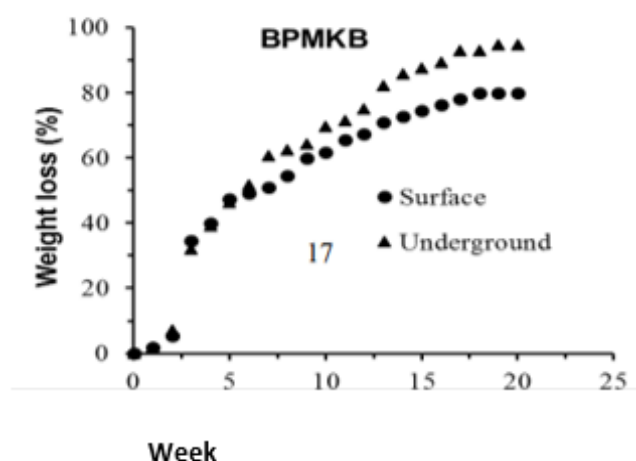


Figure 28. Weight loss of BPMKB on surface and underground

Challenges

Of the field

Polysaccharide-based biopolymers have been drawing significant attention in recent years. However there many aspects of biopolymers in general requiring a lot more investigation and the high cost of biopolymer production is still one of the greatest barriers in competing with petroleum-derived plastics. [11] One issue that was the major challenge in this literature review is that the existing information is mainly on PSIP properties and a lot less on their biodegradability. The same challenge was reported by [54] that Synthetic polymer composites reinforced with natural fibers have attracted so much attention, but most research on them only investigate their mechanical and thermal properties and not biodegradability. [3] mentioned that although there is a lot of investigation on polyvinyl alcohol/starch, the number of publications is very limited.

It is important to distinguish between biopolymers and biodegradability. There are sources offer different definitions of biopolymers. According to [69], Polymers from natural sources that are degradable are classified as biopolymers, but in fact bio-based bioplastics that are not degradable or biodegradable fit the category as well. [4]

The term green in biopolymer production, does not necessarily indicate that the material has to be 100% biodegradable to be considered biodegradable, as clear by many standards like ASTM and ISO where the criteria is a minimum of 70% biodegradation. Yet, this is how a green biopolymer is perceived in some research. Green composites, for instance, are that "they are environmentally friendly, *fully degradable* and *sustainable in every way*". An interesting fact was noticed about starch in this review paper. Starch is undoubtedly highly biodegradable, but it did not fully degrade in any soil burial experiment. Pure starch was tested in three different soils by [50]. After 6 months of degradation when equilibrium was reached, microorganisms in different soil samples showed different capabilities for metabolizing starch, "but none of them could fully metabolize the starch present." Even in a longer test by [25], about 9 months, starch was not fully consumed. Highest weight loss was 98.8% of the initial weight (see Table 2).

Of the papers

The more crystalline the PSIC, the harder is the enzymatic hydrolysis, thus biodegradation. Water diffusion is much easier in amorphous regions and enzymes get better access to polymer chains in less organized structures [9][39][22]. However, in blend of gelatin/carboxymethylcellulose/chitosan, addition of chitosan increased biodegradability which was explained by the author [38] as a result of chitosan increasing crystallinity.

Critiques on biodegradability researches

Table 8 was made to give an insight on how biodegradability tests are being conducted. This table only includes the experimental papers found for this literature.

Temperature, moisture and PH

The three influential environmental factors are given in Table 9 with the most important being temperature and humidity. Underline is for when no data is required for moisture in liquid media such as activated sludge and for PH when the test condition is being exposed to microorganisms. They affect the behavior of both the polymer and the microorganisms active in the process [14]. For instance, Half of biodegradation rate is reduced by 10°C decrease in temperature [18]. Therefore, it makes it difficult to compare results of papers when these factors are different or not mentioned. The range is 10 - 58 °C for Temperature, 35 – 100 % for humidity, 10 – 65 wt. % for moisture, and 2.5 - 8 for PH. 28% of experiments did not mention temperature, 36% did not mention humidity/moisture, and 52% did not mention PH. Overall, 44% of tests, which is less than half of papers, recorded all three parameters.

In order to have an actual biodegradability prediction, materials must be tested in real environmental setting. However, most biodegradation tests are carried at ambient temperature, from

20°C to 25°C. real environmental temperature is an average 10°C at soil depth which is not seen in any test. [18]

Testing conditions, duration, and biodegradability factor

Table 10 shows test condition and duration, and biodegradability factor that was investigated. Long term biodegradability tests like one or two years are more useful in determining actual biodegradability of a material and short-period tests do not give an insight to the final behavior of a material that would be disposed and left in the environment for ever [23]. Nonetheless, the test duration ranges from 5 days to 360 days and the average is 4 months.

Another issue is that there is little to no data on how the processing and preparation of materials affect biodegradability which might be a proof to [9] claiming that process conditions do not affect biodegradability. Only one paper, number 47, was found in which the standardized methodologies was not used, PH and moisture was not reported and was conducted in only 5 days, making it invalid.

Materials are often tested under composting conditions. Compostable refers to materials that biodegrade under special environmental conditions like temperature and humidity. All compostable materials are biodegradable but biodegradable materials are not necessarily compostable. [18] [12] However, materials are not always disposed of where composting conditions exist. However, there are no considerations of the possible disposal environment of the materials being tested in many experimental papers, which might make the results useless in real life. According to [12], although most plastic wastes are disposed of in landfills, research only has been done on biodegradation of bioplastics in landfill conditions.

An alarming problem is that methodology standards (i.e. ASTM, ISO, EN) are not often considered in biodegradability tests. Only about 20% followed standards.

Measurement methods

Popularity of biodegradability measuring methods was already discussed. Table 11 gives a confirming and more realistic insight. Physical methods, despite being an invalid method, are the most popular, making up 80% of all methods, with weight loss being 90% of it. Visual observation alone is not valid because the samples might have not gone through assimilation which is not visually detectable and just degraded, not biodegraded. Observation of how much microbes grow in a buffer solution or when exposed to microorganisms is an indication of biodegradation as for number 3 and 35 in the table, which is not problematic. Yet, the biodegradation results are not trustable for numbers 30, 32, 33 and 40, all tested in compost, where visual examination was the only method. A concerning problem is that despite respirometric methods being the only way to ensure that biodegradability has happened, only 18% of experiments applied it.

Table 8. papers

Number	Title	Reference
1	Synthesis, thermal properties, and biodegradability of propyl-etherified starch	(Teramoto et al., 2003)
2	LDPE/plasticized starch blends containing PE-g-MA copolymer as compatibilizer	(Bikiaris et al., 1998)
3	Testing of polyvinyl alcohol and starch mixtures as biodegradable polymeric materials	(Tudorachi et al., 2000)
4	Degradation of polycaprolactone/starch blends and composites with sisal fibre	(Di Franco et al., 2004)
5	Biodegradation of poly(o-caprolactone)/starch blends and composites in composting and culture environments: the effect of compatibilization on the inherent biodegradability of the host polymer	(Singh et al., 2003)
6	Processing, performance and biodegradability of a thermoplastic aliphatic polyester/starch system	(Ratto et al., 1999)
7	Biodegradable and transparent cellulose film prepared eco-friendly from durian rind for packaging application	(Zhao et al., 2019)
8	Biodegradation Behaviour of Thermoplastic Starch: The Roles of Carboxylic Acids on Cassava Starch	(Zain et al., 2018)
9	Effect of amylose contents of starches on physical properties and biodegradability of starch/PVA-blended films	(Yun & Yoon, 2010)
10	Study on the biodegradability of modified starch/ polylactic acid (PLA) composite materials	(Yu et al., 2020)
11	Biodegradation behavior of acid-containing cellulose acetate film in soil	(Yamashita & Endo, 2005)
12	Effects of Polymethacrylamide-Grafted Branch on Mechanical Performances, Hydrophilicity, and Biodegradability of Thermoplastic Starch Film	(Weerapoprasit & Prachayawarakorn, 2019)
13	Crystallization Behavior, Mechanical Properties, and Environmental Biodegradability of Poly(-hydroxybutyrate)/Cellulose Acetate Butyrate Blends	(Wang et al., 2003)
14	Physical and Degradable Properties of Mulching Films Prepared from Natural Fibers and Biodegradable Polymers	(Tan et al., 2016)
15	Biodegradability of Starch Based Self-Supporting Antimicrobial Film and Its Effect on Soil Quality	(Sen & Das, 2018)
16	Biodegradability of food-associated extracellular polysaccharides	(Ruijsenaars et al., 2000)
17	Monitoring of degradation of starch-based biopolymer film under different composting conditions, using TGA, FTIR and SEM analysis	(Ruggero et al., 2020)
18	Effectiveness of cellulosic Agave angustifolia fibres on the performance of compatibilised poly(lactic acid)- natural rubber blends	(Rosli et al., 2019)
19	Biodegradable blends of cellulose with synthetic polymers and some other polysaccharides	(S. Rogovina et al., 2013)
20	Mechanical Properties and Biodegradability of Polylactide– Polysaccharide Compositions	(S. Z. Rogovina et al., 2019b)
21	Radiation-synthesized polysaccharides/polyacrylate super water absorbents and their biodegradabilities	(Relleve et al., 2020)

22	The Soil Biodegradability of Structured Composites Based on Cellulose Cardboard and Blends of Polylactic Acid and Polyhydroxybutyrate	(Radu et al., 2021)
23	Cellulose Acetate Blends – Effect of Plasticizers on Properties and Biodegradability	(Phuong et al., 2014)
24	Effect of polymer blending on mechanical and barrier properties of starch-polyvinyl alcohol based biodegradable composite films	(Patil et al., 2021)
25	Properties and fungal biodegradation of the different cellulose derivatives structure included into castor oil-based polyurethane composites	(Oprea et al., 2019)
26	Biodegradation of polystyrene-graft-starch copolymers in three different types of soil	(Nikolic et al., 2014)
27	Controlled biodegradability of functionalized thermoplastic starch based materials	(Nevoralová et al., 2019)
28	Effect of Nanoclay Addition on the Biodegradability and Performance of Starch-Based Nanocomposites as Mulch Films	(Merino et al., 2019)
29	Properties of hydric and biodegradability of cassava starch-based bioplastics reinforced with thermally modified kaolin	(Méité et al., 2021)
30	Biodegradability and plasticizing effect of yerba mate extract on cassava starch edible films	(Medina Jaramillo et al., 2016)
31	Kraft Lignin Ameliorates Degradation Resistance of Starch in Urea Delivery Biocomposites	(Majeed et al., 2018)
32	Impact of the starch source on the physicochemical properties and biodegradability of different starch-based films	(Luchese et al., 2018)
33	Enzymatic Degradation and Pilot-Scale Composting of Cellulose-Based Films with Different Chemical Structures	(Leppänen et al., 2020)
34	Biodegradable kinetics of plastics under controlled composting conditions	(Leejarkpai et al., 2011)
35	Effect of microcrystalline cellulose on characteristics of cassava starch-based bioplastic	(Abdullah et al., 2020)
36	Preparation and Characterization of Low-Density Polyethylene/Thermoplastic Starch Composites Reinforced by Cellulose Nanofibers	(Alidadi-Shamsabadi et al., 2015)
37	Characterization of Polypropylene Green Composites Reinforced by Cellulose Fibers Extracted from Rice Straw	(Dinh Vu et al., 2018)
38	Effect of cellulose nanofibers and acetylated cellulose nanofibers on the properties of low-density polyethylene/thermoplastic starch blends	(Ahmadi et al., 2018)
39	Biodegradability of PMMA Blends with Some Cellulose Derivatives	(Bhat & Kumar, 2006)
40	Biodegradable Plasticized Blends of Poly(L-lactide) and Cellulose Acetate Butyrate: From Blend Preparation to Biodegradability in Real Composting Conditions	(Kunthadong et al., 2015)
41	Radiation modification of the properties of polypropylene/carboxymethyl cellulose blends and their biodegradability	(Abdel Ghaffar & Ali, 2016)
42	End-of-life evaluation and biodegradation of Poly(lactic acid) (PLA)/Polycaprolactone (PCL)/Microcrystalline cellulose (MCC) polyblends under composting conditions	(Kalita et al., 2020)
43	Cellulose nanocrystal effects on the biodegradability with alginate and crude seaweed extract nanocomposite films	(Doh et al., 2020)
44	Biodegradation behavior of starch-PVA films as affected by the incorporation of different antimicrobials	(Cano et al., 2016)

45	Investigation of Biodegradation Speed and Biodegradability of Polyethylene and Manihot Esculenta Starch Blends	(Abioye et al., 2019)
46	Biodegradability and biodegradation rate of poly(caprolactone)-starch blend and poly(butylene succinate) biodegradable polymer under aerobic and anaerobic environment	(Cho et al., 2011)
47	Preparation and physical properties of gelatin/CMC/chitosan composite films as affected by drying temperature	(Jahit et al., 2016)
48	The concentration of sorbitol on bioplastic cellulose based carrageenan waste on biodegradability and mechanical properties bioplastic	(Arief et al., 2021)
49	Drug release and biodegradability of electrospun cellulose nanocrystal reinforced polycaprolactone	(Hivechi et al., 2019)
50	Effect of thickness and starch phthalate/starch content on the degradability of LDPE/silane-modified nanosilica films: a comparative parametric optimization	(Datta et al., 2021)

Table 9. Temperature, Moisture and PH of experiments

Number	Temperature(°C)	Moisture (% for relative humidity and wt.% for water content)	PH
1	25	-	7.4
2	Not mentioned	-	Not mentioned
3	28	-	-
4	20	40%	Not mentioned
5	Not mentioned	Not mentioned	Not mentioned
6	30	60%	7
7	25 C	20 wt. %	6.8
8	25	70-80%	Not mentioned
9	Not mentioned	Not mentioned	Not mentioned
10	Not mentioned	Not mentioned	Not mentioned
11	30	85%	6.7
12	30	10 wt. %	7
13	25	-	Buffer:1 and 13 Natural water:7
14	10-25(by season)	35%/65 wt. %	6.05
15	26	75%	Not mentioned
16	30	Incubated	6.9
17	58	60%	6.7
18	25	Not mentioned	Not mentioned
19	30	Not mentioned (wet soil)	7.5
20	Not mentioned	Not mentioned	Not mentioned
21	35	Stated as gram water in compost	2-5.8
22	Not mentioned	Not mentioned	Not mentioned
23	Not mentioned	-	-
24	Am 27	Am70%	Not mentioned
25	30	85%	-

26	Ambient	60,50,60	6,6.5,6.5
27	52	52%	7.2
28	15	60 wt.%	5.8
29	25	Not mentioned	Not mentioned
30	Ambient	Not mentioned	Not mentioned
31	27	-	5.37
32	Not mentioned	Not mentioned	Not mentioned
33	20	84%	4.9
34	58	55 wt.%	5.1
35	37	90%	Not mentioned
36	Not mentioned	Not mentioned	Not mentioned
37	Not mentioned	Not mentioned	Not mentioned
38	32	20	7
39	Room	20 wt.%	6.7
40	45	40%	4
41	Not mentioned	Not mentioned	Not mentioned
42	58	60%	Not mentioned
43	23	64%	4.5
44	58	100%	Not mentioned
45	Not mentioned	Not mentioned	Not mentioned
46	35	Not mentioned	Not mentioned
47	25 and 45	Not mentioned	Not mentioned
48	Not mentioned	Not mentioned	Not mentioned
49	Not mentioned	Not mentioned	Not mentioned
50	25	60%	Not mentioned

Table 10. test condition, duration and investigated biodegradability factor

Number	Test condition	Test duration	Biodegradability factor investigated
1	Aerobic activated sludge	30 days	Chemical structure
2	Activated sludge	8 weeks	Polysaccharide loading
3	Incubation with isolated bacteria and fungi	28 days	Environmental effect
4	Indoor soil burial	9 months	Chemical structure/polysaccharide loading/environmental effect
5	Compost/fungal incubation	250 days for compost 15 week for fungi test	Source of polysaccharide/chemical structure/polysaccharide loading
6	Incubation with standard soil mix	168 days	Polysaccharide loading
7	Garden soil burial	4 weeks	Source of polysaccharides/chemical structure

8	Compost	30/50 days	Chemical structure
9	Soil burial	6 months	Source of polysaccharides/effect of other materials
10	Soil burial	25 days	Polysaccharide loading
11	Laboratory soil burial	60 days	Chemical structure/effect of other materials
12	Soil burial	10 days	Chemical structure
13	Hydrolytic degradation in buffer solutions and in natural lake water	20 days	Environmental effect
14	Soil burial test	49 days	Effect of other materials
15	Indoor soil burial	35 days	Chemical structure/effect of other materials
16	Soil/human fecal inoculation	5 days	Source of polysaccharides/environmental effect
17	Laboratory composting condition	45 days	Chemical structure/environmental effect
18	Compost soil burial	180 days	Polysaccharide loading
19	Soil burial	5 months	Source of polysaccharides/effect of other materials
20	Soil burial and exposure to mold fungi	3 months for starch and 9 months for chitosan blend	Source of polysaccharides/effect of other materials
21	Laboratory by MODA	-	Chemical structure
22	Outdoor soil burial	8 months	Polysaccharide loading
23	ISO 2012 incubation under controlled composting condition	200 days	Chemical structure/polysaccharide loading/environmental effect
24	Garden soil burial	3 weeks	Polysaccharide loading/environmental effect
25	Antifungal resistance test	120 days	Chemical structure/polysaccharide loading
26	Three different soils	6 months	Chemical structure/environmental effect
27	Incubation under composting condition/outdoor soil burial(uncontrolled climatic parameters)	60 days	Chemical structure/effect of other materials
28	Simulated soil burial	100 days	Chemical structure/polysaccharide loading/effect of other materials
29	Soil burial	20 weeks	Effect of other materials/environmental effect
30	Vegetal compost	12 days	Polysaccharide loading
31	Anaerobic soil burial by ASTM standard D6003-96	60 days	Effect of other materials
32	Vegetal compost	2 months	Source of polysaccharides
33	Modified EN standard 14045 in natural composting environment	12 weeks	Chemical structure

34	Incubation under controlled composting conditions according to ISO 14855-1, 2004	90 days	Source of polysaccharide
35	Immersed in potato dextrose agar (PDA) medium	21 days	Polysaccharide loading
36	Soil burial	30 days	Polysaccharide loading
37	Soil burial	50 days	Polysaccharide loading
38	Soil burial	30 days	Chemical structure/polysaccharide loading
39	Garden soil burial	30 days	Polysaccharide loading/environmental effect
40	Real aerobic composting condition	90 days	Chemical structure/polysaccharide loading/effect of other materials
41	Agricultural and desert soil burial.	6 months	Polysaccharide loading
42	Incubation in simulated composting conditions by ASTM International D5338-15 protocol	140 days	Polysaccharide loading
43	Laboratory soil burial by ASTM D2216 and lake immersion	35 days	Polysaccharide loading
44	Incubation under controlled composting conditions by EN ISO 14855-1: 2012 European Standard	45 days	Polysaccharide loading
45	Uncontrolled sandy loam soil burial	28 days	Polysaccharide loading
46	Landfill burial test in both aerobic by ISO 14851 (ISO, 1997) and anaerobic conditions by ASTM, 1992	90 days	Environmental effect
47	Soil burial	5 days	Chemical structure/polysaccharide loading/pre-treatment
48	Soil burial	7 days	Effect of other materials
49	Soil burial	4 weeks	Polysaccharide loading
50	Garden soil and vegetable waste burial	360 days	Polysaccharide loading

Table 11. measurement methods and technique

Number	Measurement method	Technique
1	Respirometric	Biochemical oxygen demand (BOD)
2	Physical	Weight loss/SEM and AFM/mechanical properties
3	Physical	Weight loss/visual examination of microbial growth
4	Physical	Weight loss/SEM
5	Physical	Weight loss
6	Respirometric/physical	CO ₂ mineralization/SEM
7	Physical	Weight loss
8	Physical	Weight loss

9	Physical	Weight loss
10	Physical	Weight loss
11	Physical	Weight loss/SEM
12	Physical	Tensile properties measurement
13	Physical	Weight loss/SEM
14	Physical/spectroscopic	Weight loss/SEM/FTIR
15	Physical	Weight loss
16	Physical	Decrease in polysaccharide sugar concentration
17	Thermal/spectroscopic/physical	TGA/FTIR/SEM/visual inspection
18	Physical	Weight loss
19	Physical	Weight loss
20	Physical	Weight loss and SEM
21	Respirometric	CO ₂ evolution
22	Physical	Weight loss
23	Respirometric	CO ₂ evolution
24	Physical	Weight loss/ visual observation
25	Physical/spectroscopic	SEM/behavior of mechanical strength/FTIR
26	Spectroscopic/physical	FTIR/SEM/weight loss
27	Physical and respirometric	Percentage of carbon mineralization/SEM/weight loss
28	Physical/spectroscopic/thermal	SEM/FTIR/TG
29	Physical	Weight loss/SEM
30	Physical	Visual examination
31	Physical/spectroscopic/thermal	SEM, AFM,FTIR, TGA
32	Physical	Visual observation
33	Physical	Visual examination of the surface disintegration
34	Repirometric	CO ₂ evolution
35	Physical	Visual examination of microbe growth
36	Physical	Weight loss
37	Physical	SEM/weight loss
38	Physical	Weight loss
39	Physical	Weight loss
40	Physical	Visual examination
41	Physical	SEM
42	Respirometric	CO ₂ evolution
43	Physical	Weight loss/SEM/ visual inspection
44	Respirometric	CO ₂ evolution
45	Physical	Weight loss
46	Respirometric	O ₂ consumption and CH ₄ generation
47	Physical	Weight loss
48	Physical	Weight loss
49	Physical/spectroscopic	Weight loss/SEM/FTIR
50	Physical	Weight loss/SEM

Conclusion and future work

Polysaccharides are intrinsically biodegradable polymers, yet show different biodegradability behaviors when incorporated into synthetic and other bio-based polymers. Factors believed to have an effect were, resources and origins, pre-treatment before preparation, process variables, modification, grafting, additives. Based on very little data existing on pre-treatment and not enough investigation on polysaccharides sources it was concluded that further research must go into the two fields in future. Biodegradability was dependent on crystallinity, chemical structure, nature and interaction of components present in the composites including host polymer, polysaccharide, and additives and hydrophilicity was the most influential element to explain the mechanism of biodegradability improvement. Increasing crystallinity, substitution of hydroxyl groups of starch and cellulose with other functional groups, grafting, and crosslinking reduced biodegradability for making the structure more complex and hydrophobic and inaccessible to microorganisms. Plasticizers and compatibilizers improved biodegradability with some exceptions. In addition, biodegradation of the same material is significantly different in various locations and weather conditions and for that, environmental conditions have to be considered in experiments.

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