Effects of Chemical and Morphological Structure on Biodegradability of Fibers, Fabrics, and Other Polymeric Materials

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The biodegradability of polymers depends on several factors. However, the most critical aspects are the accessibility of the structure for moisture and enzyme diffusion and the capacity of the microbes in the environment to assimilate the final monomers. The accessibility of the polymer structure to enzymes and water depends primarily on crystallinity, hydrophobicity, and the steric effects of the side groups in the polymer backbone. In general, biologically synthesized polymers are readily biodegradable in natural environments but synthetic polymers are either less biodegradable or degrade very slowly. However, such generalizations should be avoided. To understand the compatibility of biomaterials and the environment, both the disintegration step of the biodegradation process and the assimilation and mineralization of these fragments by microorganisms must be investigated. Mineralization occurs when the oligomers and monomers assimilated within the cells are converted to CO_2 and H_2O (aerobic), and CO_2, CH_4, and H_2O (anaerobic). Although the disintegration of the polymeric structure limits the biodegradation rate and is most easily detected, the final pieces may accumulate in the environment if they are not fully mineralized. Such accumulation could contribute to an issue with microplastics that may be much more difficult to address than the removal of macroscopic, large polymer-based debris.

Keywords: Biodegradable; Fiber; Chemical structure; Morphology; Fabric; Textile; Cellulose

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INTRODUCTION

In the last century, the utilization and production of plastic materials have increased exponentially due to the boom of the petrochemical industry (Browne *et al.* 2010; Thevenon *et al.* 2011; Geyer *et al.* 2017). Plastic materials have excellent mechanical properties, can resist water and other environmental damage, and their versatility makes them suitable for multiple applications (Browne *et al.* 2010; Thevenon *et al.* 2011). Their contributions to society in health, food, housing, and beyond have been immense. The petrochemical industry is fully developed, and its products have very competitive prices in the market. Therefore, the production and demand of plastics continue to grow (Browne *et al.* 2010; Thevenon *et al.* 2011). However, less than half of this plastic ends up in landfills or being recycled, and the rest is still in use or littering the continents and oceans (Rochman *et al.* 2013; Geyer *et al.* 2017).

The accumulation of plastics in the environment has become important in the last 50 years, especially in water bodies (Thompson *et al.* 2004). In the last decade, attention has been focused on microplastics, which are particles smaller than 5 mm in size that

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represent a hidden threat to the environment (Browne *et al.* 2011). Researchers have estimated that a minimum of 5.25 trillion plastic particles weighing 270,000 tons are floating in the world's oceans (Eriksen *et al.* 2014). This constitutes only 0.1% of the world's annual plastic production, which was 380 million metric tons in 2015 (Eriksen *et al.* 2014; Geyer *et al.* 2017).

In the textile industry, global clothing sales have doubled in the last 15 years (Cooper n.d.; Ellen Macarthur Foundation 2017). In 2015, the global consumption of apparel and footwear was 62 million tons and it is expected to increase by 63% by the year 2030, which implies a 62% rise in waste (Textile Exchange n.d.; Global Fashion Agenda & The Boston Consulting Group 2017). This represents an increase in solid waste of 57 million tons of waste generated annually (Global Fashion Agenda & The Boston Consulting Group 2017). Globally, only around 18% of clothing is collected for reuse or recycling and 57% is going to landfills (Fig. 1) (Global Fashion Agenda & The Boston Consulting Group 2017; Gwozdz *et al.* 2017). This is mainly due to the fast fashion phenomenon that involves quick style changes and low prices/quality, a combination that results in a reduction of the times that a garment is worn before it is discarded (Cooper n.d.; Eco Watch n.d.; Siegle n.d.). There are several options to reuse and recycling textile materials: reuse, fabric recycling, fiber recycling, polymer/monomer recycling, and energy recovery (Johnson *et al.* 2020). Nevertheless, these processes are still not fully implemented due to technical constraints (complex separation processes and low quality products) and limitations in the supply chain (cost, volume, collection, sorting, and transportation) (Johnson *et al.* 2020).

In addition, Boucher and Friot (2017) reported that synthetic textiles are the primary source of microplastics. Even if this portion only represents ~ 1% of the textile waste (Fig. 1), these small particles are ingested by aquatic fauna and transferred to the human food chain, potentially causing problems for the human health (Thevenon *et al.* 2011; Wagner *et al.* 2014; Rochman *et al.* 2015; Miranda and de Carvalho-Souza 2016; Kim *et al.* 2018; Liebmann *et al.* 2018). Despite being relatively inert, due their large surface-to-volume ratio and chemical composition, these particles can adsorb pollutants and pathogens and transfer them via ingestion to other trophic levels (Wagner *et al.* 2014; GESAMP 2015; Rummel *et al.* 2017; Egbeocha *et al.* 2018; Wang *et al.* 2018).

There is enough evidence supporting that synthetic and natural textile fibers and other plastics do not fully degrade in wastewater treatment systems, landfills, and the environment. Microplastics, mainly particles and fibers smaller than 100 µm, have been observed in wastewater effluents at low concentration (Browne *et al.* 2011; Magnusson and Norén 2014; McCormick *et al.* 2014; Talvitie *et al.* 2015, 2017a; b; Mintenig *et al.* 2017; Lares *et al.* 2018; Wolff *et al.* 2018). In the wastewater treatment process, more than 98% of microplastics are retained in the sewage sludge and they are transferred to the environment when used for soil amendment/fertilizer (Nizzetto *et al.* 2016; Mintenig *et al.* 2017; Talvitie *et al.* 2017b; Lares *et al.* 2018). The fibers identified in the effluents are typically from the textile industry. Mainly polyethylene terephthalate (PET) has been observed, but important quantities of cellulosic fibers such as cotton and rayon are also present (Talvitie *et al.* 2015, 2017a; b; Mintenig *et al.* 2017; Ziajahromi *et al.* 2017; Lares *et al.* 2018; Wolff *et al.* 2018). In the environment, the average size of plastic particles seems to be decreasing due to fragmentation (Barnes *et al.* 2009). In addition, Suaria *et al.* (2020) compiled a global dataset of oceanic water samples and observed that 8.2% of oceanic fibers are synthetic, 79.5% cellulosic, and 12.3% of animal origin.
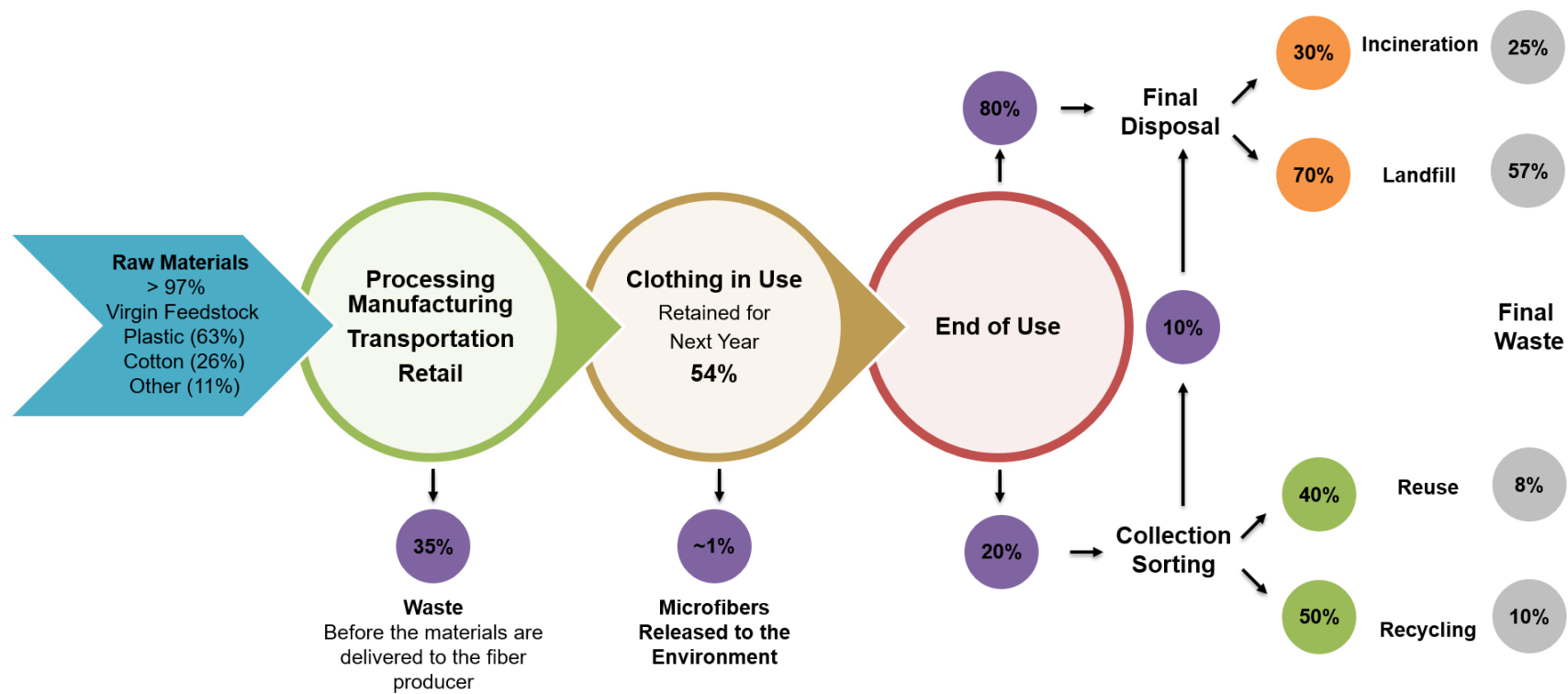
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Fig. 1. Global material flow of clothing (Ellen Macarthur Foundation 2017; Global Fashion Agenda & The Boston Consulting Group 2017).

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Moreover, microplastic/fiber fragments have been observed in landfill leachates of active (young and old) and closed facilities, which is also an indication that even under anaerobic conditions plastics are fragmentated but not fully mineralized (Kilponen 2016; Praagh *et al.* 2018; He *et al.* 2019; Su *et al.* 2019). Therefore, it is essential to understand the biodegradability of plastics, especially polymers used in the textile industry.

In early plastic development, to guarantee the durability and longevity of these materials, the production of plastics mainly focused on preventing or reducing degradation. Today, due to the concern about the fate of plastics in the environment after their intended use, the promotion of degradation is seen as a positive attribute (Krzan *et al.* 2006).

In general, petroleum-based plastics are not biodegradable, and their accumulation in the environment represents a social concern that impacts human health and the normal behavior of natural ecosystems. As a response to the problems of plastic accumulation and petroleum dependence, the production of plastics based on renewable resources is growing (Ashter 2016). Bio-based plastics can replace harmful conventional plastics (Ashter 2016). Biopolymers are produced from renewable natural sources such as chitin, gluten, corn, starch, or vegetable oil (Ashter 2016; Karamanlioglu *et al.* 2017). Bioplastics are often biodegradable, but this is not always true (Ashter 2016; Karamanlioglu *et al.* 2017). Bio-based refers to the feedstock, and biodegradable describes the end of life of the material. The biodegradability of bio-based plastic is not related to its bio-based content. Even fossil-based plastics can be designed to be biodegradable, as biodegradability depends on the polymer structure and physical properties (Ashter 2016).

The effects of chemical and morphological structure on biodegradability of fibers, fabrics, and other polymeric materials are reviewed herein to summarize and identify which aspects could be manipulated in different stages of the life cycle of materials, especially textiles, to promote or delay biodegradation.

MECHANISMS OF POLYMER BIODEGRADATION

According to the American Society for Testing and Materials (ASTM) and the International Organization for Standardization (ISO), degradation is ''an irreversible process leading to a significant change of the structure of a material, typically characterized by a loss of properties (*e.g.*, integrity, molecular weight, structure, or mechanical strength) and fragmentation. Degradation is affected by environmental conditions and proceeds over a period of time comprising one or more steps'' (Krzan *et al.* 2006; ASTM D6691 − 09 2009; ISO 14851:2019 2019). In the environment, degradation occurs due to a combination of various mechanisms and factors (Krzan *et al.* 2006) (Fig. 2).

Abiotic Degradation

Abiotic degradation factors do not involve microorganisms, but they are necessary to fragment the polymeric material and produce smaller units that can be biodegraded (Mochizuki and Hirami 1997; Krzan *et al.* 2006; Lucas *et al.* 2008). The action of mechanical stress, temperature, humidity, solar light exposure, rain, and wind, *etc*. can weaken polymeric materials. Many transformations occur, such as changes in mechanical, physical, and chemical properties (Krzan *et al.* 2006; Lucas *et al.* 2008). The most important abiotic processes are oxidation and hydrolysis.

In synergy with light degradation, the O_2 or O_3 present in the atmosphere produce free radicals that can attack covalent bonds in polymers; they can also generate crosslinking or chain scissions (Lucas *et al.* 2008). Likewise, hydrolysis depends on water activity, temperature, pH, time, and the presence of hydrolyzable covalent bonds (ester, anhydride, amide, carbamine, or ester amine). Diffusion of water or oxygen inside the material structure is limited by its crystallinity and the molecular architecture, polar nature, and molecular mobility properties of the polymer (Mochizuki and Hirami 1997; Lucas *et al.* 2008).

Biotic Degradation

Biodegradation, or biotic degradation, is the breaking of polymeric bonds associated with the action of enzymes in living organisms (Krzan *et al.* 2006). Microorganisms, such as bacteria, protozoa, algae, and fungi, can grow on the surface or inside the polymeric material, form biofilms, and secrete slime matter, acids, and enzymes that can penetrate the surface of the material and disrupt its pore structure (Lucas *et al.* 2008).

Of all these factors, enzyme action is most often the determinant step during biodegradation. Enzymes are proteins that act as catalysts decreasing the activation energy of some chemical reactions (Lucas *et al.* 2008). There are different types of enzymes, such as endo-enzymes (catalytic action within the polymer chain), exo-enzymes (catalytic reactions that occur mainly at the ends of the polymer), constitutive enzymes (non-substrate specific), and inductive enzymes (substrate-specific enzymes) (Lucas *et al.* 2008). Enzymes are too molecularly large to be involved in bulk erosion and have poor diffusion characteristics in bulk materials; thus, they are only responsible for surface deterioration (Lucas *et al.* 2008).

After the polymer backbone is reduced to oligomers and monomers by depolymerization under the action of the factors mentioned above, these simpler compounds can penetrate the cell wall of microorganisms, providing the energy and elements necessary for living, growing, and reproduction, which is called assimilation (Lucas *et al.* 2008). After assimilation, the complete degradation of a substance occurs within the cell, which is called mineralization (Pagga 1997). The mineralization catabolic pathway depends on the environment where the microorganism can grow (Lucas *et al.* 2008). Microorganisms digest the organic products of plastic degradation under aerobic or anaerobic conditions (Krzan *et al.* 2006). During aerobic biodegradation O_2 is available, and aerobic microorganisms control the process and form CO_2, H_2O, and biomass as final products (Fig. 2) (Gu 2003). Anaerobic biodegradation occurs in the absence of O_2, and anaerobic consortia of microorganisms are responsible for polymer deterioration (Gu 2003). The primary products are microbial biomass, CO_2, CH_4, and H_2O under methanogenic conditions or H_2S, CO_2, and H_2O under sulfonic conditions (Fig. 2) (Gu 2003). During both processes, aerobic or anaerobic, microorganisms need a carbon source for growth and reproduction.

More details about the specific mechanisms of disintegration and mineralization of plastics and other polymeric materials are presented in several published reviews (Pagga 1997; Gu 2003; Krzan *et al.* 2006; Lucas *et al.* 2008; Gewert *et al.* 2015; Tiwari and Maurya 2018)
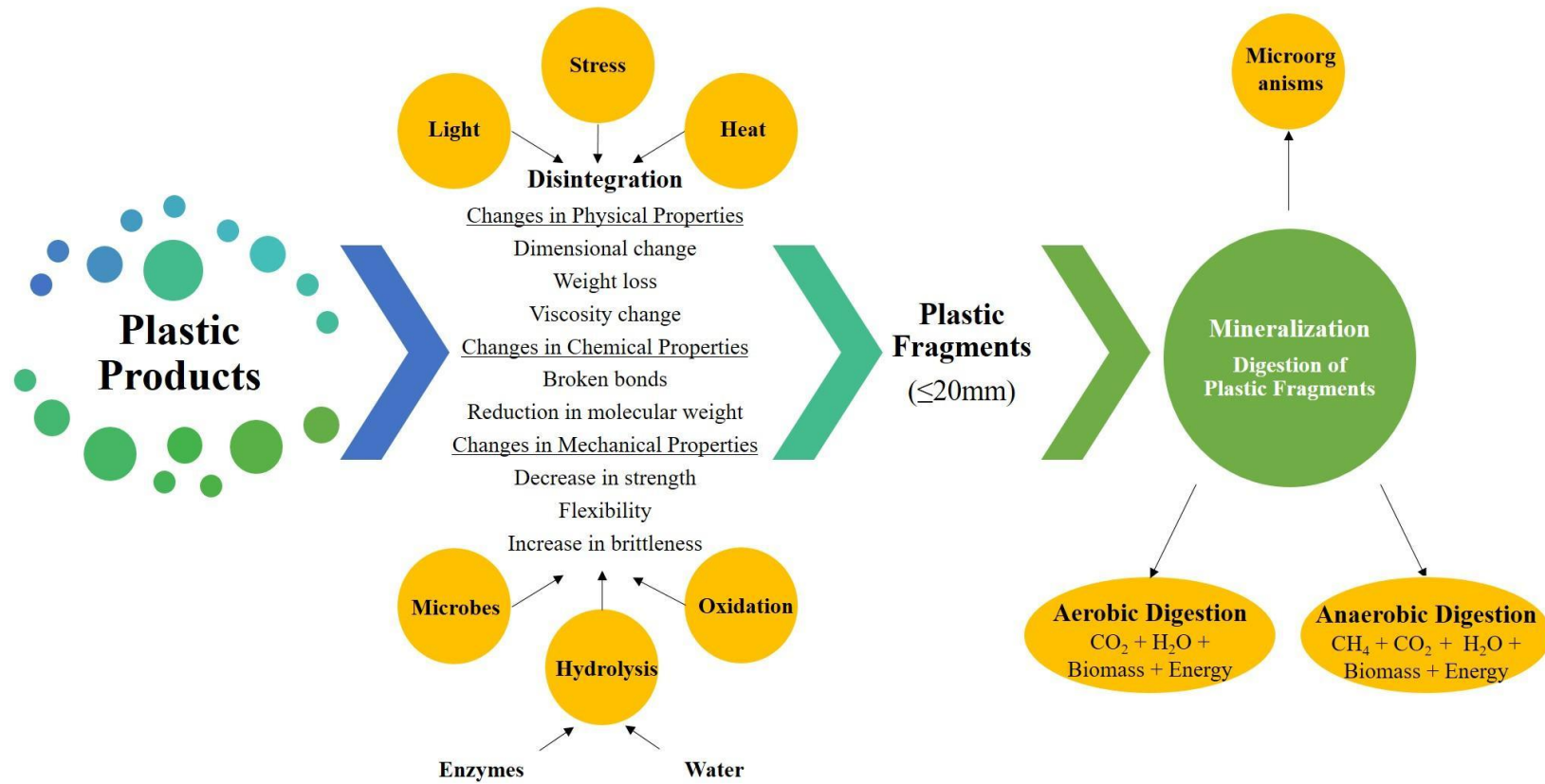
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Fig. 2. Schematic representation of plastics degradation processes in the environment, adapted from Krzan *et al.* (2006)

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FACTORS THAT AFFECT POLYMER DEGRADATION

The biodegradation of polymeric materials depends on the characteristics and properties of the material, such as molecular composition of the polymer, presence of functional groups, the intermolecular interactions, balance between hydrophobicity and hydrophilicity, crystallinity, level of orientation, morphology, configuration, surface structure, and molecular weight (Mochizuki and Hirami 1997; Gu 2003; Eyerer *et al.* 2010). Biologically synthesized polymers are generally readily biodegradable in natural environments, whereas synthetic polymers are either less biodegradable or degrade very slowly (Gu 2003). In addition to the polymer characteristics, biodegradation also depends on the environmental conditions that affect microbial growth and the presence of microbial communities able to generate the appropriate enzymes, assimilate, and metabolize the polymer (Gu 2003).

This review aims to summarize how the properties of textile materials affect the biodegradability of the polymers in the structure. The literature reviewed contains textile studies and studies on films and composites and how their properties influence degradation, as these studies also have implications for fiber and fabric behavior.

Crystallinity, Solid-State Morphology, and Moisture Diffusion

Crystallinity is one of the most critical factors during degradation (Mochizuki and Hirami 1997). In general, crystallinity is measured by X-Ray Diffraction (XRD), solid-state 13C NMR, infrared (IR) and Raman spectroscopies, and differential scanning calorimetry (DSC) (Szcześniak *et al.* 2008; Park *et al.* 2010; Linares *et al.* 2019). The amorphous regions of the polymers are easier to degrade, chemically and enzymatically, than crystalline regions. This is related to the primary chemical structure of the polymer, which controls how the molecules pack in the crystalline matrix. However, this is not the only factor; the kind of process involved in the manufacturing of materials defines the orientation, packing, and crystalline structure of the final good.

Table 1. Tensile Tenacity and Ultimate Elongation of PCL Fibers at Different Draw Ratios and Effect of Enzymatic Degradation in the Crystallinity and Orientation of PCL Fibers (Adapted from Mochizuki *et al.* (1995))

Draw Ratio	Tensile Tenacity (g/d)	Ultimate Elongation (%)	Crystallinity (%)		Orientation (%)	
			Before Degradation	After Degradation	Before Degradation	After Degradation
DR = 1 (Undrawn)	1.05	2485.4	40.0	38.7	65.3	63.3
DR = 5 (Drawn)	4.65	126.0	63.3	57.3	94.4	95.3
DR = 7 (Drawn)	5.22	58.6	65.0	61.8	95.3	95.1
DR = 9 (Drawn)	7.15	20.9	69.3	63.9	95.7	95.3

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One of the main methods to enhance the mechanical properties of fibers is the drawing process. The influence on the enzymatic hydrolysis by lipase of polycaprolactone (PCL) fibers at different draw ratios was evaluated (Mochizuki *et al.* 1995). At higher draw ratios, there was an increase in the orientation of the polymers within the fiber; therefore, there was an increase in crystallinity and tensile tenacity, and a decrease in ultimate elongation (Table 1). This study showed that the draw ratio was inversely related to the extent of the enzymatic hydrolysis of the fibers, which can be seen in Fig. 3 by the decrease in total organic carbon (TOC) formation (measured by combustion catalytic oxidation) and weight loss. It was also suggested that the enzymatic attack occurred preferentially in the amorphous or less ordered regions because the enzymes had more free space to move and bind to the polymer. Crystalline regions seem to be susceptible to degradation after the amorphous part of the material is consumed (Mochizuki *et al.* 1995).
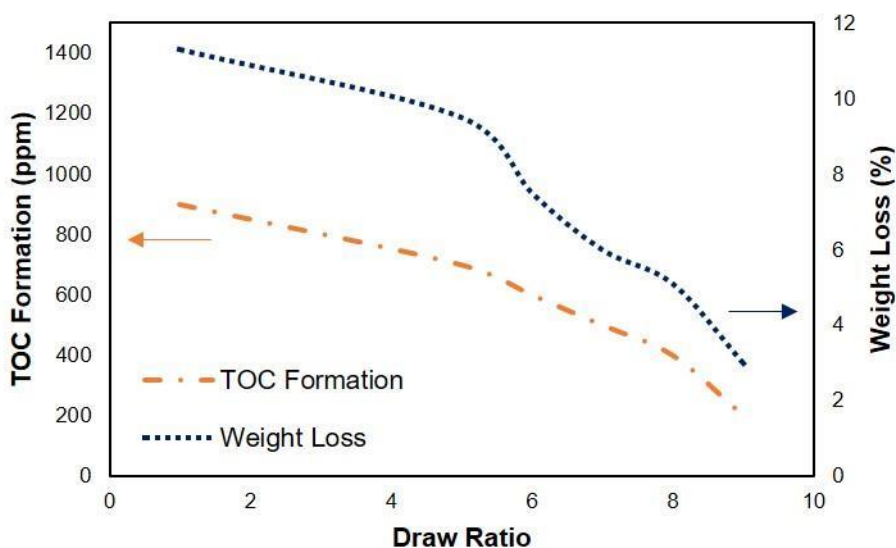

Fig. 3. The TOC formation and weight loss of PCL fibers with different draw ratios after 16 h in the aqueous solution containing lipase of *Rhizopus arrhizus* at 30 °C (adapted from Mochizuki *et al.* (1995))

According to the SEM images shown in Fig. 4, the degradation occurs from the surface and then proceeds from erosion of the surface to the inside of the fiber structure. The undrawn fibers showed deterioration on the surface and an important decrease in diameter after enzymatic hydrolysis in comparison to the drawn fibers. The presence of spherulites are an indication of the low orientation in the undrawn fibers, which made them susceptible to the enzymatic attack of the endo-enzyme lipase. In drawn fibers, the existence of highly-oriented fibrillar stripes parallel to the fiber axis indicated that the spherulites were extended and modified during the drawing process, which generated the highly crystalline structure that is resistant to lipase hydrolysis.

The effect of structure on the enzymatic hydrolysis of poly(butylene succinate-co-ethylene succinate)s (P(BS-co-ES)s) was studied using lipases obtained from several microorganisms to degrade hot-pressed co-polyester films (Mochizuki *et al.* 1997). The degradation was monitored by water-soluble total organic carbon (TOC) formation. Figure 4 shows the relation between crystallinity, chemical structure, and enzymatic degradation.
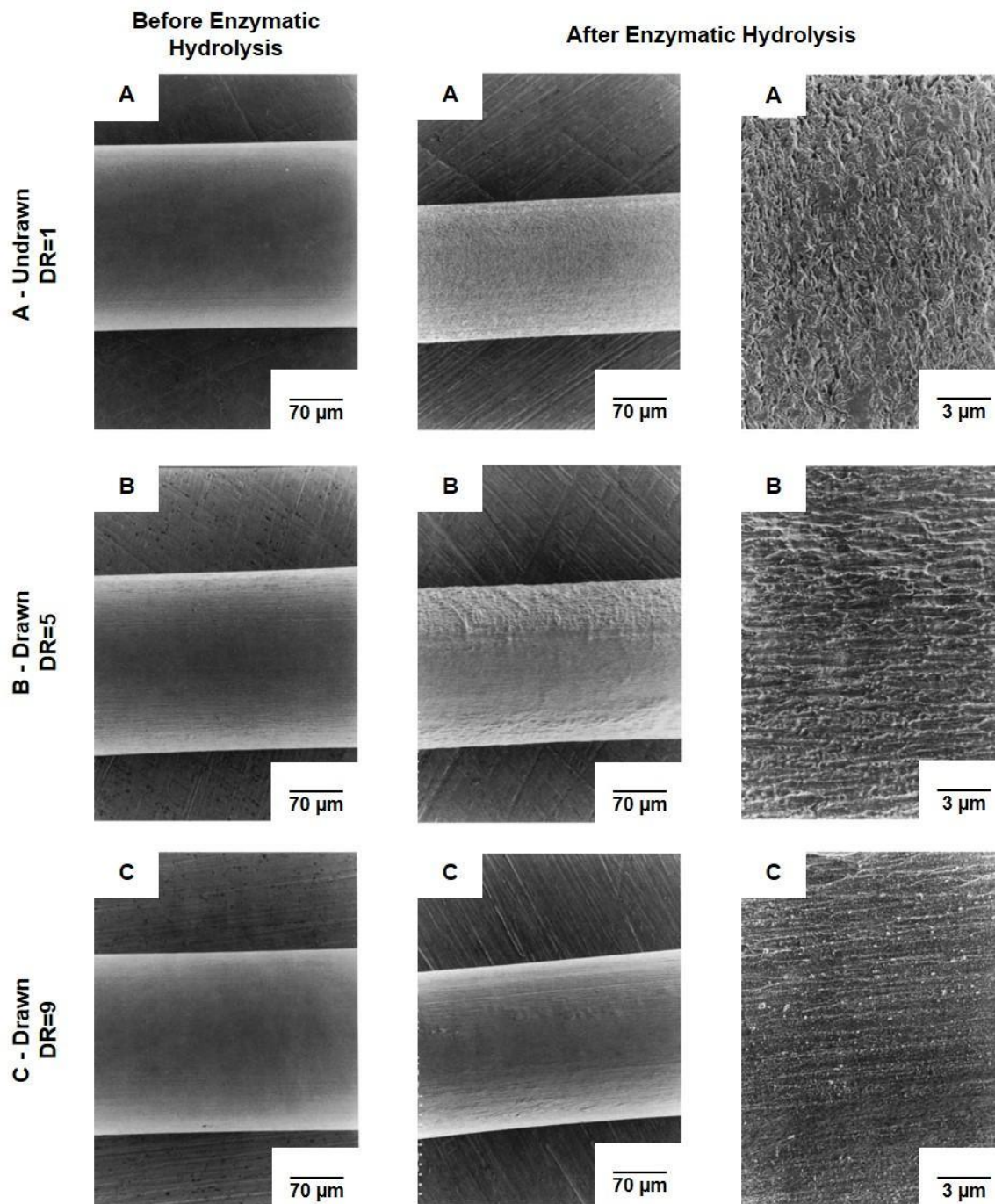
Fig. 4. The SEM images of PCL fibers with different draw ratios before and after enzymatic degradation (adapted from Mochizuki *et al.* (1995))

At 53 mol% of ES, there was a minimum in crystallinity, which coincided with the maximum rates of enzymatic hydrolysis for two lipases from *R. arrhizus* (not shown) and *P. nitens* (Fig. 5). The optimum biodegradation point was attributed to the presence of mostly amorphous or less ordered structures in films. This study concluded that both the chemical primary structure of the polymer and the decrease in crystallinity that impacts the accessibility of the polymer to microbial attack critically affect the rate of degradation.
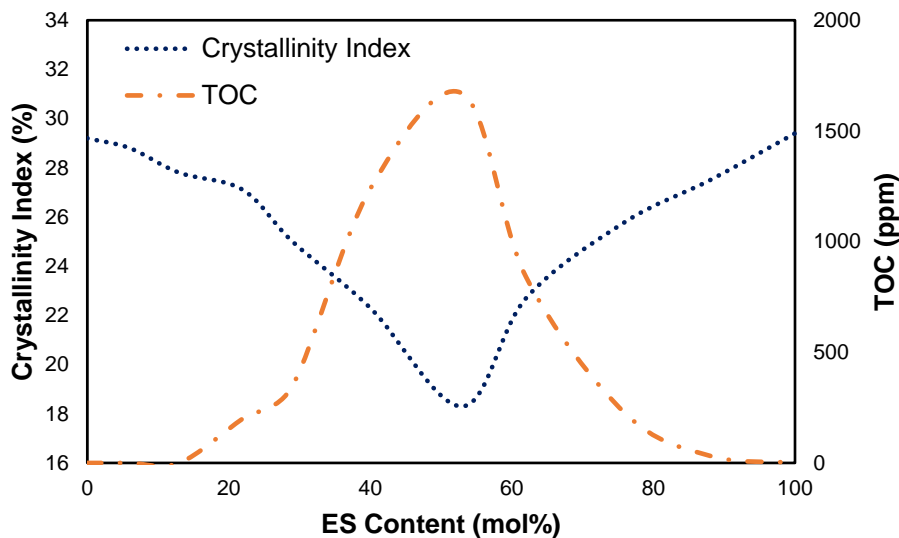
Fig. 5. Changes in X-ray crystallinity index and TOC formation profile of P(BS-co-ES) films after 4 h in the aqueous solution containing lipase of *P. nitens* at 30 °C *vs.* ES content in P(BS-co-ES) films (adapted from Mochizuki *et al.* (1997))

Similar results were observed by Bi *et al.* (2018) during the enzymatic degradation of poly(butylene succinate-co-hexamethylene succinate), p(BS-co-HS), by a lipase from *Candida rugose*. The rate of enzymatic degradation, crystallinity, and thermal properties were found to depend on the ratio of butanediol (BS) to hexanediol (HS) in the copolymer. Co-polyesters with more HS content were more susceptible to enzymatic attack due to the changes in crystallinity and melting point. Between 40% and 64% of HS, there is low crystallinity (13% - 20%) and the melting point of the co-polyesters is within 30 °C of the incubation temperature (37 °C). The 50/50 co-polyester showed the highest degradation rate and lowest crystallinity. In addition, all polymers showed an increase in crystallinity after incubation, supporting the fact that amorphous regions are easier to degrade. However, the influence was higher in more equimolar co-polyesters. In terms of molecular weight, no significant influence was observed in biodegradation rate and the molecular weight distribution was constant after degradation, supporting the proposed random endo-type scission mechanism.

On the other hand, Alzate Marin *et al.* (2018) created blended PLA/PHA films by solvent casting. The incorporation of PHA in the films increased the crystallinity of PLA, especially at the 60/40 PLA/PHA ratio (Table 2). Crystallized PHA acted as a nucleating agent for PLA, increasing crystallinity and reducing the water-vapor permeability (Table 2). The crystals decrease the volume of amorphous phase and create a bigger tortuosity in the film structure reducing the mass transfer through the film. After 50 days of soil burial test, the changes in morphology, chemical structure, and thermal properties indicate that both phases degraded to some extent. PHA is highly biodegradable in composting and soil at environmental conditions; however, PLA is biodegradable in industrial compost at higher temperatures and in soil at a slow rate. In Fig. 6, it can be observed that the degradation is more intense as the ratio of PLA/PHA decreases, especially from 40/60 to 20/80. The decrease in the PHA transition enthalpy of melting during DSC indicated depolymerization within the structure. In addition, the characteristic ATR- FTIR bands lost definition after the soil burial test. For all the samples, the peaks in the 4000 to 3000 cm^{-1} range were broadened due to the formation of hydroxyl and carboxylic groups during

biodegradation. In addition, it is important to mention that at a PLA/PHA ratio of 60/40 the crystallinity is higher and the water permeability lower (Table 2), which is in accordance with the low disruption of the matrix after biodegradation in soil (Fig. 6).

Table 2. Crystallinity and Moisture-vapor-barrier Properties of Polyhydroxyalkanoates (PHA) and Polylactic Acid (PLA) Films (Adapted from Alzate Marin *et al.* (2018)).

PLA/PHA	CD (%)	WVP * $(\times 10^{11}$ g s^{-1} m^{-1} Pa^{-1})
100/0	14.3	1.73(0.25)[b]
80/20	16.9	0.62(0.06)[a]
60/40	21.8	0.68(0.07)[a]
40/60	18.5	0.72(0.05)[a]
20/80	14.8	2.22(0.38)[b]
0/100	18.3	2.24(0.30)[b]
Note: CD Crystallinity Degrees WVP Water-Vapor-Barrier, lower values indicate lower water vapor permeability * Different letters indicate significant differences ($p < 0.05$) among samples.		

Moreover, Antipova *et al.* (2018) studied the biodegradation of poly-ε-caprolactones (PCL) and poly-l-lactides (PLA) by fungi. The biodegradation rate depended on the fungal strain used. All of them were able to degrade the polymers but at different rates. In addition, the most degradable PCL sample was shown to have the lowest molecular weight and polydispersity and higher crystallinity.

Generally, the biodegradability of a polymer increases with lower molecular weight (easier depolymerization) and crystallinity. The molecules in the amorphous regions are more susceptible to the action of hydrolases. However, in this case the lower molecular weight has a more dramatic effect on biodegradability than the other parameters. For the PLA samples studied, the most biodegradable polylactide DL-PLA had the lowest crystallinity due to the stereochemistry differences between the L and D configurations of PLA. Among the PLA samples having only poly-L-lactide, a similar molecular weight and polydispersity was observed; however, the sample with highest crystallinity was less biodegradable.

In addition, the effect of the stereochemistry on the biodegradation of polymers was also observed by Arcana *et al.* (2005) in poly(R,S)-β-hydroxybutyrate (PHB) and its copolymer with δ-valerolactone (δ-VL). The biodegradation was studied using activated sludge in an aerobic medium. The biodegradation rate was the highest in P(R)-HB with 100% (R) isotactic structure (bacterial PHB) and the final biodegradation was reached at around 94% after incubation time of 35 days. Stereoregular synthetic P(R,S)-ß-HB degraded at a lower extent and rate than the bacterial PHB (88%) and the degradation decreased even more when VL was co-polymerized in the structure. The decrease in the biodegradation could be related with the fact that isotactic P(S)-HB polymer is not degraded by PHB depolymerase; this enzyme is not able to hydrolyze the (S)-HB units. In addition, PVL (poly-valerolactone) is biodegradable but at a lower rate than naturally produced PHB (bacterial), 25% *vs*. 94%. The homopolymer PVL has higher crystallinity compared to PHB.
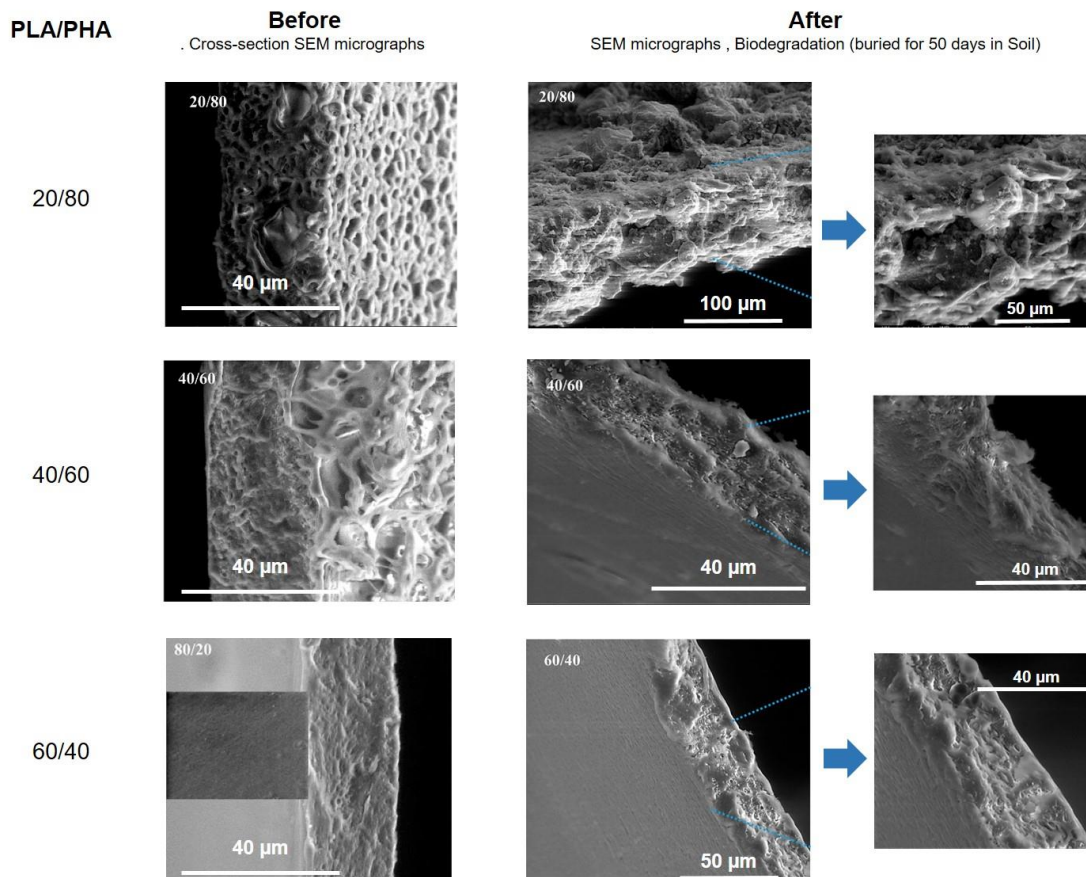
Fig. 6. SEM micrographs of PLA/PHA blended films before (cross section, only) and after 50 days of biodegradation by soil burial test. Adapted from Alzate Marin *et al.* (2018)**.**

In general, the same behavior has been reported for other aliphatic polyesters with different chemical structures, additives, and morphologies; the material resulting in lower crystallinity has higher tendency/susceptibility to enzymatic hydrolysis and biodegradation (El-Hadi *et al.* 2002; Bikiaris *et al.* 2006; Tserki *et al.* 2006; Pantani and Sorrentino 2013; Gigli *et al.* 2014; Hsu *et al.* 2014; Genovese *et al.* 2016; Prudnikova *et al.* 2017; Pan *et al.* 2018; Wang *et al.* 2019; Iozzino *et al.* 2019; Kuo and Wu 2019; Li *et al.* 2019; Quattrosoldi *et al.* 2020; Tang and Simon 2020).

For cellulose fabrics, the influence of crystallinity has also been reported to affect biodegradability. Park *et al.* (2004) assessed the biodegradability of different types of cellulose fabrics made with natural fibers (cotton and flax) and regenerated fibers (viscose rayon and cellulose acetate). Three methods were used: tracing the CO_2 produced by degradation by the action of activated sludge, measuring the loss in tensile strength of fabrics by soil burial test, and the formation of total organic carbon (TOC) by enzymatic hydrolysis using cellulase. According to this study, the biodegradability of the fabrics evaluated is higher in rayon, followed by cotton and cellulose acetate fibers. The higher rate of degradation of rayon compared to cotton is attributed to differences in crystallinity in the fibers. In the case of cellulose acetate fibers, the most influential factor is the presence of acetate groups that replace hydroxyl in the cellulose chain, which makes these fibers more hydrophobic and less prone to biodegradation, despite their low crystallinity.

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Though linen fabrics are made of natural flax fibers and have higher crystallinity than cotton, in soil burial tests, linen fabric showed the highest biodegradability; nevertheless, in the activated sludge and the TOC tests, this fabric was less biodegradable than cotton. This inconsistency with linen may be related to the microorganisms present in the soil sample used and the high content of a non-cellulosic material such as lignin.

Similarly, Niu *et al.* (2012) studied the biodegradability of cotton, ramie, and viscose rayon under anaerobic conditions in activated sludge. Though the chemical structure of the cellulose chains that compose these fabrics are similar, there is one slight change that modifies the crystalline structure of these materials; natural fibers are composed of cellulose I (parallel) and regenerated cellulose fibers are made of cellulose II (antiparallel) (Niu *et al.* 2012). In addition, cotton has a higher molecular weight and degree of polymerization (~ 6,000 to 10,000 units) than rayon (~ 400 and 700 units) (Warnock 2011)**.**

The antiparallel configuration of cellulose II is accompanied with a lower crystallinity and lower orientation in rayon compared to the native form of cellulose in cotton and ramie, which makes it more susceptible to biodegradation as indicated by the results of (Niu *et al.* 2012) (Fig. 7) and Park *et al.* (2004). Hou *et al.* (2013) also showed that the rate of biodegradation of regenerated cellulose fabrics in soil (production of CO_2), composting (weight loss), and cellulase hydrolysis (weight loss) is higher than cotton fabrics.
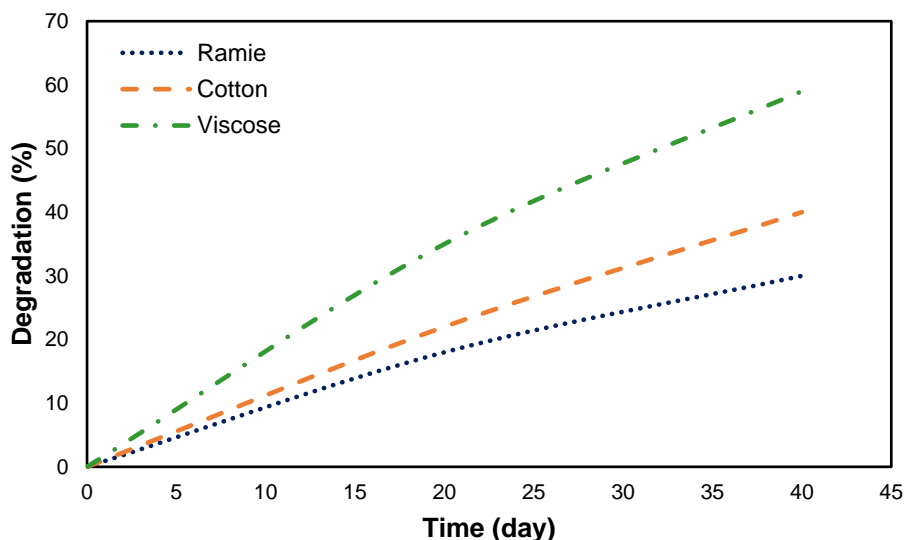
Fig. 7. The degradation of the fabrics in the activated sludge (adapted from Niu *et al.* (2012))

The behavior reported by Niu *et al.* (2012) for fabrics made of fibers with different cellulose crystalline structures (cellulose I and cellulose II) during enzymatic hydrolysis is supported by the work of Wada, Ike, & Tokuyasu (2010) (Fig. 8). Both forms of cellulose II have a higher degradation than cellulose I. Nevertheless, hydrated cellulose II showed higher saccharification during enzymatic hydrolysis; the structure of the material is already swollen, and the presence of water assists the mobilization of enzymes and other chemicals that promote degradation.
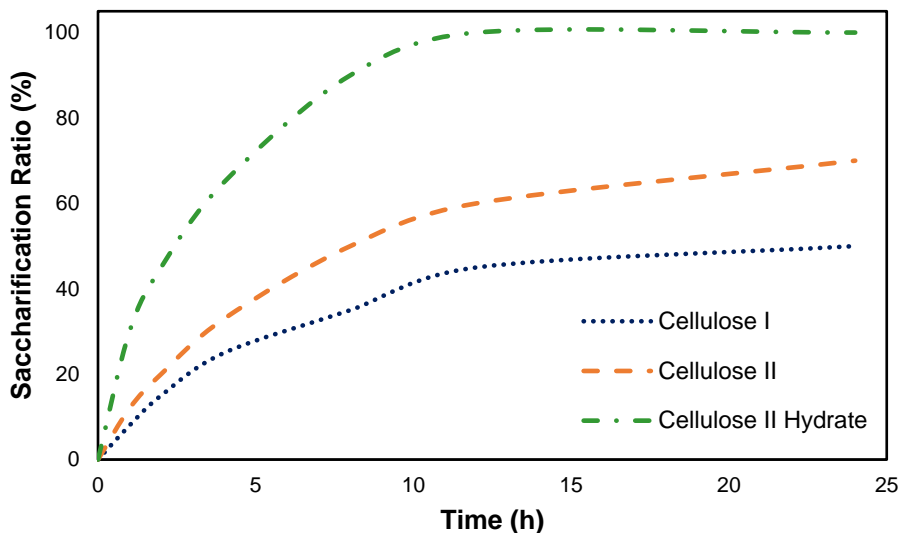
Fig. 8. Changes in the enzymatic saccharification ratio of cellulose I, cellulose II hydrate, and cellulose II with time (up to 24 h) (adapted from Wada *et al.* (2010))

Another factor that affects the biodegradation of polymers is moisture diffusion in the polymeric matrix. The degradation rate for cellulose acetate fabrics is lower than other cellulose fabrics with equal or higher crystallinity, and the hydrophobicity of this molecule blocks the moisture diffusion in the fiber matrix (Park *et al.* 2004). Though this study did not present any data on moisture regain, it was concluded that the level of crystallinity of the material is closely related to moisture regain and biodegradability. Further, cellulose fibers have a good capacity to absorb water due to the hydroxyl groups within the polymer chain, and the water absorption rates increase in materials with lower crystallinity. Rayon (regenerated cellulose) has higher moisture regain than cotton, which also helps to explain why rayon was degraded to a greater extent than cotton in the study conducted by Park *et al.* (2004). It is important to understand the effect of both crystallinity and moisture sorption capacity during biodegradation.

A strong relationship between crystallinity, water sorption capacity, and tensile properties in the biodegradability of polymeric materials was reported by Spiridon *et al.* (2015). Their primary purpose was to study the morphology and structure of composite films made of potato starch and cellulose modified with toluene diisocyanate (TDI) and the behavior of these composites under enzymatic hydrolysis using α-amylase from *Bacillus subtilis* and cellulase from *Aspergillus niger* at optimized conditions. They reported that composites reinforced with cellulose fibers showed an increase in tensile strength due to reinforcement from high crystallinity cellulose (Table 3). In addition, the carbamate moiety in the modified cellulose and the crosslinking between cellulosic chains by TDI increased the H-bonding intensity within the composite, which improved the mechanical properties and made the materials less susceptible to water sorption and enzymatic attack (Spiridon *et al.* 2015). The hydrolytic degradation of PLA/RH (rice hulls) composites at different temperatures was studied by Ndazi and Karlsson (2011) to evaluate the effect of hydrolytic degradation on thermal properties, crystallinity, chemical structure, molecular weight, and surface morphology. The hydrolytic degradation of PLA and PLA/RH composites was greatly influenced by the temperature of the water. The diffusion rate of water increased with the temperature, and the increment was more important above the glass transition temperature of the polymer (T_g).

Table 3. Enzymatic Hydrolysis of Composites with 10 U/g of α-amylase and 10 U/g of cellulase at 25 °C (Adapted from Spiridon *et al.* (2015))

Parameters	Sample		Starch Film	Composite A	Composite B
	Composition		Potato Starch	Potato Starch 30% Organosolv Cellulose	Potato Starch 30% TDI Modified Cellulose
Mechanical Properties	Young's modulus (MPa)		7.5	6.8	2.3
	Tensile strength (MPa)		1.7	2.5	3.2
	Elongation at break stress (mm)		20.00	7.86	10.80
Water Sorption Capacity	Mo* (g water/g)		0.0902	0.0885	0.0722
Enzymatic Hydrolysis 25 °C 10 U/g	$K \times 10^{-3}$ ** (s^{-1})	Amylase	3.6	3.374	2.079
		Cellulase	-	2.88	2.699
	Amylase ¥ Product after 1400 min	Maltose (mmol/mL)	12	10	9
	Cellulase ¥ Product after 1400 min	Glucose (mmol/mL)	0.5	2.7	2.25

*Mo – Monolayer moisture constant from the Guggenheim–Anderson–de Boer (GAB) model for moisture sorption isotherm;
**K - Velocity rate constant (1/s);
¥ - Higher enzymatic degradation rate is indicated by the increase in concentration (mmol/mL) of maltose and glucose

At temperatures close to the T_g of PLA (51 °C), the composites showed notable degradation. The addition of rice hulls also indirectly promoted PLA disintegration, as the filler disrupted the polymer structure and enhanced water absorption and swelling. During hydrolytic degradation, the composite exhibited fragility and fractures. In this study, hydrolytic degradation was demonstrated by the reduction in thermal stability of the materials tested, which is related to a decrease in the average molecular weight of the polymer at higher water immersion temperatures. In addition, the crystallinity increased after hydrolysis, whereas amorphous regions were more susceptible to hydrolysis due to the higher free volume in this area that allows the diffusion of water and enzymes that cleaves the -C-O- ester bond. However, the crystallinity will decrease if the hydrolysis is extended to crystalline regions. This behavior was also observed in other studies related to enzymatic hydrolysis and biodegradation of polymers (Hsu *et al.* 2014; Lipsa *et al.* 2015; Muniyasamy *et al.* 2016; Stoleru *et al.* 2017; Zhuikov *et al.* 2017; Blackwell *et al.* 2018; Cesur 2018; Vasile *et al.* 2018; Chasse *et al.* 2019; Iozzino *et al.* 2019; Kalita *et al.* 2019; Karimi and Biria 2019; Puchalski *et al.* 2019; Shamsah *et al.* 2020). However, other studies show just a steady decrease in crystallinity, suggesting that in some polymers the biodegradation can occur simultaneously in both amorphous and crystalline regions (Pan *et al.* 2018; Sajkiewicz *et al.* 2018).

Similar results were observed by Avolio *et al.* (2015) in poly(butylene succinate-co-butylene adipate) (PBSA) biocomposites using cellulose as a filler. The water vapor permeability of the composites increased when adding cellulose fillers due to the intrinsic hydrophilicity of cellulose. However, composites containing amorphous cellulose (15 %

crystallinity) had a slightly lower permeability than those containing long fibers (> 50 % crystallinity); such fibers create a preferential path for water molecules inside the composite. Despite this, composites containing amorphous cellulose undergo faster degradation in soil compared to pure PBSA or composites reinforced with cellulose fibers. In addition, Badia *et al.* (2017) observed an increase in crystallinity and a decrease in molecular weight on PLA/sisal composites during biodegradation in soil when increasing the sisal content on the composite. The hydrolytic chain scission provoked a reduction of molar mass and a slight increment of crystallinity degree during biodegradation. The sisal fibers act as a nucleating agent, increasing the crystallinity of the composite, but also increasing their hydrophilicity, making them more susceptible to biodegradation.

Therefore, these studies are in agreement with the finding that amorphous regions are more susceptible to degradation than crystalline regions. In addition, oxidation and hydrolysis occur more easily in the amorphous regions of the polymers than in organized crystalline structures that block the diffusion of O_2 and H_2O (Lucas *et al.* 2008).

For typical applications, the temperature of the environment is rarely close to the melting point of most polymers. However, higher temperatures can promote reorganization of the macromolecular structure of the polymers. Above the glass transition temperature (T_g) of polymers, the amorphous regions have high molecular mobility and are susceptible to chemical and biological attacks due to the free volume available for diffusion (Lucas *et al.* 2008).

Degree of Chemical Substitution

The degree of substitution (DS) in acetylated cellulose fibers affects their mechanical and moisture properties and, therefore, their biodegradability. Buchannan *et al.* (1993) demonstrated that the biodegradation rate of cellulose acetate (CA) fibers and films in environments favorable to its degradation depends mainly on the degree of substitution. The degree of substitution and the molecular weight of cellulose acetate fibers (DS = 2.5) decreased with the biodegradation. Cellulose acetate films with DS of 1.7 degraded 80% in 5 d, 12 d were required for extensive degradation of CA films with DS of 2.5, and no changes were observed after 28 d for cellulose triacetate (DS = 3) films using cellulose acetate degrading enrichments. The same behavior occurred in samples incubated in the aeration basin of a wastewater treatment plant, but a lower rate of degradation was observed.

In addition, the biodegradation of ^{14}C radiolabeled side groups in cellulose acetate and propionate samples was evaluated by capturing [14]CO$_2$ using an *in vitro* aerobic system with naturally derived mixed microbial communities from activated sludge (Komarek *et al.* 1993). The ^{14}C polymeric carbon in the cellulose acetate samples was significantly converted to [14]CO$_2$ in 14 d to 31 d; over 80% was converted for CA with a DS of 1.85, and only 60% was converted for CA with DS of 2.07 and 2.57. In the case of cellulose acetate propionate, only low DS (1.77 and 1.84) samples showed around 70% to 80% conversion of ^{14}C to [14]CO$_2$ in 29 d, whereas samples with a DS of 2.11 to 2.64 showed a much lower conversion rate than the other materials.

In a composting environment, the situation was the same for cellulose derivatives. The disintegration of cellulose acetate films with low DS (< 2.20) was comparable to that of polymers such as poly(hydroxybutyrate-co-valerate) (PHBV) and PCL (Gardner *et al.* 1994). Similar to the results presented by Buchannan *et al.* (1993), cellulose acetate film samples with high bio-disintegration rates had lower DS and molecular weight. In samples with high DS (2.97) and low disintegration rates, the molecular weight increased at the end

of the composting experiment, which was likely due to the lower molecular weight fractions in the sample being preferentially degraded. In a study by Gross *et al.* (1995) on mineralization with microorganisms of cellulose acetate powders, it took 24 d to reach 70% of theoretical CO_2 produced with a DS of 1.7, whereas it took 60 d for a DS of 2.5. Gross *et al.* (1995) observed that a decrease in the moisture level of the compost decreased the biodegradability of the cellulose esters to a great extent.

Moreover, losses in enzymatic and anaerobic degradability with increasing DS have also been reported for xylan, cellulose, and starch derivatives (Glasser *et al.* 1995; Rivard *et al.* 1995). The groups of substitution are usually substituting the hydroxyl groups in the sugar structures. Basically, there are steric interferences that do not allow cellulases and beta-glucosidases, or amylases to access the glycosidic bonds and produce the hydrolysis.

In addition, the size of the substituting group also affects the biodegradability of these materials. This effect was already mentioned above with regard to cellulose acetate and propionate in the work done by Komarek *et al.* (1993). Rivard *et al.* (1995) found a clear correlation between DS, the carbon chain length of the ester groups, and biodegradability in anaerobic systems for starch esters (Fig. 9). The anaerobic bioconversion of starch esters declines with increasing DS and chain length of the ester substituting group.
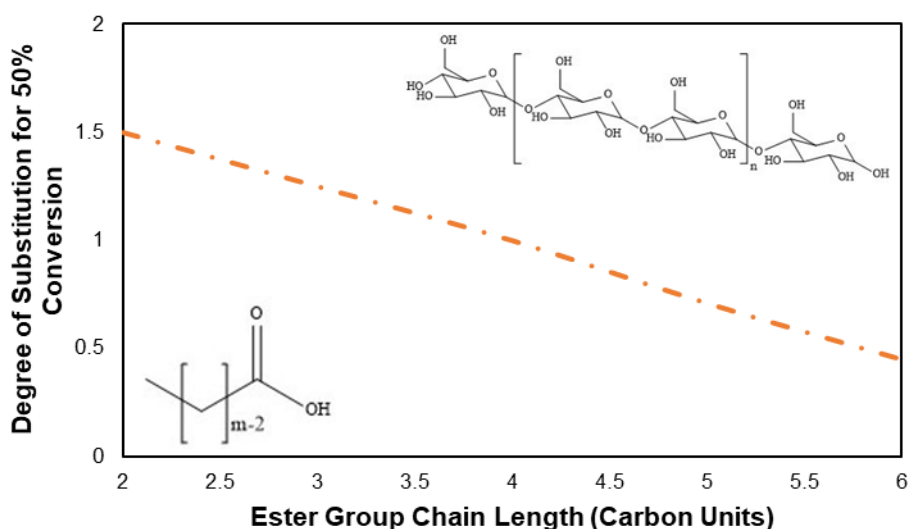
Fig. 9. The effect of increasing ester group chain length (m) on the minimum DS for starch esters, which allows for 50% anaerobic conversion (adapted from Rivard *et al.* (1995))

In addition, cotton fibers have higher biodegradability than cellulose acetate fibers (DS = 2.5) (26% and 5%, respectively) in aerobic aquatic systems with 1% of inoculum from municipal sewage sludge (Suh *et al.* 1996). Similarly, the same behavior was observed in aerobic biodegradation tests (Sturm Test) when comparing cellulose acetate and aminated cellulose with kraft paper, cellophane, sausage casing, and cotton fabric; non-substituted cellulose materials showed more than 60% conversion to CO_2 and substituted cellulose showed less than 10% conversion (Itavaara and Viikari 1999). The tendency was the same when comparing the enzymatic hydrolysis rate of these materials using cellulase and β-glucosidase (Itavaara and Viikari 1999).

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As previously mentioned, crystallinity is an important aspect of the biodegradation process. However, for cellulose acetates, the DS is the principal aspect of the process, despite the crystallinity of the sample. Samios *et al.* (1997) observed that the crystallinity of CA increased when DS decreased, and high DS CA samples were amorphous. Nonetheless, in terms of biodegradability, it was easier to degrade low DS cellulose acetates. Samios *et al.* (1997) proposed a mechanism for the biodegradation of cellulose acetate. First, esterase deacetylates the polymer. Then, when the DS drops to a certain level and there is enough space, cellulase de-polymerizes the cellulose chain. At high DS (> 2.5), the steric effect of the acetyl groups does not allow the attack of esterase.

Similarly, in electrospun starch acetate (SA) nanofibers, a DS of 2.3 was shown to retain 78% and 48% of tenacity after 16 d and 32 d, respectively, of exposure to an environment with 90% relative humidity and 50 °C, whereas lower values of 77% and 40.2% were observed for SA nanofibers with a DS of 1.1 (Xu *et al.* 2009). Higher DS values of the SA decrease the hydrolysis of the polymer matrix. In contrast, SA nanofibers with low DS have more hydroxyl groups available to interact with water, which favors the water migration within the polymer and the swelling of the structure, which increases hydrolysis and decreases tenacity. Though this paper was not directly related to biodegradation, the effects of DS on water interactions and biodegradation are correlated. When fewer groups are available to interact with water, it is more difficult for enzymes or chemicals to access and disrupt the polymeric matrix.

On the other hand, the degree of deacetylation in chitin/chitosan fibers significantly influenced the crystallinity and, therefore, the degradation of these fibers. A change in the degree of deacetylation from 67.4% to 70.6% increased the crystallinity from 9.5% to 12%, making these fibers more resistant to in vitro degradation by lysozyme in phosphate buffer. In addition, when these fibers were subjected to methanol drying, the fiber structure was completely dehydrated (more hydrophobic) which caused a further increase in crystallinity (~14%), tensile strength, fiber density, and durability (Judawisastra *et al.* 2015). Similar results were observed by Tomihata and Ikada (1997); it was found that a higher degree of deacetylation showed more resistance to degradation.

Crosslinking

Crosslinking treatments are widely used to improve the mechanical properties of materials. However, this also affects biodegradability. In methylcellulose films, crosslinking with glutaraldehyde not only increased the glass transition temperature and the tensile modulus of the films but it also decreased moisture absorption capacity and biodegradability (Rimdusit *et al.* 2008).

In cellulose fibers, crosslinking agents are used as easy-care finishing to connect the cellulose macromolecules from the hydroxyl groups within the non-crystalline regions (Tomšič *et al.* 2007). This treatment enhances the crease-recovery and crease-resistance properties of the fabrics due to the reduction in the swelling and shrinkage of the cellulose fibers (Tomšič *et al.* 2007). The decrease in hydrophilicity of the fibers and fabrics after the application of the easy-care finishing, which also affects the biodegradability at the end of the use of the modified fabric, is shown in Table 4 by the increase in the penetration rate of water. In this case, the sites where the crosslinking occurs also block the accessibility of cellulases to the glycosidic bonds, preventing hydrolysis and therefore the biodegradation. Tomšič *et al.* (2007) studied the influence of an easy-care finishing imidazolidinone (1,3-dimethyl-4,5-dihydroxyethylene urea) on the biodegradability of cellulose fibers by soil burial test and enzymatic hydrolysis. The cellulose fabric modified by imidazolidinone

(finished cotton fabric) showed irrelevant morphological changes and a smaller decrease in breaking strength and polymer solubility than the untreated cotton fabric (Table 4). In addition, the analysis of the FT-IR spectra showed the characteristic bands of the protein produced by microbial growth, amine I and amide II bonds (1640 cm^{-1} and 1548 cm^{-1}, respectively), and substantial structural damage to the untreated cotton fabric alone.

Table 4. Properties Related to the Biodegradability of Cellulose Fabrics Modified with Imidazolidinone as Easy-care Finishing (Adapted from Tomšič *et al.* (2007))

Properties	Biodegradation Test	Untreated Cotton Fabric	Finished Cotton Fabric
Penetration Rate of Water* (s/cm^2)	Before	1.56	6.54
Color Difference ($\triangle E*$)	After 12 d in soil burial test	31	16
Loss of Breaking Strength (q_{red})	After 12 d in soil burial test	0.25	0
Total Organic Carbon of Water-Soluble Compounds (ppm)	After 24 h of enzymatic hydrolysis at 44 °C and pH 4.7	1600	450
*A higher number indicates lower water penetration.			

The effect of crosslinking (polyisocyanate (PMDI) to glyoxal ratios) on the mechanical properties, water resistance, and biodegradability of composites made of wood flour and soybean protein was studied by Yue-Hong *et al.* (2015). Using different proportions of crosslinking agents, mechanical properties, water absorption, and the biodegradability of materials were balanced. The proper combination of crosslinking agents, glyoxal (good dispersion but weaker bonds), and PMDI (strong bonds and bad dispersion), with desired interfacial adhesion and excellent crosslinking efficiency improved the mechanical properties and water resistance of the wood/protein composite.
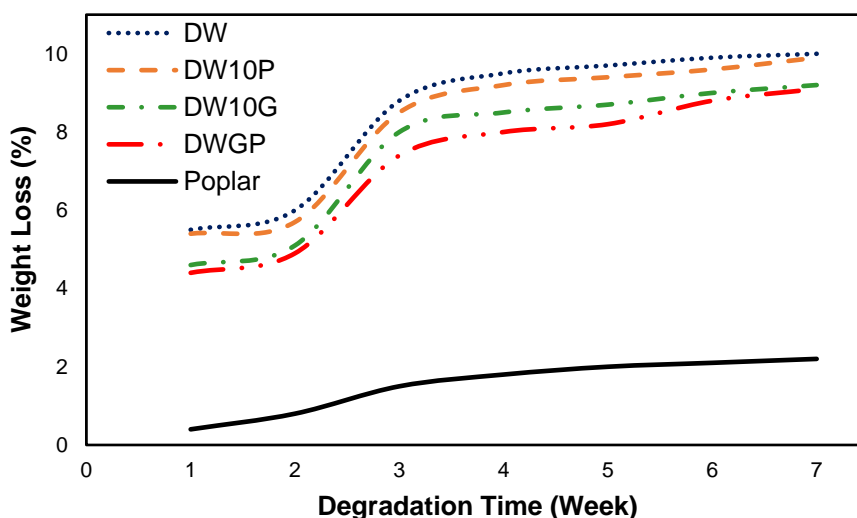
Fig. 10. The weight loss results of some composites and poplar wood control under incubation with *Aspergillus niger* (ASTM G21-09 2009) (adapted from Yue-Hong *et al.* (2015))

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The excellent dispersion capacity of glyoxal is associated with low tensile strength and high water sorption capacity, as is reported in Table 5. Likewise, the aggregation generated by PMDI in the composite, despite the strong bonds that PMDI forms during crosslinking, causes the mechanical properties to be poor (Table 5). The composite that showed better performance during mechanical experiments, water absorption, and resistance tests contained the same amount of glyoxal and PMDI (Table 5). However, the biodegradation seems to be negatively affected by the crosslinking efficiency in these composites. In Fig. 10, the composite with the optimum mechanical properties, DWGP (Table 5), exhibited lower weight loss rates than the other composites studied (Yue-Hong *et al.* 2015).

Table 5. Properties of Soybean Protein-wood Flour Composites and their Weight Loss after 7 d of Incubation with *Aspergillus niger* (ASTM G21-09 2009) (Adapted from Yue-Hong *et al.* (2015))

ID	Crosslinker Composition	Tensile Strength (MPa)	Water Absorption (%)	Water Boiling Test	Weight Loss (%)
SW	No crosslinking	6.21 ± 0.76	143.81 ± 2.60	Failed (35 min)	-
DW	No crosslinking	10.84 ± 0.53	96.81 ± 0.94	Failed (2 min)	10
DW10G	10% G	18.34 ± 0.72	61.54 ± 1.12	Passed	9.2
DW3GP	7.5% G 2.5% P	22.32 ± 1.28	59.02 ± 0.43	Passed	-
DWGP	5% G 5% P	27.23 ± 1.14 (Maximum)	56.99 ± 0.67 (Minimum)	Passed	9.1 (Minimum)
DWG3P	2.5% G 7.5% P	21.74 ± 1.41	62.97 ± 0.39	Passed	-
DW10P	10% P	15.96 ± 0.61	66.52 ± 0.31	Passed	9.9

Note: W, G, and P refer to wood flour, glyoxal, and PMDI, whereas S and D refer to the form of the soybean protein (native or denatured, respectively). The protein (S or D) to wood ratio is 15:85.

Surface Characteristics

Both the bulk properties (crystallinity and water sorption capacity) and the surface characteristics affect the rate of degradation, as the biodegradation process starts at the surface. The importance of surface properties on biodegradation was shown for PLA and PHBV films *via* plasma treatments on the surface (Kim and Masuoka 2009). The biodegradation rate of PLA and PHBV is too slow in nature and human bodies to meet reasonable criteria of biodegradability. Due to the high demand for biopolymers for medical applications, PLA and PHBV hydrophilicity and bioactivity need to be optimized to improve the interaction of these polymers with human cells. According to the results presented by Kim and Masuoka (2009), the employment of CO_2-plasma treatment enhances the biodegradability in aqueous mediums of PLA and PHBV films. After CO_2-plasma treatment, the hydrolysis rates increased tremendously under all pH conditions, except for PLA in a basic pH environment (Fig. 11). Figure 11 shows that the highest weight loss was achieved with basic conditions, followed by acidic and neutral conditions, respectively.
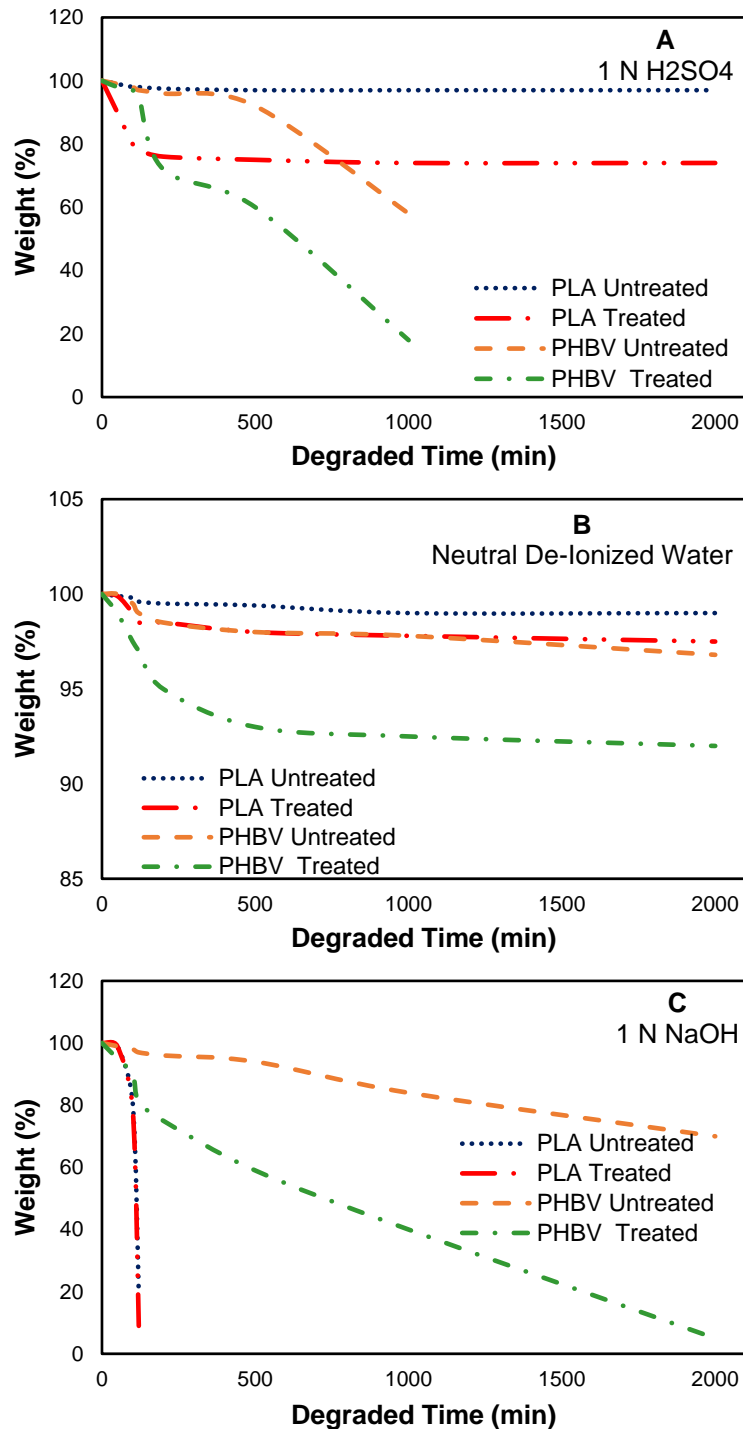
Fig. 11. The weight losses of the untreated and plasma treated PLA and PHBV-copolymer films after degradation for approximately 2000 min in (a) 1 N H2SO4, in (b) neutral de-ionized water, and in (c) 1 N NaOH solutions (adapted from Kim and Masuoka (2009))

Further, the changes in morphology after biodegradation were more obvious in films treated with CO_2-plasma (Fig. 12). This finding is associated with the increased surface roughness of the film. Additionally, the polymer became more hydrophilic by the formation of polar groups and oxidation of the surface (mainly carbonyl and carboxylic

groups), which increased its wettability. Primc *et al.* (2016) also observed a significant increase in the biodegradability of cotton fabrics in soil when subjected to oxygen plasma treatment. This was observed even in the presence of ZNO nanoparticles, which act as antimicrobials and tend to suppress biodegradation.
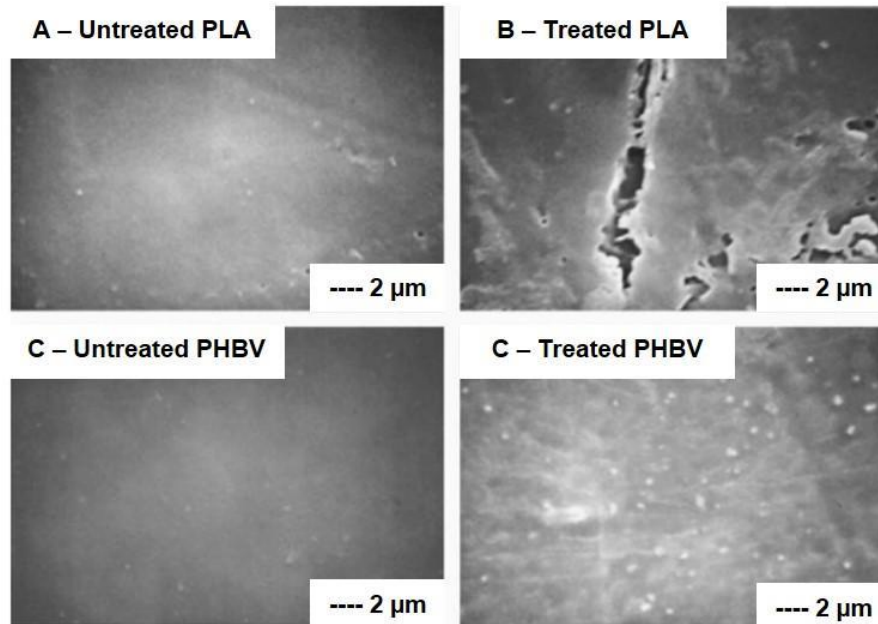
Fig. 12. Untreated and plasma-treated films after hydrolysis in a 1 N H_2SO_4 solution (Kim and Masuoka 2009)

Similarly, Abisegapriyan *et al.* (2018) showed that to increase the biocompatibility and controlled biodegradation of polycaprolactone (PCL) and polycaprolactone /nano-hydroxyapatite (PCL/nHA) electrospun scaffolds, Mg–Zn–Ca thin film metallic glasses were sputtered over their surface. This treatment increased considerably the hydrophilicity and wettability of the surface, and their hydrolysis in phosphate buffered solution (PBS, pH =7.4), at 37 °C for 28 days.

Shibata *et al.* (2016) showed that the biodegradation of a poly(lactic-co-glycolic acid) (PLGA) following irradiation with femtosecond laser pulses depends on the wavelengths used for the pre-treatment. Laser pulses at shorter wavelength dissociated the chemical bonds efficiently increasing the degradation rate at an early stage of degradation. This assessment was done by microscopic observations, water absorption, and mass change measurement. The XPS and FTIR analyses of the PLGA films showed that there was a reduction in the quantity of C–O bonds and C=O bonds following laser irradiation, especially at a wavelength of 400 nm. This surface treatment created craters on the film surface. The degradation also was manifested as an increase in water retention values and the decreased in molecular weight at 400 nm. The authors related the degradation improvement to a decrease in crystallinity and photolysis of chemical bonds in the areas where traces of melting can be observed. The melted site is associated with the presence of an amorphous phase, but no significant changes were observed in the XRD spectra. This indicated a reduction in crystallinity, though this change was only in the surface. This work has potential to control the degradation and sustainability of a structure following its fabrication. In addition, Shibata *et al.* (2017) evaluated the biodegradability of PLGA

irradiated with femtosecond laser pulses at a lower wavelength than the previous study (266 nm) by the measurement of the change in mass of PLGA during water immersion. In this case, the results showed faster water absorption and rapid mass decrease in comparison with the previous findings, confirming that lower wavelengths promote better degradation.

Tanaka *et al.* (2014) showed a method to suppress the biodegradability of PLA during usage and the acceleration of biodegradability after disposal by the introduction of photo-dissociable protecting groups (o-nitro-benzyl alcohol) into the carboxyl end groups and deactivating this protection by ultraviolet irradiation. The modification did not affect the tensile strength of the material and increased the resistance of hydrolytic degradation; however, the deprotection of these groups was successfully and efficiently induced by UV irradiation, accelerating the hydrolysis process.

Similarly, Chaudhary and Vijayakumar (2020) observed an acceleration in the biological degradation of high-density polyethylene (HDPE) by *Cephalosporium* species when treating the surface with nitric acid. This chemical treatment induces the formation of carbonyl and nitro functional groups in HDPE making the surface more susceptible to microorganisms. Anyways, the degradation is not significant compared to a biodegradable material, and there is evidence of deterioration and degradation of this plastic.

Moreover, Chen and Cluver (2010) showed that the biodegradability in soil of naturally colored cottons is affected by the higher amounts of wax that protect those fibers. All the fabrics tested showed severe degradation (loss of fabric strength and fiber structural damage); however, the rate of biodegradation is much slower in naturally colored cottons than in white cotton or conventional dyed cotton. The wax layer in naturally colored cotton is a hydrophobic barrier that microbes and enzymes need to disrupt to degrade the fiber.

Synthetic *versus* Natural Polymers

Natural polymers are synthesized by nature and can be extracted with minimal manufacturing processes, whereas synthetic polymers are derived from non-renewable sources, such as the petroleum oil industry. In general, fibers from fossil-based resources are not biodegradable, whereas natural fibers can be assimilated easily in the environment. Thus, the more the chemical structure of a synthetic polymer approaches the structure of a natural polymer the more susceptible it is to biodegradation. However, not all biopolymers are designed to be similar to naturally occurring polymers (Ashter 2016).

The differences in biodegradability of fabrics made of natural and synthetic fibers at the end of their lifecycle were studied by Li *et al.* (2010) under natural soil aerobic conditions in a laboratory and a large-scale composting facility. The study used 100% cotton jersey fabrics and a polyester shirt from a retail store. All cotton fabrics were scoured and bleached. As a control, cotton fabrics without finishing were used (cotton nf, no finish). Then, softener was added (cotton softener only) followed by the addition of resin (cotton resin). Figure 11A shows that cotton fabrics with softener added were degraded more than any other samples in natural soil under aerobic conditions with moisture present. The softener formulation is composed mainly of surfactants that can promote the attachment of different microorganisms to the surface of the fabric to improve the biodegradation rate in soil. The softener containing cotton also had the highest degradation rate in composting and by enzymatic hydrolysis with cellulase. However, cotton fabrics with resin added had a higher hydrophobicity, which impedes the degradation process in soil, under the action of cellulase during hydrolysis and in composting, relative to the cotton alone (Fig. 13A, Fig. 13B, and Fig. 13C). Nevertheless, polyester showed the lowest degradation rate in all cases (Fig. 13).
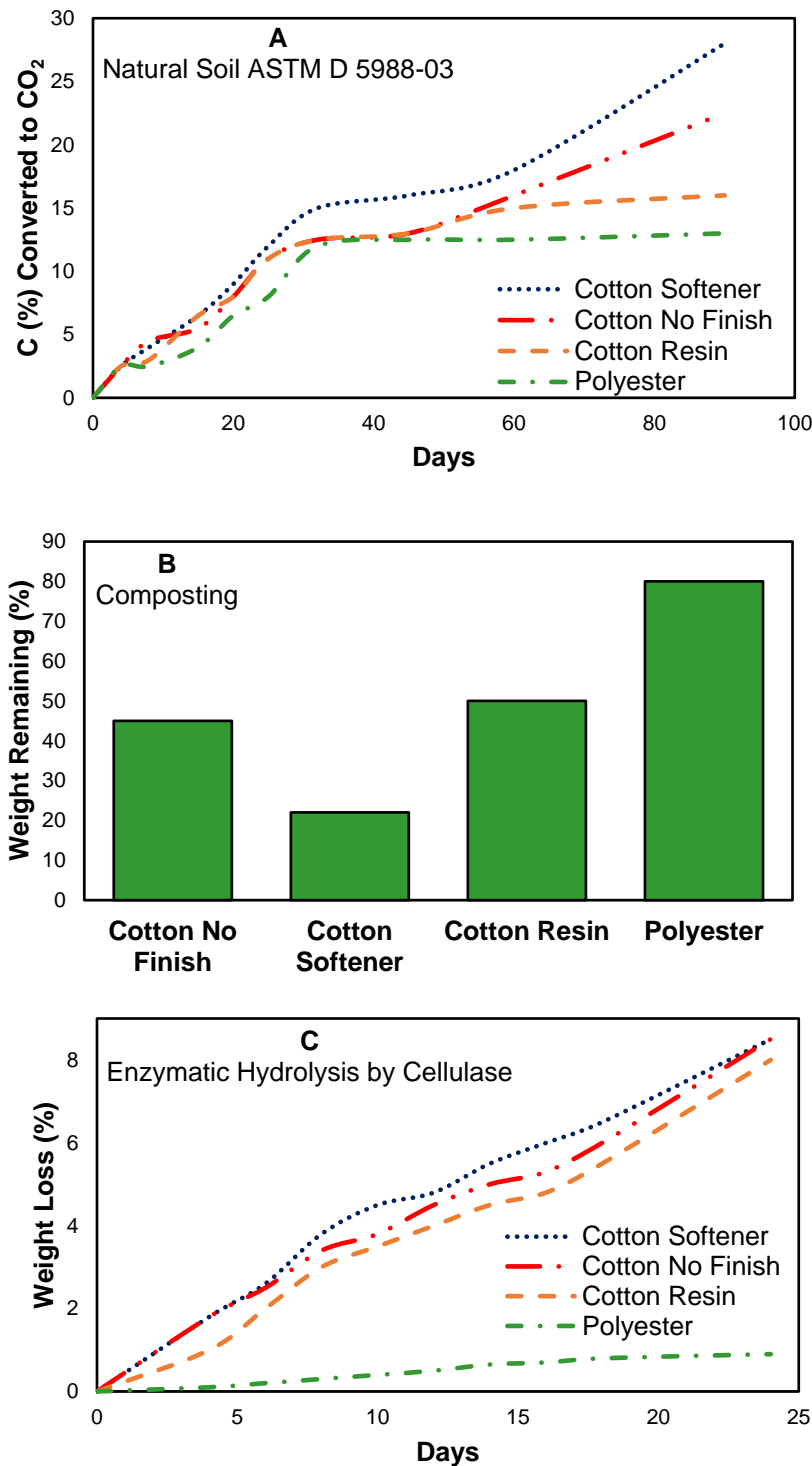
Fig. 13. Biodegradation of fabrics: A - natural soil according to ASTM D 5988-03 (2003), B - composting, and C - enzymatic hydrolysis by cellulase (adapted from Li *et al.* (2010))

Since it is a synthetic polymer, polyester does not have good affinity with the typical microbial communities in the environment and is less susceptible to fragmentation of the structure by hydrolysis due to its high hydrophobicity and low moisture regain. The

damage of the fiber structure within the fabric was more important under composting conditions, high temperature, and in the presence of active microbial communities than under controlled laboratory conditions, room temperature, and soil microbes. In all the tests, the structure of polyester remained intact after degradation. The action of cellulase was less prominent than the complex microbiome in compost and soil for all fabrics. In accordance with these results, it was concluded that cotton fabrics are compostable, while polyester fabrics are not (Li *et al.* 2010).

Table 6. Biodegradation of Textile Yarns in Different Aquatic Environments (Adapted from Zambrano *et al.* (2019, 2020))

Inoculum	30 ppm of Activated Sludge TSS from Neuse River WWTP	Lake Water	Seawater	30 ppm of Activated Sludge TSS from Neuse River WWTP
Reference	Zambrano *et al.* (2019)	Zambrano *et al.* (2020)	Zambrano *et al.* (2020)	Zambrano *et al.* (2020)
Oxygen Measurements	Manual dissolved oxygen measures	Automatic respirometer	Automatic respirometer	Automatic respirometer
Method	ISO 14851 (2005)	ISO 14851 (2019)	ASTM D6691 (2009)	ISO 14851 (2019)
Material Added per Bottle	1000 mg	80 mg	80 mg	80 mg
Liquid Media Added per Bottle	400 mL	500 mL	500 mL	500 mL
Incubation	243 d	35 d	33 d	38 d
Samples	**Biodegradation (%)** Plateau Phase Mean ± Standard Error			
MCC (Microcrystalline Cellulose)	84	81.06 ± 0.24	71.02 ± 0.49	105.42 ± 0.4
100% Cotton Spun Yarns	75.90 ± 12.35	77.22 ± 0.41	48.50 ± 0.21	89.12 ± 0.48
100% Rayon Spun Yarns	62.21 ± 13.29	72.71 ± 0.20	45.87 ± 1.20	87.01 ± 0.58
50/50 Polyester/Cotton Spun Yarns	39.76 ± 3.52	32.84 ± 0.36	14.40 ± 0.48	45.22 ± 0.33
100% Polyester Spun Yarns	4.05 ± 0.75	Not appreciable	4.24 ± 0.42	5.22 ± 0.15
TSS: Total suspended solids				

Similar behavior was observed in an aerobic aquatic environment under the action of activated sludge from a wastewater treatment plant inoculum at low concentration of total suspended solids (TSS), lake water, and seawater as inoculum to simulate aquatic environments (Zambrano *et al.* 2019, 2020). Rayon, cotton, polyester, and 50/50 cotton/polyester spun yarns were incubated in the liquid media in the presence of dissolved oxygen in different environments, and no biodegradation was observed in the polyester, but over 48% biodegradation was achieved by rayon and cotton yarns in all cases (Table 6) (Zambrano *et al.* 2019, 2020). The scanning electron microscopy (SEM) images in Fig.

14 show the progression of biodegradation on the fibers over time in simulated aquatic environments. The polyester fibers remained intact after the experiment, and cotton and rayon fibers completely disintegrated. In general, the biodegradation trend was the same in all the cases: cotton > rayon > polyester/cotton > polyester (Zambrano *et al.* 2019, 2020). Despite the higher crystallinity of the cotton fibers than the rayon fibers, the biodegradation of cotton was slightly higher than that of rayon, and small differences in crystallinity seem to play a less critical role in complex systems (Zambrano *et al.* 2019, 2020).
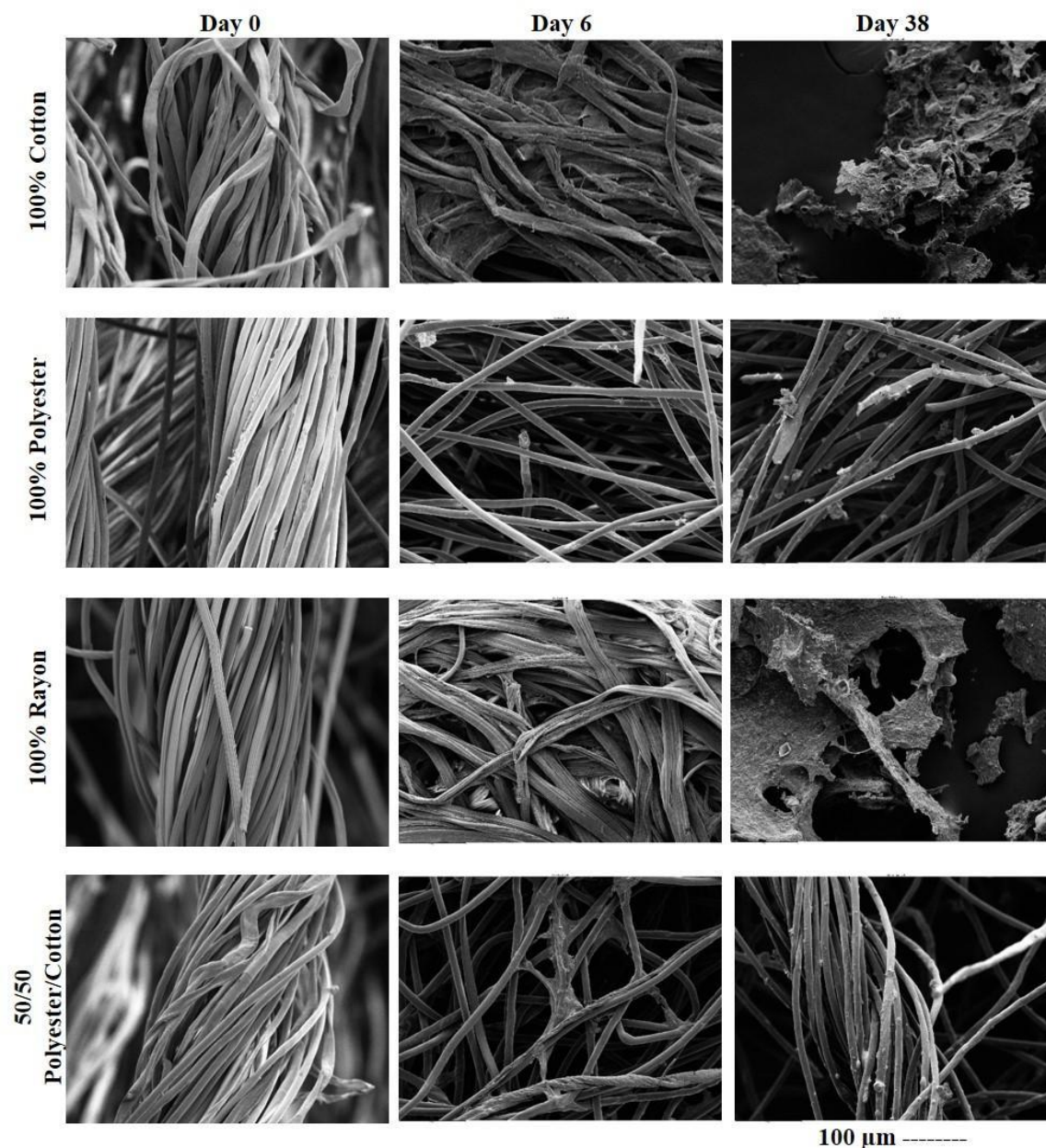

Fig. 14. SEM images of the spun yarns during biodegradation using an inoculum 30 ppm of TSS of activated sludge from the Neuse River WWTP (Zambrano *et al.* 2020)

The study on the influence of the environment on the biodegradation of textile fibers shows that caution must be taken when interpreting biodegradability claims. Since these studies indicate potential behavior rather than absolutes in nature, other factors, such as light, water quality, nutrients, microorganisms, and mechanical actions, could promote or delay biodegradation in the environment (Zambrano *et al.* 2020).

Zambrano *et al.* (2020) also studied the interaction of the fibers during the biodegradation process with the microbiome in the different inoculum systems considered. This study shows the incompatibility of polyester with the bacterial communities in the environment; bacterial communities related to the assimilation and mineralization of complex carbohydrates were promoted with the cellulosic samples, and polyester showed the same behavior as did bottles that lacked degradable materials (Zambrano *et al.* 2020).

As previously mentioned, the main problem with the degradation of synthetic polymers is finding microorganisms and enzymes in the environment having affinity and activity towards these synthetic materials. This is difficult because these materials are not normally synthesized in nature. However, some bacteria can develop the ability to break down synthetic polymers if they are exposed to the appropriate environment. After 5 years of screening microbial communities in a polyethylene terephthalate (PET) bottle-recycling plant in Japan, Yoshida *et al.* (2016) isolated a bacterial species that can use PET as its primary source of food and energy. This bacterium was called *Ideonella sakaiensis* 201-F6 (NCBI Identifier 1547922) due to its similarity with the gene *Ideonella*. Degradation was assessed by evaluating the morphological changes in PET films and measuring its weight loss under the action of the different microbial consortia. The action of this bacterium is noticeably higher than the action of activated sludge, soil, and cellulase reported in Fig. 13 and Table 6 for polyester fabrics, which indicates that this bacteria has a high affinity for PET.
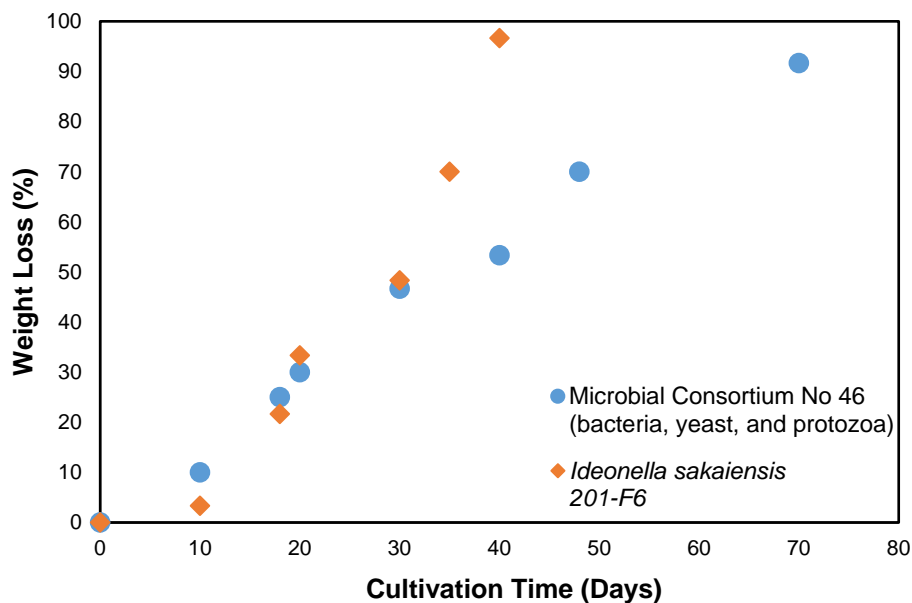
Fig. 15. Weight loss (%) of PET film (60 mg, 20 mm × 15 mm × 0.2 mm) by microbial consortium no. 46 (bacteria, yeast, and protozoa) at 30 °C and *Ideonella sakaiensis* 201-F6 at 30 °C (adapted from Yoshida *et al.* (2016)

The bacteria were isolated from microbial consortium No. 46, and several analyses were done to identify the enzymes responsible for PET degradation and the specific interactions with low-crystallinity (1.9%) PET films (Yoshida *et al.* 2016). The action of the isolated bacteria was more effective in PET degradation than the original microbial consortium (Fig. 15), and the amorphous film was almost fully degraded in 40 d. In addition, *Ideonella sakaiensis* 201-F6 was found to have a high affinity with the PET surface, which is essential to the progression of the enzymes to erode the polymeric matrix.

By studying the behavior *of Ideonella sakaiensis* 201-F6 when grown on PET, it was observed that the enzyme capable of hydrolyzing PET (PETase) produced the reaction intermediate, mono(2-hydroxyethyl) terephthalic acid (MHET), and then the enzyme MHETase hydrolysed MHTE to its environmentally benign monomers, terephthalic acid, and ethylene glycol. These products and intermediates were identified by ^{1}H-NMR spectroscopy and High- performance liquid chromatography (HPLC) (Yoshida *et al.* 2016). PETase and other common PET-degrading enzymes were produced by synthetically expressing their genes in *E. coli*; after purification, the activity of these recombinant proteins was measured in different carbon substrates (aliphatic and aromatic polyesters). PETase was not able to degrade aliphatic polyesters, which illustrates the high selectivity of this enzyme to the PET substrate. In addition, PETase can degrade high crystallinity PET. However, the degradation was lower than the low crystallinity PET. The influence of temperature on the activity of these enzymes was also studied, and they were found to lose their activity above a maximum temperature.

Recently, Austin *et al.* (2018) characterized the structure of PETase and found common features with cutinases and lipases that were improved by mutation to optimize PET degradation, which produced an enzyme with better performance than PETase. Additionally, they found that PETase is also active in polyethylene-2,5-furandicarboxylate (PEF), which is a semi-aromatic emerging biopolyester that could replace PET due to its superior barrier properties. These findings suggest that optimization of the mechanism of PETase activity is a promising solution for PET recycling. Although the development of enzymes with effective action on synthetic polymers may be envisioned as having some potential for specialized composting and plastic recycling, these enzymes are not ever expected to influence the fate of plastic in the environment.

The biodegradation of cotton, jute, linen, and wool woven fabrics and fibers was assessed by soil burial test using microscopic and visual observations, FTIR, and TGA (Arshad *et al.* 2014). In addition, a non-woven of flax fibers supported by PET was also evaluated. Fibers containing cellulose (cotton, jute, and linen) degraded similarly. However, the linen fabric degraded faster due to the low twist of yarns and loose structure, and that allowed a better diffusion of moisture and microbes in the soil. The flax/PET nonwoven showed the lowest degradation, the PET fibers were intact at the end. Only the cellulose in the flax fibers were degraded. In the case of wool, this material is more resistant to the attack of microorganisms. The highly crosslinked structure of keratin, which has high concentration of sulfur crosslinks. The surface of wool is covered by a water-repelling membrane that stops the penetration of microorganisms and enzymes into the fiber. A similar trend was observed by other authors (Peacock 1996; Rijavec 2011; Tomšič *et al.* 2014), wherein protein fibers such as wool, silk, or soy protein fibers are more resistance to biodegradation than cellulosic fibers, and linen was also observed to be less resistant than cotton. Esmaeilzadeh and Rashidi (2018) also showed promising results with linen fabrics in composting conditions, in 90 days this fabric lost 55% of its weight.

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In the case of jute fabrics, their degradation for geotextiles application was evaluated in different soils and water by the changes in tensile strength (Ghosh *et al.* 2019). The jute fabrics were chemically treated with an antimicrobial formulation (butyl isothiazolinone derivative), a combination of an antimicrobial (isothiazolinone) and a water repellent (a fluorocarbon derivative) formula, and blended with polypropylene (PP) to increase their resistance. In this study the characteristics of the soil influence the biodegradation of jute fabrics. Soils with high alkalinity with higher microbial growth showed more biological activity against these fabrics. The combined antimicrobial/water repellent treated jute fabric showed more efficacy protecting the fibers against degradation, followed by the antimicrobial treatment. In addition, the jute-PP blended fabric also showed more stability against soil degradation than the control fabrics, whereas the PP did not show any sign of degradation. Similarly, Ramaswamy (2002) compared the biodegradation of kenaf and PP non-woven by soil burial test; no damage or loss in mechanical properties was observed in the PP. Although the authors claim that blending kenaf fiber with PP improves the biodegradation of the fabric, there is no evidence showing PP degradation, only the kenaf fibers in the blend are disintegrated, helping with the loss of integrity of fabric.

Nam *et al.* (2016) evaluated the disintegration in aerobic conditions in field soil of low-weight nonwoven fabrics made with raw cotton, rayon, polypropylene (PP), and polylactic acid (PLA). The temperature of the soil was between 40 $^{\circ}$ C (summer) and 5 $^{\circ}$ C (winter). The most common raw material for nonwovens, PP, did not disintegrate or show loss of its mechanical properties in the 140 days of the experiment. The PLA fabric was also resistant to soil degradation, but there was a decrease in breaking and burst strength. Despite some changes in chemical structure and surface appearance, no weight loss was observed in PP and PLA nonwovens. In contrast, cotton and rayon disintegrated completely in 30 days; however, rayon had a slightly faster disintegration than raw cotton due to the differences in crystallinity already discussed in this review. Similar results were reported by Warnock (1997), showing that cotton nonwovens are susceptible to soil biodegradation, while PET and PP does not suffer changes. This work also showed that the disintegration of the non-woven fabrics depends on the type of soil used for the incubation.

Sülar and Devrim (2019) also observed the difference between natural and synthetic polymers in the biodegradation of fabrics by soil burial test. All cellulosic fabrics (cotton, viscose, modal, and Tencel or Lyocell) tested disintegrated significantly during the 4 months of the experiment. Around 90% weight loss was observed in cotton, viscose, and modal, whereas Tencel fabrics only lost 60% of their weight. However, the synthetic fabrics (polyethylene teraphtalate, PET, and polyacrylonitrile, PAN) did not show any deterioration. Only PLA fabrics lost some weigh (3%), but no morphological or chemical changes were observed. Cellulosic fabrics were greatly colonized by bacteria and fungi, whereas synthetic fibers did not support the growth of the microorganisms in soil. In this study, a slight resistance was observed for biodegradation from Tencel fabrics; this might be due to the higher thickness of this fabric in comparison to the other cellulosic fabrics tested. However, Warnock (2011) observed a similar behavior when comparing the biodegradation of cellulosic fabrics (cotton, rayon, and Lyocell) by a soil burial test. In general, the main difference between regenerated cellulose fibers is the processing method. Lyocell fibers are produced by dissolving wood pulp with N-methyl-morpholine-N-oxide, and the spun fibers are usually stronger than Modal and Viscose Rayon due to post-processing by drawing. For that reason, Lyocell is highly crystalline with great strength properties, while Rayon, as already mention, has lower crystallinity than cotton. In these

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studies, no crystallinity data is presented; however, Warnock (2011) tested Lyocell fabrics with superior tensile and tear strength than cotton, which suggest a higher crystallinity and orientation of the fibers that limits the migration of moisture and enzymes in the structure.

There is not much data in the literature about anaerobic biodegradation in landfills of fabrics, however Zheng *et al.* (2013) classified natural fabrics such as cotton as biodegradable in landfills whereas synthetic fabrics made of acrylic and polyurethane fibers were recalcitrant under this condition based on the biochemical methane potential.

Influence of a Biodegradable Polymer in a Synthetic Polymer Matrix

There have been efforts to increase the degradability of materials by blending biodegradable polymers with synthetic polymers. Using radiolabeled carbon measurements, the biodegradation of cellulose acetate with a high degree of substitution (2.5) was shown to improve when blended with biodegradable cellulose acetate (DS = 2) and a plasticizer (Buchanan *et al.* 1996). Similarly, in blends of cellulose acetate (DS = 2.5) and cotton fibers, the synergy between the two fibers during the aquatic aerobic biodegradation process using activated sludge from a municipal WWTP seems to induce an increased production of cellulases and esterases, which makes the biodegradability of the blends superior to that of the individual materials (Suh *et al.* 1996).

In addition, the influence of cotton fibers on the degradation process in the soil of composites prepared from a commercial thermoplastic starch-blend (Mater-Bi KE) was studied (Moriana *et al.* 2010). During accelerated soil burial testing, the polymeric matrix and the reinforced composite showed a decrease in the C=O (carbonyl of ester group) of the synthetic component and a decrease in the proportion of C=O (polyester) to C-O-C (polysaccharides) signals by FTIR. In addition, the crystallinity index decreased for the synthetic polymeric matrix and the reinforced composite as the degradation time increased, and the change was more important for the reinforced composite. There was also more damage to the surface of the reinforced composite. These results suggest that the presence of cotton fibers enhanced and promoted the biodegradation of the synthetic portion of the blended matrix due to the disruption of the polymeric matrix and the increase in the available surface for microbial attack and free volume that become available once the biodegradable portion is degraded.

This behavior has been also reported elsewhere, and biodegradable materials are known to be able to induce degradation in the synthetic portion of the blend; however, this has not been fully demonstrated, and the mechanisms need to be better understood (Leja and Lewandowicz 2010).

For example, several researchers have claimed that the addition of starch to a synthetic polymeric matrix such as polyethylene or propylene enhances the biodegradability of the final composite, but only the disintegration or the mechanical properties of the material were measured in their studies (Imam *et al.* 1992; Arévalo-Niño *et al.* 1996; Dave *et al.* 1997; Thakore *et al.* 2001; Park *et al.* 2002; Datta and Halder 2018; Ndon *et al.* 2018). The addition of starch in a polymeric matrix increases the hydrophilicity of the material. Then, when the material is exposed to different environments, the structure is disrupted faster, and the mechanical properties decrease faster or to a greater extent than the synthetic polymer alone (Imam *et al.* 1992; Arévalo-Niño *et al.* 1996; Dave *et al.* 1997; Thakore *et al.* 2001; Park *et al.* 2002; Datta and Halder 2018; Ndon *et al.* 2018). Thus, the disintegration step in the biodegradation process is accelerated by the disruption of the polymeric matrix due to the fast degradation of the starch in the blend, but that does not imply that the synthetic portion is assimilated by microorganisms. Similarly, the addition

of cellulose whiskers from bleached sugar cane bagasse kraft pulp in natural rubber nanocomposite films enhances the thermomechanical properties of the films but reduces their resistance to water vapor permeation and accelerates disintegration in soil (Bras *et al.* 2010).

The claim of biodegradability enhancement just by blending synthetic and natural materials has also been made by Singh *et al.* (2009) in grafted films of polystyrene (PS) with gelatin (50/50). However, in the soil biodegradation and a microbial degradation by *Pseudomonas fluorescens* data (weight loss), it can be appreciated that only the gelatin in the mix was degraded, no more than 50% degradation was achieved. Similarly, Usman *et al.* (2020) showed an enhancement in the degradation of recycled PP when preparing composites with groundnut shell powder; however, the weight loss shown is mainly related to the biodegradable part and not the synthetic polymer. On the contrary, Karimi and Biria (2019) reported evidence of degradation of low density polyethylene (LDPE) when blending with starch. The weight reduction in the presence of α-amylase aqueous solution after 31 days of incubation was higher (48%) than the initial starch amount (25%) in the samples. In the study, evidence of the fragmentation of the LDPE polymer backbone and its branches was presented. An increase of crystallinity by DSC was shown, as well as a reduction on intensity of the related FT-IR peaks. In addition, a reduction in the percentage of carbon atoms in the blend by energy dispersive X-ray spectroscopy (EDXS), a significant decrease in the molecular weight, and viscosity of LDPE was observed. Despite the mechanism is not well understood, there is a co-metabolic process wherein the complex starch-amylase or a product of their reaction influences the PE breakdown. With respect to LDPE, an important improvement in mineralization in soil and aquatic media has been observed when adding pro-oxidant/pro-degradant iron and cobalt stearates to LDPE films due to combination of abiotic and biotic factors such as temperature, UV light, oxygen, and the action of microorganisms (Kérouani *et al.* 2018). A similar behavior has been observed in PP when adding an organic pro-degradant additive consisting in benzoin/potassium salt free of transition metals (Montagna *et al.* 2014, 2015).

Blending lignin with polyolefin plastics under the action of lignin-degrading microorganisms or enzymes could result in partial degradation of the synthetic matrix. The lignin portion in the composite acts as an initiator of radical reactions, and lignin-degrading microorganisms produce hydroxyl radicals that result in oxidative degradation of the polyolefin, such as polyethylene and polypropylene, which is also enhanced by the ultraviolet light in the environment (Mikulášová and Košíková 1999; Mikuláová *et al.* 2001).

Therefore, the best approach in blended polymers to avoid the formation of persistent microplastics in the environment is to adjust the properties of biodegradable polymers, such as PLA, polyvinyl alcohol (PVA), PCL, and others, for the desired application by the addition of natural components, such as starch, lignocellulosic fibers, hemicellulose, chitosan, CNC (cellulose nanocrystals), pectin, and proteins, that increase the disintegration step during the biodegradation process (Muniyasamy *et al.* 2013; Dharmalingam *et al.* 2015; Makhijani *et al.* 2015; Yuksekkaya *et al.* 2016; Stoleru *et al.* 2017, 2020; Vasile *et al.* 2018; Kalita *et al.* 2019; Bulatović *et al.* 2019; Tanjung *et al.* 2020; Kuciel *et al.* 2020; Liao *et al.* 2020; Nevoralová *et al.* 2020).

Antimicrobial Finishes and Additives

The biodeterioration of textiles during wear, use, storage, and aging is problematic, especially in natural organic fibers, because it can cause strength loss, elongation,

discoloration, unpleasant odors, and changes in appearance at early stages of the textile life cycle (Montegut *et al.* 1991; Szostak-Kotowa 2004). There are different ways to protect the textile materials against the attack of the microbial organisms in the environment, such as the control of the environmental conditions to inhibit microbial growth (temperature, humidity, and pH), the addition of antimicrobial agents (biocides or hygienic finishes) during the textile manufacturing process that inhibit the growth or kill a diverse group of microorganisms, the chemical modification of the fibers or fabrics *via* acetylation, the application of water or oil repellent, and durable press finishes to make the fabrics less susceptible to microbial attack (Montegut *et al.* 1991; Szostak-Kotowa 2004). These treatments are crucial for historical textiles and to ensure the durability of clothing, but they could cause problems during material disposal.

The decrease in biodeterioration of the finished cellulose fibers and fabrics has demonstrated the effectiveness of some antimicrobial agents such as silver (Ag) and titanium dioxide (TiO_2) nanoparticles (Klemenčič *et al.* 2010; Tomšič *et al.* 2011; Lazic *et al.* 2015; Milosevic *et al.* 2017). In these studies, the biodeterioration of the cellulose fabrics has been assessed mainly by changes in morphology, color, tensile strength, and degree of polymerization after soil burial testing (Klemenčič *et al.* 2010; Tomšič *et al.* 2011; Lazic *et al.* 2015; Milosevic *et al.* 2017).

Klemenčič *et al.* (2010) studied the influence of different chemical forms of silver on the biodegradability of cellulose fibers. The silver finishes tested were nanoparticles of silver in elemental form (average particle size of 30 nm), a dispersion of AgCl, and colloidal silver at different concentrations. Their antimicrobial activity depends on the release of Ag^+ cations by oxidation in the presence of water and oxygen from the surface of the fibers. Both forms of silver, nanoparticles and Ag^+ cations, interact with microorganisms by attraction, and they can also penetrate the cell wall. Inside the cell, they bind to the thiol group of enzymes or nucleic acids, inhibiting the cellular metabolism and eventually causing the death of the microorganisms (Klemenčič *et al.* 2010). In this case, only AgCl and the colloidal silver released enough Ag^+ in the presence of the soil moisture to protect the fibers against biodegradation. These results showed that the rate and degree of biodegradation of these fibers depend on the chemical form and particle size of the silver antimicrobial finishing.

Similarly, Tomšič *et al.* (2011) compared the antimicrobial activity of dispersions of colloidal silver (Ag) and 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (Si-QAC) on a 100% cotton fabric and a blended fabric (cotton and polyester). These agents have different mechanisms of action against microbes; Ag is a leaching agent that is physically bonded to the fabric, whereas Si-QAC acts as a bio-barrier chemically bonded to the fabric. The biodeterioration of the polyester in the blend is not influenced by the presence of these antimicrobial agents, and the fibers remain undamaged due to their chemical nature, morphology, and biological resistance. However, in the case of cotton, only Ag was able to protect the fibers against microbial attack during the soil burial test at longer exposure times, regardless of the concentration.

The influence of Ag and TiO_2 nanoparticles on the biodegradation of cotton fabrics was studied by Lazic *et al.* (2015). Not only the disintegration of the fabrics by soil burial test was evaluated but also the rate of biodegradation of these fabrics by the measurement of CO_2 production during the aerobic biodegradation in soil as per ASTM D5988-03 (2003). The effects were measured of these antimicrobial agents during enzymatic hydrolysis by cellulase, and the microbial activity of the soil (dehydrogenase activity) also was measured. Both agents were found to inhibit the biodegradation of the cotton fabrics

and the microbial activity of the soil used during this study, but TiO_2 nanoparticles had a greater effect (Table 7). It seems TiO_2 can alter the bacterial composition and diversity in soil. In addition, TiO_2 increased the hydrophobicity of the cotton fabrics, which is a major factor hindering biodegradation. Recent studies showed that TiO_2 nanoparticles and 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride did not hinder the biodegradation of natural fabrics (cotton, wool, and silk) fabrics; however these studies are only showing a visual inspection of the fabric or changes in color, no quantitative data is presented for disintegration (weight loss) and mineralization (CO_2 production) (Tomšič *et al.* 2014; Marković *et al.* 2019).

Table 7. Biodegradability of Cellulose Fabrics Impregnated with Ag and TiO_2 Nanoparticles from Colloidal Solutions (Adapted from Lazić *et al.* (2015))

Test	Variable	Untreated Cotton Fabric	Ag Impregnated Cotton Fabrics		TiO$_2$ Impregnated Cotton Fabrics	
			Ag10 25.9 ± 2.5 µg Ag/g Fabric	**Ag50x2** 209.6 ± 17.5 µg Ag/g Fabric	**TiO$_2$0.05** 3.59 ± 0.12 mg TiO$_2$/g Fabric	**TiO$_2$0.1x2** 11.18 ± 0.71 mg TiO$_2$/g Fabric
Aerobic biodegradation in soil, 3 months at 18 °C as per ASTM D5988-03 (2003)	% C Converted to CO$_2$	No data	17%	14%	18%	11%
Dehydrogenase activity of the microorganisms in soil, after 3 months of aerobic biodegradation in soil as per ASTM D5988-03 (2003)	a (mg/g*h)	110	42	35	20	12
Soil burial test, 95 d	Weight loss (%)	50%	47.5%	37.5%	27%	17.5%
Enzymatic hydrolysis with cellulase, 14 d at 50 °C	Weight loss (%)	55%	52.5%	47.5%	25%	12.5%

In addition, Milosevic *et al.* (2017) performed a similar study on cotton and cotton/polyester fabrics impregnated with Ag/TiO_2 nanoparticles that confirms the previous findings that antimicrobial agents hinder the biodegradation in soil of cellulose fabrics.

Bras *et al.* (2017) also showed that antimicrobial treatments significantly decrease the biodegradation of cotton and polyester/cotton (50/50) blended woven fabrics in a soil burial test (ISO 11721). In this case, the fabrics were pre-treated with oxygen plasma, an organofunctional trialkoxysilane was applied for the creation of a silica matrix, and in situ synthesis of silver chloride was performed. The plasma treatment increased the sorption capacity of the antimicrobial treatment, making the treatment more effective. However, it

is important to mention that the plasma treatment (only) increased the degree of fiber biodegradation compared to untreated samples due to the increase in hydrophilicity of the fibers. The biodegradability was tested by changes in color, visual observations, and IR.

SUMMARY

Much is known about biodegradation of polymers, and several of the controlling parameters have been identified in this review, but there is still more to learn. Most of the polymer biodegradation literature is focused on the degradation under composting and soil conditions, and several recent studies have focused on aquatic environments. In addition, a complete evaluation of the mineralization of the fragments generated during the disintegration process is needed. Most of the degradation measurements reported are representative of the disintegration step during the mechanism of biodegradation: weight loss, TOC formation, changes in mechanical properties, *etc*. With these measurements alone, it is not possible to assess whether or not there is a buildup of the smaller fragments that could be contributing to the microplastics accumulation in the environment. In addition, several studies that show biomaterials suitable for different applications claim biodegradability without testing or reporting the conditions favorable (temperature, pH, soil, composting, liquid media, *etc*.) and the timeframe for the biodegradation (Honma *et al.* 2003; Torres-Giner *et al.* 2008; Zhang *et al.* 2012; Binoj *et al.* 2016).

According to this review, there are additives and treatments used to improve the properties in textiles that could reduce their biodegradability. Thus, there is a trade-off between biodegradation and performance in use that needs to be balanced according to the application to meet the requirements during the life cycle of the textile material and the desired biodegradability after disposal. The determination and control of this balance is a critical research challenge.

A consistent observation from the literature is that, in materials made with polymers of similar chemical structure, higher crystallinity is more resistant to degradation (Table 8). Amorphous regions degrade more quickly than crystalline regions due to the higher free volume, which increases the rates of diffusion of water, chemicals, and enzymes within the polymeric matrix. Diffusion rates affect the degradation process in combination with other parameters such as the primary chemical structure, moisture diffusion, hydrophilicity/ hydrophobicity balance, morphology, and surface characteristics. However, crystallinity becomes less important when comparing materials made with polymers having different chemical structures, such as cellulose and polyester, or a series of similar polymers with different substituents and degrees of substitution. In those cases, the most important factors are the steric interference by the groups of substitution, the hydrophilicity and moisture diffusion of the structure, and how easily these materials can be hydrolyzed and swollen by water to allow enough space in the structure for enzymatic attack (Table 8). Another important factor is the microbiome. The microorganisms are specific, and they are better at degrading materials typically present in their environment, which contributes to the recalcitrance of some synthetic materials. Under the appropriate conditions, microorganisms can develop the ability to use synthetic polymers as the main source of carbon and energy. Designing new enzymes to degrade polymers is very beneficial. However, the development of these enzymes is slow, and their efficient implementation in the recycling industry is challenging, as it requires specific processing conditions and is to date not feasible.

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Table 8. Determinant Factors That Influence the Biodegradability of Polymeric Materials

Type of Materials		Similar Chemical Structure	Different Chemical Structure
Determinant Factors	Increase in biodegradability	Hydrophilicity Moisture diffusion Lower molecular weight	Hydrophilicity Moisture diffusion
	Decrease in biodegradability	Crystallinity High degree of substitution Crosslinking	Crosslinking
	All	Environment (temperature, humidity, and the presence of O₂); Microorganisms and enzymes affinity; Type of polymer (natural *vs.* synthetic)	

ACKNOWLEDGMENTS

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