Chapter

ASSESSMENT OF POLYMER-BASED NANOCOMPOSITES BIODEGRADABILITY

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ABSTRACT

The management of solid waste is a growing concern in many countries. Municipal solid waste is a major component of the total solid waste generated by society, and the composting of municipal solid waste has gained some attention even though a composting treatment for it is not yet widespread. It may not be realistic to replace large portions of these plastics with biodegradable materials, and it may be more important to separate plastics unsuitable for the composting process at the generating spots. However, for food packaging, there is still a great deal of interest in using biodegradable plastics that are difficult to sort at the generation spots. Under these circumstances, nanocomposites of biodegradable polymers as matrix and nanoparticles, that can be degraded along with organic wastes during composting could be a solution.

Therefore, this chapter aims to give an overview on the biodegradability studies of bio-nanocomposites. It will focus on different polymers, nanocomposites containing different clay types and inorganic particles exposed under different environments.

Keywords: Bio-nanocomposites; Biodegradability; TPS, PLA, PCL, PHA

INTRODUCTION

Since the industrial revolution, in particularly after World War II, the breakthrough in materials research increased fast, and resulted in the wide use of non-conventional materials, such as, polymers, metals, semi-conductors and agricultural chemicals (e.g., pesticides and fertilizers) [1]. Fossil fuel based plastics have brought many benefits to human life and

became to be used in different applications, including textiles, electronics, healthcare products, toys and packaging [2]. What was attributed to their high specific strength, lightness, resistance to water and water-borne microorganisms, along with their long durability [3]. The production of these materials, to meet the demands of a growing population, exceeded 260 billion kilograms of plastic in 2009, which resulted in regional and global environmental problems ranging from air, water and soil pollution, to climate changes [2].

Nowadays society has become increasingly aware of more sustainable paths towards environmental preservation [4]. The principle of sustainability is based on the assumption that a good could be produced or an activity carried out without limiting the opportunities of the future generations to produce that good or carry on that activity [5]. Sustainability therefore depends on minimizing environmental pollution and reusing, recycling or transforming each of the components of a product or by-products of an activity. Given the large quantities of plastics that are currently used, they are limited both by their "source", since petroleum is currently the main feedstock to produce plastics, and by their "fate"; the high costs related to the correct collection, removal, disposa, and recycling. Used plastics have resulted in their uncontrolled disposal in landfills, with consequent production of a wide range of harmful chemicals [4, 5]. For these reasons, renewability and biodegradability have become key criteria for sustainable plastic production and utilization [5]. Similarly to other areas, the plastics industry started looking for alternative sources of raw materials and a research on the development of biodegradable polymers began [6, 7].

Several definitions of biopolymers, biodegradable polymers, biocomposites and other bio-words have been suggested during de last years [8]. One of the proposed definition for biopolymers involved materials consisting of units that are entirely or in part derived from biomass (e.g. materials with biological origin). Among biopolymers it is necessary to distinguish natural polymers, which are defined as polymeric materials obtained from nature, e.g. cellulose, starch, proteins. Therefore, all natural polymers can be considered as biopolymers, but not all biopolymers are natural polymers [8, 9].

The American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO) define degradable plastics as those that undergo significant changes in chemical structure under specific environmental conditions. These changes result in a loss of physical and mechanical properties, measured by standard methods [10]. The definition of biodegradable plastics is not consistent. In fact, several different designations have been published by national and international standardization bodies and organizations (Table 1) [11].

According to ASTM, biodegradable means that the material can undergo decomposition into carbon dioxide, methane, water, inorganic compounds or biomass, in which the predominant mechanism is the enzymatic action of microorganisms that can be measured by standard tests, over a specific period of time, reflecting available disposal conditions [5, 12]. ISO definition, request only a chemical change of material (e.g. oxidation). CEN and DIN, in contrast, demand the conversion of plastics into microbial metabolic products. Other definitions adapted from the area of degradation of low molecular-weight chemicals, such as inherent biodegradability or ultimate biodegradability, can also be applied to polymers [11]. Biodegradable polymers are then defined as those that undergo microbially induced chain scission leading to the mineralization, with specific conditions of pH, humidity, oxygenation and the presence of some metals [13].

Table 1. Definitions of biodegradable plastics used by different organizations
(from Müller, 2005 [11])

DIN FNK 103.2	Biodegradable plastics[1] A plastic material is called biodegradable if all its organic compounds undergo a complete biodegradation process. Environmental conditions and rates of biodegradation are to determined vy standardized test methods. Biodegradation[3] Biodegradation is a process, caused by biological activity, which leads under change of the chemical structure to naturally occurring metabolic products.
ASTM sub-committee D20-96	Biodegradable plastics[1] A degradable plastic in which the degradation results from the action of naturally occurring microorganism such as bacteria, fungi and algae.
Japonese Biodegradable Plastics Society	Biodegradable plastics[1] Polymeric materials, which are change into lower molecular weight compounds where at least one step in the degradation process is though metabolism in the presence of naturally occurring organisms.
ISO 472	Biodegradable plastics[1] A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standards test methods appropriate to the plastic and the application in a period of time that determine its classification. The change in the chemical structure results from the action of naturally occurring microorganisms.
CEN	Biodegradable plastics[1] A degradable material in which the degradation results from the action of microorganisms and ultimately the material is converted to water, carbon dioxide and/or methane and a new cell biomass. Biodegradation[2] Biodegradation is a degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of a material. Inherent biodegradability[2] The potential of a material to be biodegraded, established under laboratory conditions. Ultimate biodegradability[2] The breakdown of an organic chemical compound by microorganisms in the presence of oxygen to biodegradability carbon dioxide, water and mineral salts of any other elements present (mineralization) and new biomass or in the absence of oxygen to carbon dioxide, methane, mineral salts and new biomass. Compostability[2] Compostability is a property of a packaging to be biodegraded in a composting process. To claim compostability it must have been demonstrated that a packaging can be biodegraded in a composting system as can be shown by standard methods. The end-product must meet the relevant compost quality criteria.

[1]Pagga (1998) [14]; [2]Calmon-Decriaud and co-worker (1998) [15]; [3]DIN V 94900 (1998).

A vast number of biodegradable polymers or their monomers are chemically synthesized or biosynthesized during the growth cycles of all organisms and they can be classified in four different categories, depending on the polymers origin [16]:

- polymers from biomass such as the agro-polymers from agro-resources;
- polymers obtained by microbial production;
- polymers chemically synthesized using monomers obtained from agro-resources;
- polymers whose monomers are obtained by chemical synthesis from fossil resources.

BIONANOCOMPOSITES

The non-biodegradable and non-renewable nature of plastics has led scientist to research for biopolymers derived from renewable sources as potential alternatives for conventional plastic materials. Biopolymers include plant-derived materials (starch, cellulose, other polysaccharides, proteins), animal products (proteins, polysaccharides), microbial products (polyhydroxybutyrate) and polymers synthesized chemically from naturally derived monomers (polylactic acid) [17]. Nonetheless, when compared to conventional polymers, biopolymers have some drawbacks, such as relatively poor mechanical and barrier properties, processability and thermal stability, which limit its industrial application. Recently, a new class of materials, bio-nanocomposites, has proven to be a promising option to improve the properties of biopolymers [18]. Formed by combination of polymers coming from natural resources (biopolymers) or synthetic biofunctional polymers and with fillers (e.g. natural or modified clays or lignocellulose fibres) that having at least one dimension in the nanometric range (1 to 100nm), bio-nanocomposites combine the intrinsic properties of natural polymers, as biocompatibility and biodegradability, with the typical properties of nanoparticles, such as mechanical properties, high thermal stability and barrier properties. Then, these novel environmental-friendly materials open a wide range of biodegradable polymers applications, with potential perspectives for medicine, coatings, automotive, packaging, etc [19].

Concerning food quality and shelf life, great improvements have been achieved followed by reducing of plastic waste, which stimulates the exploration of new bio-nanocomposites for packaging [20, 21]. Nevertheless, the improvements on mechanical and thermal properties make this materails very attractive in the automotive and construction industries [22]. The balance between mechanical properties, functionalities, and biocompatibility make bionanocomposites very interesting for applications in the biomedical field [23].

NANOFILLERS

The idea of developing a multiple-phase nanocomposites to improve properties and materials characteristics is not recent. This has been a common practice since civilization started and humanity began to produce more efficient materials for specific purposes. Examples of man-made nancomposites can be found in green bodies of china ceramics, blue Maya pigments and some prehistoric frescos. Compared with conventional fillers, nanometer-size fillers have a huge interfacial area per volume of particles, large number density of particles per particle volume, and particle-particle correlation arising at low volume fraction [20, 24-26].

Nanofiller is the designation attributed to a material that has at least one componemt with dimensions less than 100 nm. Based on its dimensions they can be divided in four different types: (i) zero-dimension nanoparticles (all dimensions <100 nm); (ii) one-dimensional nanofibers, such as carbon nanotubes (CNTs) (diameter <100 nm); (iii) two-dimensional layered silicates such as clays (thickness <100 nm); (iv) three-dimensional interpenetrating networks, such as polyhedral oligomeric silsesquioxanes (POSSs) (all dimensions <100 nm) [20]. The nanofiller selection is made according the application requirements. Such as, to

improve the barrier properties, two-dimension nanofillers are preferred. Nevertheless, to improve optical and electrical properties, spherical nanoparticles are more suitable, while for rigidity and strength, fiber-like nanofillers are preferred. Ray, divided the most common nanofillers (silicates, CNTs, POSSs, metals, metal-oxide ceramics, and metal nonoxide ceramics) into four different groups, metals, metal-oxide ceramics, silicates and non-oxide ceramics, describing the potential inherent characteristics for each one (Figure 1) [20].
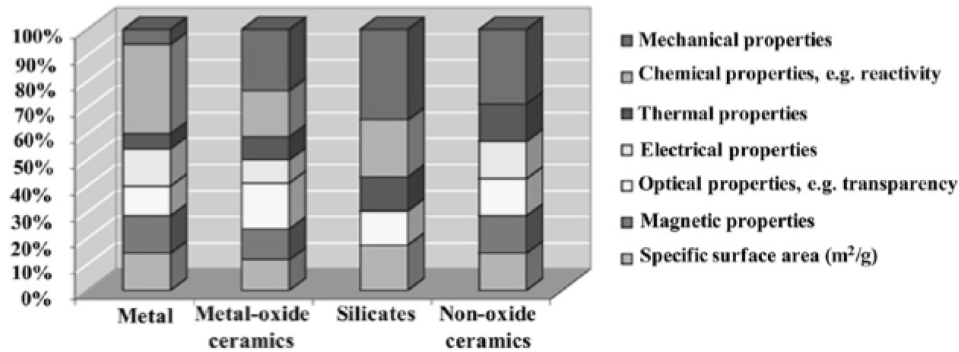

Figure 1. Properties of the most commonly used nanofillers for polymer nanocomposites (from Ray [20]).

PREPARATION METHODS

During nanocomposites preparation, the main goal is to achieve a nanolevel dispersion, since it increases the interfacial or surface area for polymer-filler interaction, exploiting unique synergisms between the combined materials [27]. Polymeric bio-nanocomposites can be prepared by four main routes (Figure 2): (i) solution method, starting from the dissolution of polymers in adequate solvent with nanoscale particles together with evaporation of solvent or precipitation; (ii) melt-mixing, involving the direct melt-mixing of polymers with nanofillers; (iii) in situ polymerization, where the nanofillers are first dispersed in liquid monomer or monomer solution, followed by polymerization in presence of nanoscale particles; and (iv) template synthesis, where polymers is used as template and the nanofillers are synthesized from precursor solution [28, 29].
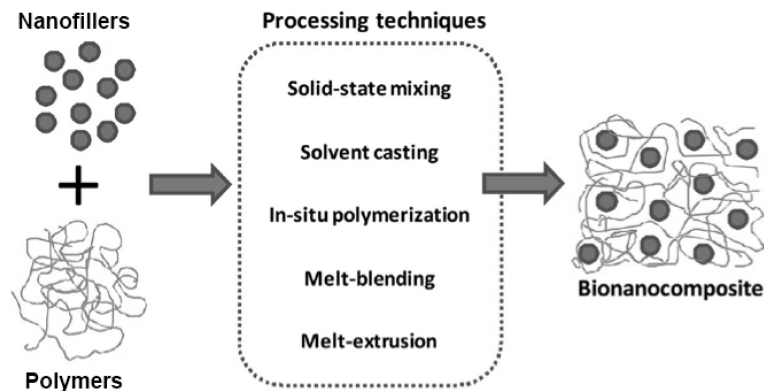
Figure 2. Methods generally used for polymer bio-nanocomposites preparation.

BIO-NANOCOMPOSITES BIODEGRADABILITY

Biodegradation can follow one or several mechanisms, such as: chemical hydrolysis, microbial, enzymatic and thermal degradation. Nonetheless, following Bikiaris, the majority of polyesters is degraded by enzymes as lipases, which are only active after conformational changes induced by adsorptive binding at the substrate surface [27]. This fact is due to the size of extracellular enzymes that are too large to penetrate deeply into the polymeric material, being a surface erosion process. Other drawback is related to lower water solubility and the size of the polymer molecules, which turn the microorganisms unable to transport the polymeric material directly into the cells where most biochemical processes take place [27, 30]. Then, microorganisms first excrete extra-cellular enzymes that depolymerize polymers outside the cells until generate water-soluble intermediates, which can be transported into the microorganisms and fed into the appropriate metabolic pathway(s) (Figure 3) [11].
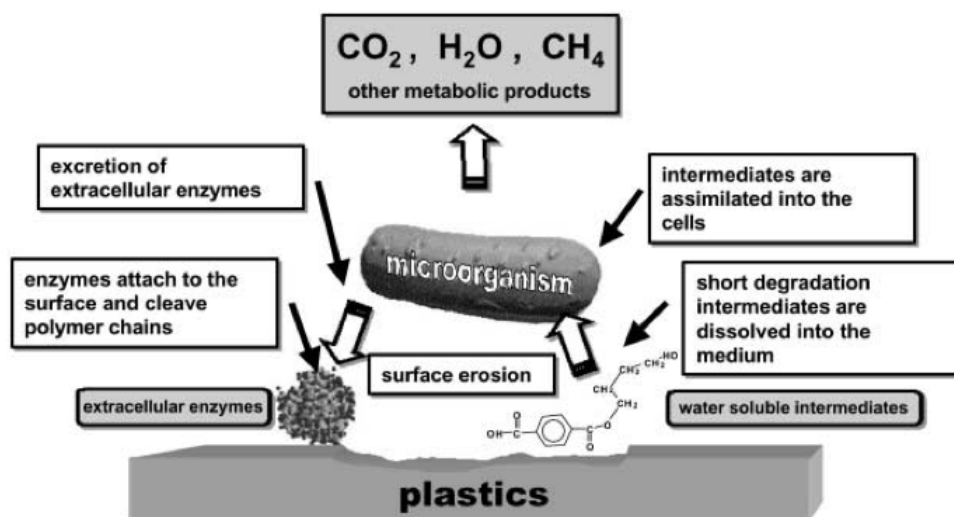

Figure 3. General mechanism of plastics biodegradation (from Müller [11]).

Plastic materials biodegradability can be performed in different compost media (liquid, inert or compost medium). Compostability, where biodegradability is assessed in a compost medium, is one of the most used methods (see Table 2 and Table 3). However, depending of the standard to be followed (ASTM, EN, ISO) different composting conditions (humidity, temperature cycle) can be used to determined the level of biodegradability. This makes difficult or impossible the comparasion of results obtained from different satandards methods [31, 32].

ASSESSMENT METHODS - STANDARDS

The biological effect of microorganisms on man-made materials and vice versa has been assessed by several methods for many years. Nevertheless, the increase concerne about environment and ecological impact of chemical compounds present in the products after these being disposal, led to the stablishment of standardized tests to harmonize the obtained results. This becomes an essencial step when attempting to bring a new chemical product to the marketplace.

The main international organizations that have established standards or testing methods in the field of polymers biodegradation are the International Organization for Standardization (ISO), the American Society for Testing and Materials (ASTM) and the European Committee for Standardization (CEN). In addition, there are also a number of national standardization bodies, such as the Austrian Standard Institute (ÖNORM), the British Standards Institute (BSI), the French Association Française de Normalisation (AFNOR), the German Deutsches Institut für Normung (DIN), the Italian Ente Nazionale Italiano di Unificazione (UNI), the Biodegradable Plastics Society (BPS) and Japanese Industrial Standards (JIS) of Japan [33-35].

The first standard testing practice for biodegradability and compostability of plastic products was issued by ASTM in 1999, although prior to that (1992-1997) several standard practices for testing biodegradation of organic compounds in aqueous media had already been issued by ISO [33]. Different norms and standards have been established to access biodegradability of plastic materials depending on the media and the parameter measured (Table 2) [36]. The biodegradation tests can be classified by the test environment, such as an aqueous solution, a compost, and soil [37], by the presence or absence of oxygen and by the parameters monitored. In aerobic biodegradation ($O_2 > 6\%$ according to ASTM D 5338), microorganisms break the polymer chains down using oxygen during the metabolism process and as a result, carbon dioxide gas and water are released to the atmosphere. Biodegradation in a compost pile is predominantly aerobic. In contrast, anaerobic biodegradation happens in an oxygen-absent environment. Instead of CO_2, methane gas (CH_4) and water are generated and released. Examples of anaerobic conditions include those in sewage and in landfills where CH_4 is collected [38]. The standards vary in system requirements, complexity, and capability. However, in all cases the determination of the biodegradation process is assessed by measuring one of the following parameters: carbon dioxide (CO_2) and/or methane (CH_4) evolution, the consumption of biochemical and chemical oxygen demand (BOD and COD), or the reduction of the dissolved organic carbon (DOC) [33].

Table 2 presents a list of active ASTM and ISO standards tests to assess biodegradation of polymers. Both series of standards have some similar or equivalent standards [38].

Apart from the active standards for the Assessment of biodegradation of plastics, ASTM and ISO also present standards with definitions and specifications about biodegradation. For example, ASTM D6400 and ISO 17088 address the compostability of plastics, and standard specifications and terminologies for biodegradable plastics as well as guidelines for using specific test methods.

According to ASTM 6868, materials of natural origin are accepted as being biodegradable without testing, but should be characterized to identify their chemical composition, presence of heavy metals or other hazardous substances, organic carbon content and total dry and volatile solids.

ASTM standard test methods usually include the use of thin-layer chromatography cellulose as a positive control and if sufficient biodegradation (a minimum of 70 % for

cellulose) is not observed within the duration of the test, the test must be regarded as invalid and should be repeated with fresh inoculum.

Table 2. List of active ASTM and ISO standards biodegradation of plastics

	Number	Title	Conditions/ Parameters monitored
ASTM	D5210 - 92(2007)	Standard Test Method for Determining the Anaerobic Biodegradation of Plastic Materials in the Presence of Municipal Sewage Sludge.	Liquid Anaerobic CO_2 and CH_4
	D5338 - 11	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures.	Compost Aerobic CO_2
	D5511 - 12	Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions.	Solid Anaerobic CO_2 and CH_4
	D5526 - 12	Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions.	Solid Anaerobic CO_2 and CH_4
	D5988 - 12	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in Soil.	Soil Aerobic CO_2
	D6340 – 98(2007)	Standard Test Methods for Determining Aerobic Biodegradation of Radiolabeled Plastic Materials in an Aqueous or Compost Environment.	Liquid/Compost Aerobic $14CO_2$
	D6691 - 09	Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium or Natural Sea Water Inoculum.	Marine Environment Aerobic CO_2
	D7081 - 05	Standard Specification for Non-Floating Biodegradable Plastics in the Marine Environment.	
	D7475 - 11	Standard Test Method for Determining the Aerobic Degradation and Anaerobic Biodegradation of Plastic Materials under Accelerated Bioreactor Landfill Conditions.	
ISO	13975 (2012)	Determination of the Ultimate Anaerobic Biodegradation of Plastic Materials in Controlled Slurry Digestion Systems -- Method by Measurement of Biogas Production.	Biogas production
	14851 (1999)	Determination of the Ultimate Aerobic Biodegradability of Plastic Materials in an Aqueous Medium -- Method by Measuring	Liquid Aerobic BOD

		the Oxygen Demand in a Closed Respirometer.	

	Number	Title	Conditions/ Parameters monitored
	14852 (1999)	Determination of the Ultimate Aerobic Biodegradability of Plastic Materials in an Aqueous Medium -- Method by Analysis of Evolved Carbon Dioxide.	Liquid Aerobic CO_2
	14853 (2005)	Determination of the Ultimate Anaerobic Biodegradation of Plastic Materials in an Aqueous System -- Method by Measurement of Biogas.	Liquid Anaerobic Biogas production
	14855-1 (2012)	Determination of the Ultimate Aerobic Biodegradability of Plastic Materials Under Controlled Composting Conditions -- Method by Analysis of Evolved Carbon Dioxide -- Part 1: General Method.	Compost Aerobic CO_2
	14855-2 (2007)	Determination of the Ultimate Aerobic Biodegradability of Plastic Materials Under Controlled Composting Conditions -- Method by Analysis of Evolved Carbon Dioxide -- Part 2: Gravimetric Measurement of Carbon Dioxide Evolved in a Laboratory-Scale Test.	Compost Aerobic CO_2
	15985 (2004)	Determination of the Ultimate Anaerobic Biodegradation and Disintegration Under High-Solids Anaerobic-Digestion Conditions -- Method by Analysis of Released Biogas.	Anaerobic Biogas production
	16929 (2013)	Determination of the Degree of Disintegration of Plastic Materials Under Defined Composting Conditions in a Pilot-Scale Test.	Compost
	17556 (2012)	Determination of the Ultimate Aerobic Biodegradability of Plastic Materials in Soil by Measuring the Oxygen Demand in a Respirometer or the Amount of Carbon Dioxide Evolved.	Soil Aerobic BOD or CO_2
	20200 (2004)	Determination of the Degree of Disintegration of Plastic Materials Under Simulated Composting Conditions in a Laboratory-Scale Test.	Compost

Given the importance of composting, which is considered to be the most ecological waste treatment method, it is not surprising that the majority of the published standards is related to aerobic degradation tests in composting conditions [33]. The number of standards is continuously changing to take into account the scientific advancements in the design and production of new materials or products and ever changing applications. Biodegradable plastics should meet stringent norms with regards to their complete biodegradability, compost quality and product safety, under specific conditions related to a given application [34, 36, 39].

Multiple test procedures are necessary to evaluate the material biodegradability because some tests are subject to false-positive interpretations and consequently incorrect conclusion if degradation or biodegradation occurred. For example, measure weight loss may not result from polymer degradation, but from the leaching of additives, including plasticizers. Carbon dioxide production might result from the degradation of low molecular weight fraction of the polymer, without degradation of longer chains.

Table 3 presents a list of work items currently under development by ASTM and ISO, some are revision of current standards and others are new.

Table 3. List of work items currently under development by ASTM and ISO

Number	Details
ASTM WK29802	New Specification for Aerobically Biodegradable Plastics in Soil Environment.
ASTM WK32805	New Test Method for Disintegration of Compostable Plastics and Products in a Pilot Scale Aerobic Composting System.
ASTM WK34454	New Test Methods for Standard Method for Determining the Disintegration of Compostable Plastics and other Materials in Aerobic Industrial Composting Environments.
ASTM WK34780	New Specification for Plastic Materials that Anaerobically Biodegrade in Landfills.
ASTM WK35342	New Specification for Home Composting of Biodegradable Plastics.
ASTM WK40316	Revision of D6954 - 04 Standard Guide for Exposing and Testing Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation.
ASTM WK40538	Revision of D6691 - 09 Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium or Natural Sea Water Inoculum.
ASTM WK41850	New Test Method for Determining the Rate and Extent of Plastics Biodegradation in an Anaerobic Laboratory Environment Under Accelerated Conditions.
ASTM WK42572	Revision of D5338 - 11 Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures.
ASTM WK42833	New Test Method for Determining Aerobic Biodegradation of Plastics Buried in Sandy Marine Sediment Under Controlled Laboratory Conditions.
ISO/DIS 15985	Determination of the Ultimate Anaerobic Biodegradation And Disintegration Under High-Solids Anaerobic-Digestion Conditions -- Method By Analysis Of Released Biogas.
ISO/CD 18830	Test Method for Determining Aerobic Biodegradation of Plastic Materials Sunk at the Sea Water/Sandy Sediment Interface.
ISO/DIS 20200	Determination of the Degree of Disintegration of Plastic Materials Under Simulated Composting Conditions in a Laboratory-Scale Test.

*DIS: Draft International Standard.
*CD: Committee Draft.

Standards give the guidelines to perform and assess the degradability of plastic materials. The selection of the appropriated standard to follow depends the type of tests to be applied and the conclusions, which can be drawn [11]. Müller, subdivided tests into three categories: field tests, simulation tests and laboratory tests (Figure 4).

From the application point of view, field tests represent the ideal approach to assess the biodegradability of plastic materials. Buried samples in the soil, placed in a lake or river to perform a full-scale composting process gives the most real results. However, serious drawbacks are associated at these types of test [11]. Parameters, as temperature, humidity or pH cannot be totally controlled due to complexicity and undefined environment. Moreover, the application of analitic technics to follow and analyse the degradation process are limited.
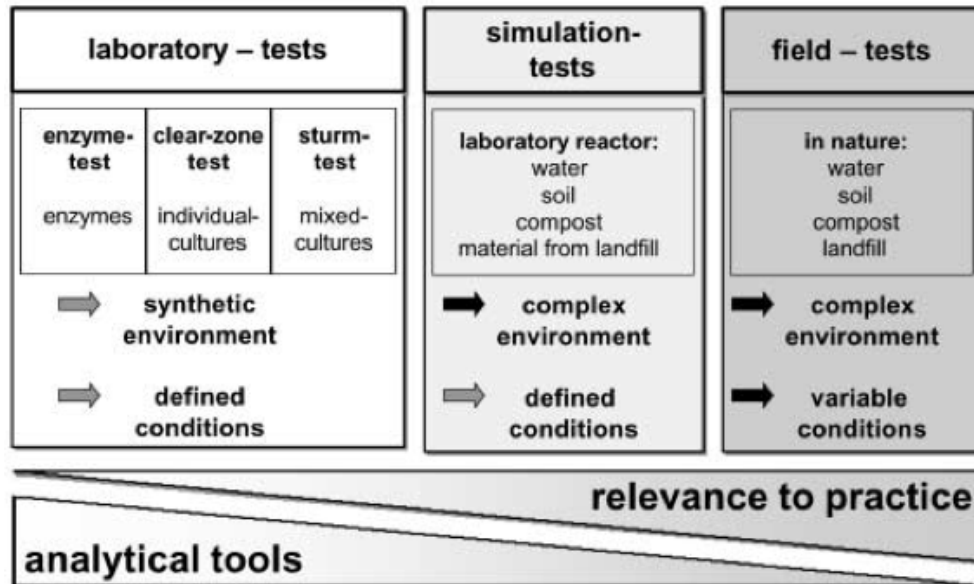
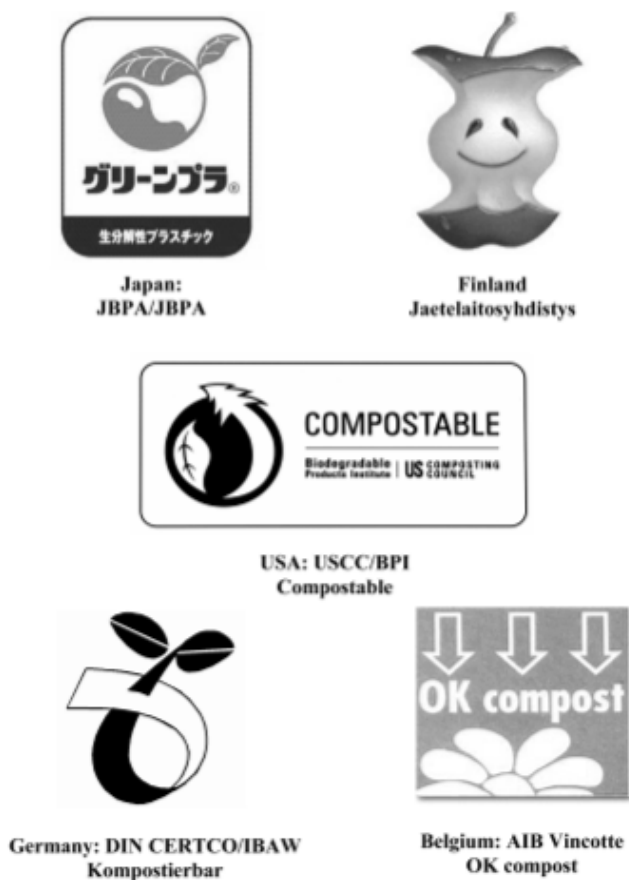Figure 4. Schematic overview on tests for biodegradable plastics (from Müller [11]).

Figure 5. Currently used logos for biodegradable plastics (from Sudesh [49]).

As alternative to field tests, laboratory tests, where a defined media is used and the inoculated microbial population is tightly controlled allow the most reproducible results. This is useful when basic mechanisms of polymer biodegradation are the object of study. However, due to its restricted nature, only limited conclusion about absolute degradation rate of the plastic material can be draw.

Simulation tests are the ones that offer best correlation, these studies can be preformed in compost, soil or sea or lake-water in a controlled reactor. Being the environment really close to the one find in the field tests, complete control over the external parameters allow to employe analytical technics to determine with precision the degradation evololution as well as the resulting products. Examples of such tests included soil burial (Pang et al., 2013; Briassoulis and Rudnik, 2011; Schlemmer et al. 2009) [40-42], controlled composting (Leejarkpai et al. 2011; Kale et al. 2007) [43, 44], test simulating landfills (Tollner et al. 2011; Campos et al. 2011) [45, 46] and aqueous tests (Funabashi et al. 2007; Machado et al. 2013) [47, 48].

More than be capable to determine the plastic biodegradability, several countries have also created attractive logos to identify products made from biodegradable polymers (Figure 5). Such logos, besides to facilitate the classification of plastic in the waste stream, increase the public awareness and promote the use of biodegradable products [49].

BIODEGRADATION OF POLYMER-BASED NANOCOMPOSITES

Biodegradable polymer or biopolymers are a growing field due to the reasons enumerated before. In 2011, production capacities increased to approximately 1.2 million tonnes being the forecasts production capacities to European Bioplastics market to roughly 6 million tonnes by 2016 [50]. The best examples of biopolymers based on renewable resources are: cellulosic plastics, polylactides (PLA), poly(ε-caprolactone) (PCL), starch plastics, and soy-based plastics. Microbial synthesized biopolymers, as polyhydroxy alkanoates (PHAs) polymers, have also attracted much attention recently [51].

Poly(lactic acid) (PLA), one the most used biodegradable polymer, is obtained from renewable resources, such as corn starch, corn, potato or sugar beet. With a glass transition temperature between 55 – 60ºC and a maximum melting temperature of 175ºC (depending of the optical purity), it is produce from L-lactic acid monomer or by ring opening polymerization of lactide. Fukushima and co-workers, 2013, report the effect of two layered silicate clays (montmorillonite (CLO30B) and fluoro-hectorite (SOMMEE)) on the biodegradation process in compost of PLA [52]. Bio-nanocomposites were prepared by melt mixing using a co-rotating twin screws extruder and the degradation study followed the Standard ISO 527. The degradation evolution was followed by percentage of weight lost coupled with differential scanning calorimetry (DSC) to establish the changes in the structure. Authors observed, especially for SOMMEE specimens, morphological differences after 21 days of degradation (Figure 6). The opacity, which is a consequence of degradation, results in polymer matrix crystallinity change [53, 54]. Actually, the hydrolytic degradation of the polyester chains is known to take place at a higher rate in the amorphous zones of the matrix, this phenomenon is expected to increase the relative crystallinity of the sample, which results in an opacity increased of the material [55]. Regarding to DSC analysis, PLA/SOMMEE upon degradation show a complete disappearance of the cold crystallization and melting peaks after only 14 days of degradation in compost. Neat PLA and CLO30B base materials shift Tcc and Tm to lower values after 14 and 21 days, especially upon addition of 10% of clay. Therefore, it was demostrated that the addition of clays accelerated the process of PLA biodegradation in compost at 40°C. Moreover, higher clay contents resulted in higher biodegradation, probably due to hydroxyl groups of silicate layers and/or of their organic modifiers [52].
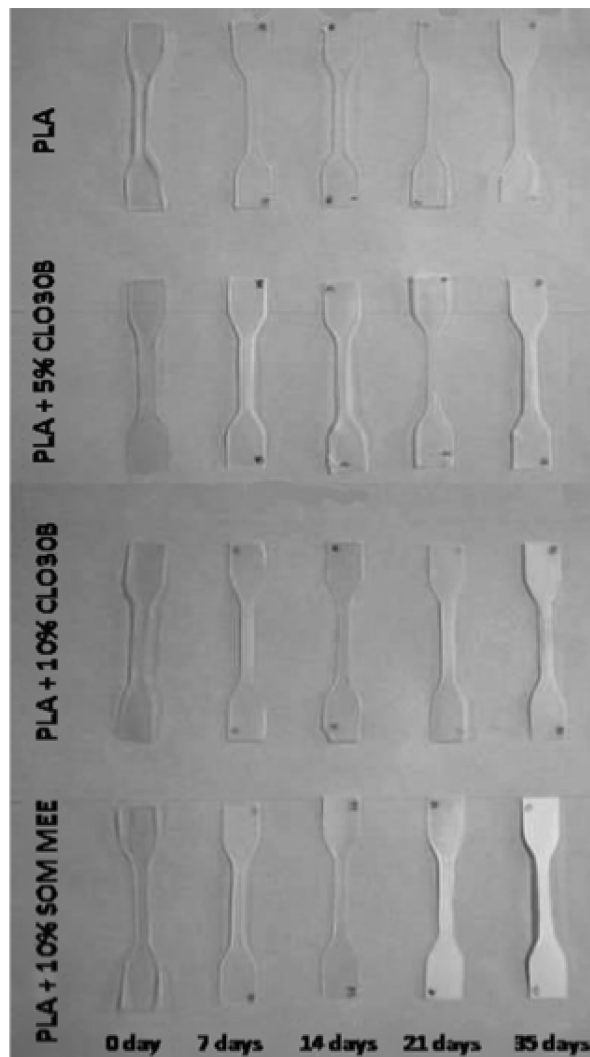
Figure 6. PLA and PLA/nanocomposites before (0 day) and after biodegradation in compost (from Fukushima [52]).

Machado and co-workers, 2013, assessed the PLA and PLA nanocomposites biodegradability in aqueous and composting mediums [56]. PLA nanocomposites with three different nanoclays (Cloisite 30B, Cloisite 15A, and Dellite 43B) were prepared by melt-mixing.

Their biodegradability, in aqueous medium, was determined by biochemical oxygen demand test following the standard procedure ISO-14851. The biodegradation in compost was performed following the procedure described by Camino [57] at 40 ºC. In agreement with other studies, an increase of the biodegradability was detected for nanocomposites (Figure 7). According to the authors, this was due to the presence of clays that increased the hydrophilicity of a PLA matrix, allowing an easier permeability of water and activating the hydrolytic degradation process. Moreover, a good correlation between both tests was obtained, showing the same trend of biodegradability.

Additionally, the extention of PLA and nanocomposites biodegradation in compost was followed by gel permeation chromatography (Figure 8). The results confirmed that biodegradation was not homogenous along the sample and that white zones correspond to smaller molecules, i.e., where the hydrolytic degradation was more intense.
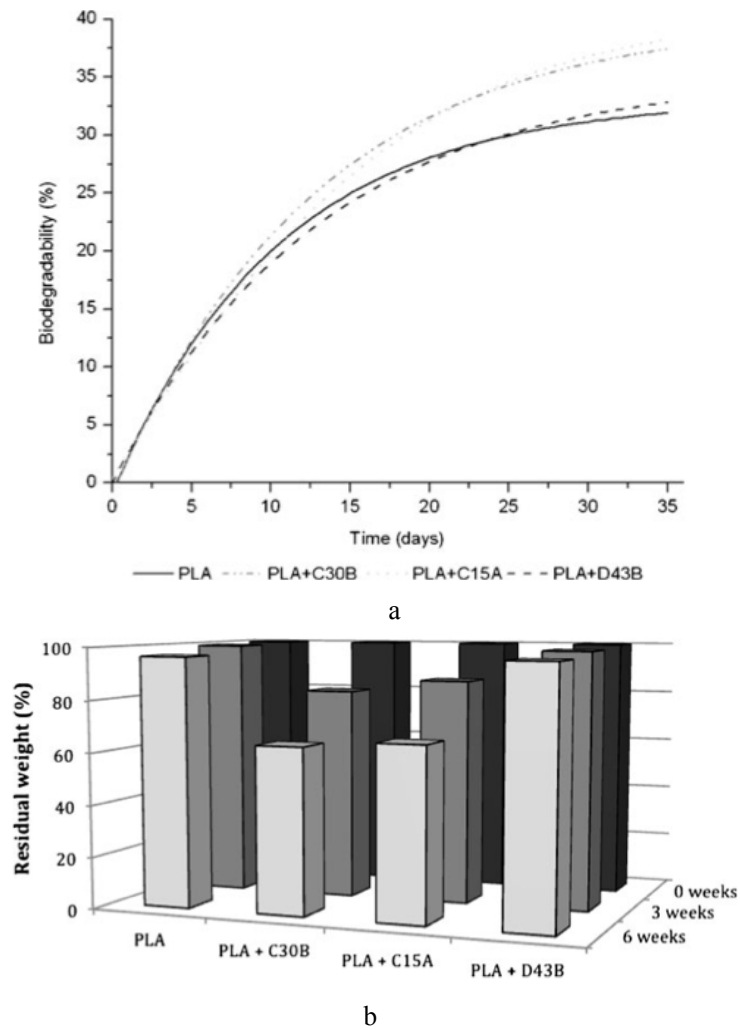

a

b

Figure 7. PLA and nanocomposites biodegradation results obtained by aqueous and composting tests (from Machado [56]).
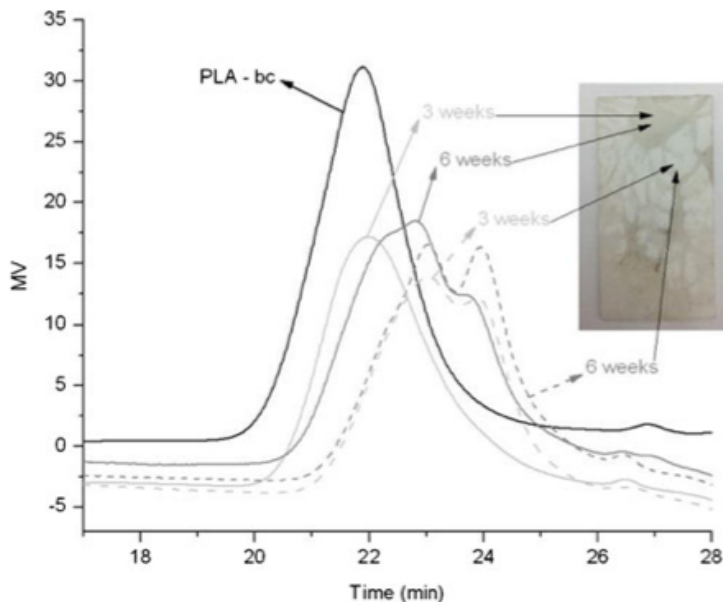
Figure 8. Retention time curves of PLA before (bc), and after 3 and 6 weeks of degradation in compost (from Machado [56]).

Although, the chemical hydrolysis degradation of PLA under composting conditions is well established, the role of microorganisms in the process still unclear [58]. The most accepted mechanism described the PLA biodegradation as a two-step process, in which chemical hydrolysis occurred in the presence of water at elevated temperatures followed polymer mineralization by microorganisms, which generate carbon dioxide under aerobic conditions and methane under anaerobic conditions [59-63]. Agarwal and co-workers, 1999, reported that microorganisms do not enhance PLA degradation. According to them polymer cleavage proceeds solely through abiotic hydrolysis of ester linkages in the presence or absence of microorganisms [64]. However, other studies showed that microbial enzymes are capable of directly biodegrade high molecular weight PLA [65-67]. Pranamuda and co-workers, 2001, were the first to isolated PLA-degrading microorganisms of Amycolatopsis strain from soil environment, which were capable of biodegrade 60% of the PLA film after 14 days [65]. One of PLA biodegradability limitations is related to the distribution of its biodegradable microorganisms that are not widely spread in the natural environment. Therefore, PLA is less susceptible to microbial attack in the natural environment than other synthetic aliphatic polyesters like PHB, PCL, and poly(butylenes succinate) (PBS).

Poly(ε-caprolactone) (PCL) is a linear synthetic aliphatic polyester, which can be synthesized by ring-opening polymerization of ε-caprolactone. Biodegradable by a variety of microorganisms, it is mainly used in packaging, drug delivery systems and also applied in bone repair, as a soft- and hard-tissue compatible material [68]. Machado and co-workers, 2013, reported the study of PCL/titanium nanocomposite biodegradability. The bio-nanocomposite was prepared by sol-gel process in solution and its biodegradability was assessed in aqueous environment under aerobic conditions according to the standard ISO14851:1999. According to the results, the titanium nanoparticles had a catalytic effect increasing in 30% the PCL biodegradability [48]. Wu and co-worker, 2009, assessed the

effect on unmodified sodium montmorillonite (Na$^+$-MMT) on PCL biodegradability. Samples buried during 40 days into compost showed a mass loss decrease with the increase of Na$^+$-MMT content. In this case, the addition of Na$^+$-MMT decrease the PCL biodegradability, indicating that silicate layers acted like a barrier rather than a catalyst [69]. Lee and co-workers, 2005, also study the effect of MMT clays on PCL biodegradability, in this study organically modified MMT, Cloisite 15A and 30B were used. They observed a much faster biodegradation of the nanocomposites than pristine polymer. However, due to barrier effect that prevents hydrolysis, clay amounts higher than 7 wt% start to provoke a delay on biodegradation [70].

Authors concluded that for low contents, modified MMT has a catalytic effect on PLA and PCL biodegradability, accelerating the hydrolysis process. However, Fukushima and co-workers, 2010, observed that PCL loaded with 5 wt% of Cloisite 30B and Nanofil 804 decrease the biodegradability [71].

As depicted in Figure 9, all samples exhibit a significant surface degradation with areas more degraded than others, indicating that the degradation proceeds through an inhomogeneous mechanism. Moreover, it was verified again that nanoclay layers play a barrier role toward microbial attack, which slows down the diffusion of enzymes into the polymer matrix.
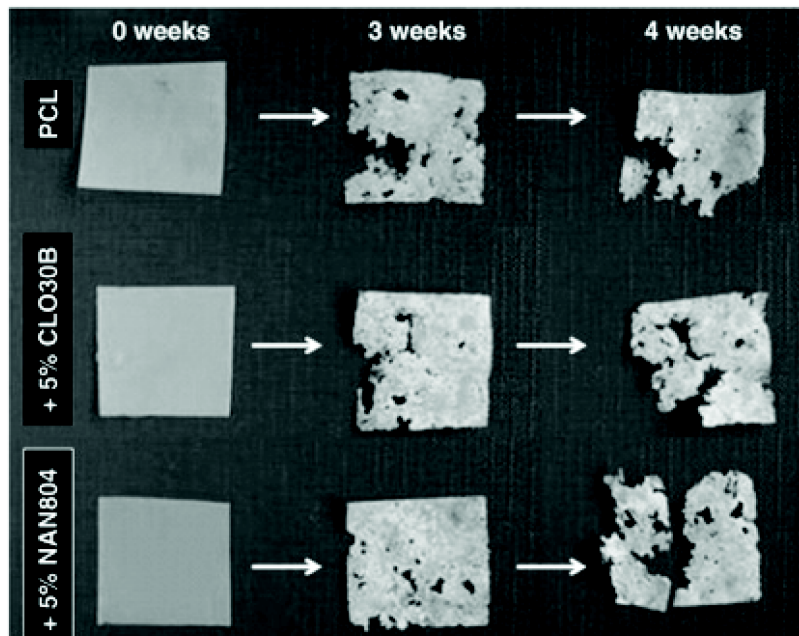

Figure 9. PCL and nanocomposites based on CLO30B (+ 5% CLO30B) and NAN804 (+ 5% NAN804) before degradation (0 weeks) and after 3 and 4 weeks of degradation in compost (from Fukushima [71]).

Starch, among biopolymers is the one that has lowest production cost, wide availability, fully biodegradability and is a renewable agriculture resource [72, 73]. Composed by a mixture of two α-glucose polymers, linear amylose and a highly branched amylopectin. Starch is not a real thermoplastic, but in the presence of a plasticizer (water, glycerol, sorbitol, etc.), high temperature, and shearing, it melts and fluidizes, enabling its use in injection,

extrusion and blowing equipment. Thermoplastic starch (TPS) due to its sensitivity to humidity and poor mechanical properties cannot be used in many applications [74]. Magalhães and Andrade, 2009, study the effect of MMT Cloisite 30B on mechanical and biodegradability properties of TPS. The TPS/Cloisite 30B nanocomposites were prepared in a single-screw extruder and its biodegradability assessed at room temperature by weighing specimens, after being buried in composted soil. The variation in weight loss showed curves of the same type (Figure 10). However, biodegradation rate of TPS was significantly enhanced by addition of Cloisite 30B, reached 85 wt% degradation in 120 days in spite of 187 days needed for TPS [75]. Agnantopoulou and co-workers, 2012, study the biodegradability of TPS and lignocellulosic fibers composites from wood flour. Prepared in an internal mixer Haake-Buchler Rheomixer, the biodegradation of the specimens was assessed according to ISO 846. Results show that composites had lower biodegradability than native TPS (Table 4). Moreover, the wood species had influence on biodegradation rate. They justified the different behaviours according to fungi affinity to wood fibers and its moisture content [76, 77]. They shown that decomposition does not occur at moisture content levels below 20% [77].
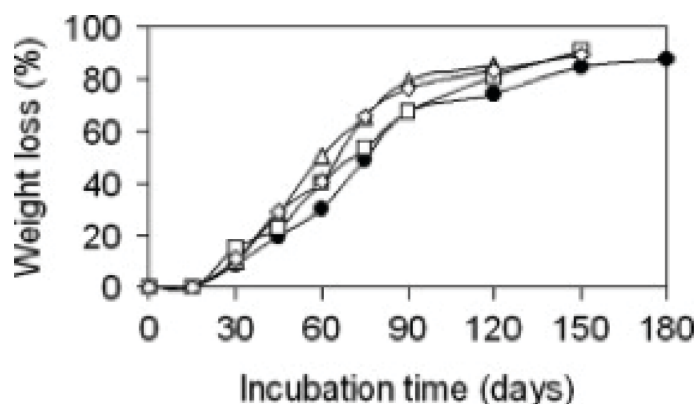

Figure 10. Weight loss for TPS alone (●), and for TPS/Cloisite 30B hybrids, plasticized with 25 wt% glycerol, with 0.34 wt% clay (Δ), with 6.0 wt% clay (□), and with 11.65 wt% clay (◇) (from Magalhães and Andrade [75]).

Table 4. Average weight loss for TPS and composites after 2 and 10 months burial in the soil

Composite type	Weight loss (%)	
	2 months	*10 months*
TPS	7.02	45.21
TPS-spruce (30 wt%)[a]	5.58	36.40
TPS-spruce (50 wt%)[a]	5.52	32.01
TPS-pine (50 wt%)[a]	1.68	30.07
TPS-beech (50 wt%)[a]	5.85	44.23
TPS-poplar (50 wt%)[a]	2.64	32.03
TPS-spruce (<150 μm)[b]	5.48	28.82
TPS-spruce (500-750 μm)[b]	7.11	37.41

[a] Particle size 150-250 μm.

[b] Wood flour content 50%.

Cellulose, the most abundant natural polymer, can be obtained from plants and also secreted extracellularly as synthesized cellulose fibres by some bacterial species, which is called bacterial cellulose (BC) or microbial cellulose (MC) [78]. Considered almost inexhaustible source of raw material to make face the increasing demand for environmentally friendly and biocompatible products, the full potential of cellulose has not yet been exploited because of the lack of an environmentally friendly method and the limited number of common solvents that readily dissolve it [79, 80]. Cellulose products have a long undustrial history started in 1878 with Celluloid, the first thermoplastic polymer produced by Bayer's subsidiary, Wolff Walsrode AG [81]. Cellulosic plastics, such as cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) are common thermoplastic materials produced through esterification of cellulose. The main drawback of cellulose is that its melt processing temperature exceeds its decomposition temperature, making necessary to substitute the hydroxyl groups [81, 82]. However, the degree of OH groups substitution per anhydroglucose unit influences the cellulose biodegradability, which is associated to the sterical demand for enzymatic attack [81]. Figure 11 exemplifies the equilibrium between biodegradability and degree of substitution.
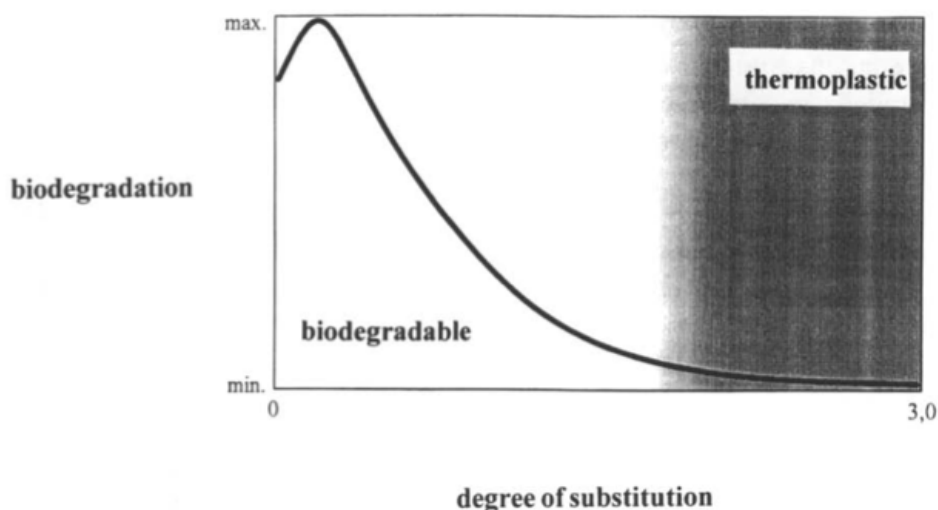

Figure 11. Biodegradation and thermoplasticity of substituted celluloses (from Simon [81]).

Besides to use cellulose as polymer matrices, it has attracted significant attention manly as potential nanoreinforcement for different biodegradable polymers [83, 84]. With a theoretical modulus estimated of 167.5 GPa, native cellulose is one of the strongest and stiffest natural fibers available [85, 86]. Highly crystalline rod-like nanostructures obtained from cellulose, called cellulose nanowhiskers (CNW) or cellulose nanocrystals (CNC) are examples of cellulose nanoreinforcements.

Mathew and co-workers, 2005, explore the effect of microcrystalline cellulose (MCC) dispersed in a PLA matrix as crystalline nanoreinforcements compounded in a twin-screw extruder [71]. MCC has the capability to disintegrate into cellulose nanowhiskers improving the mechanical properties of PLA. The biodegradability of PLA/cellulose nanocomposites were studied at 58 °C according to the ASTM D5338 standard. Figure 12, depicts the

different biodegradation stages of PLA/cellulose nanocomposites recovery samples. Clearly, nanocomposites had a slower degradation rate when compared to pure PLA. This was atributed to the resistance in water uptake and diffusion through the composite compared to pure PLA. Moreover, morphological analysis showed that the MCC was remaining as aggregates of crystalline cellulose fibrils, which resulted in poor mechanical properties.
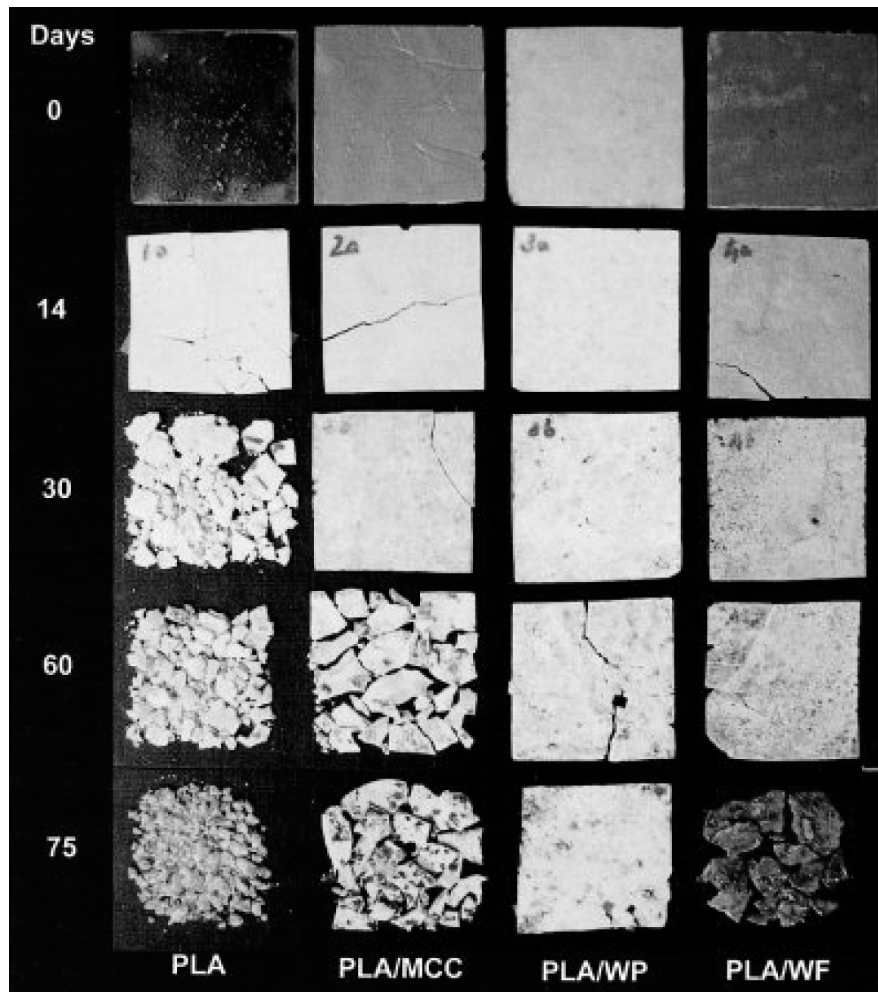

Figure 12. Photographs showing different stages of biodegradation of PLA/cellulose nanocomposites in compost soil (from Mathew [71]).

Jayaramudu and co-workers, 2013, aiming to developed a completely biodegradable composite, reinforced pure cellulose matrix with *Sterculia urens* short fiber (SUSF) [87]. Biodegradation of pure cellulose (matrix) and SUSF/cellulose composite were studied by the soil burial method as described by Potts, Clendinning, and Ackart (1972) [88], with a slight modification.

Polarized optical micrographs showed that the degradation behavior was approximately linear. At 25 days soil burial an average of 70 % weight decrease was noticed, followed by roughness increased and cracks (Figure 13). After 45 days, no remains of the composite films

were found in the soil, indicated that bacteria directly attacked and metabolized the matrix and SUSF composite films [87].
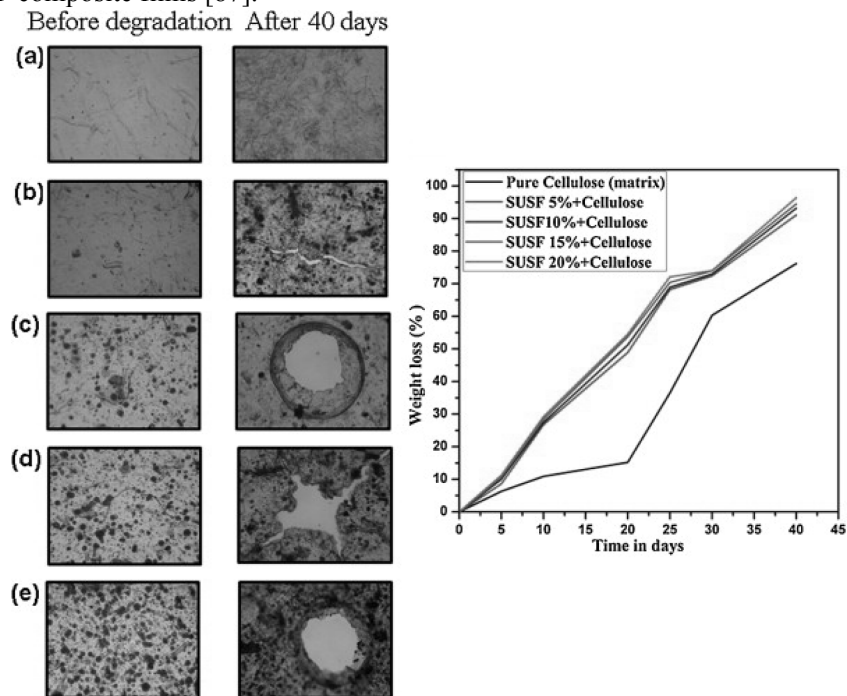

Figure 13. Polarized optical microscope of pure cellulose with SUSF/Cellulose composite films before and after 40 days degradation in soil: (a) pure cellulose (matrix), (b) SUSF5% + cellulose, (c) SUSF10% + cellulose, (d) SUSF15% + cellulose and (e) SUSF20% + cellulose at the same magnifications and including weight loss graph also (from Jayaramudu [87]).

Polyhydroxyalkanoates (PHAs) are microbial storage polymers with properties similares of the main commodity plastics [49]. Discovered in 1845, PHAs were only studied and characterized in the 1920s [49, 89, 90]. Produce from renewable resources, such as plant oils [91-93], sugars [94-96], and carbon dioxide [97, 98], PHAs are completely biodegradable in the natural environment [99]. Steinbüchel and Lütke-Eversloh, 2003, identified approximately 150 different constituents of PHAs as homopolymers or as copolymers [100]. Then, these allow to obtained materials with a large range of properties and applications.

PHAs seem to be the most interessant from commercial point of view, since their physical and mechanical properties resemble the properties of common commodity thermoplastics. Such as, PHAs are poly(3-hydroxybutyrate) [P(3HB)], poly(3-hydroxybutyrate-co-3-hydroxyvalerate) [P(3HB-co-3HV)], poly(3-hydroxybutyrate-co-4-hydroxybutyrate) [P(3HB-co-4HB)] and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [P(3HB-co-3HHx)] [49].

Corrêa and co-workers, 2012, investigated nano-biocomposites of poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) and Cloisite C30B [101]. Prepared by melting compounding, biodegradability evaluation was performed according D6003 and G160 ASTM standards. The results obtained demonstrate that the weight lost (Figure 14) were globally low (less than 10%) even after 3 months of biodegradation with exception of the bio-nanocomposite. The latter evidenced a significant improvement in biodegradation. This was explained by the

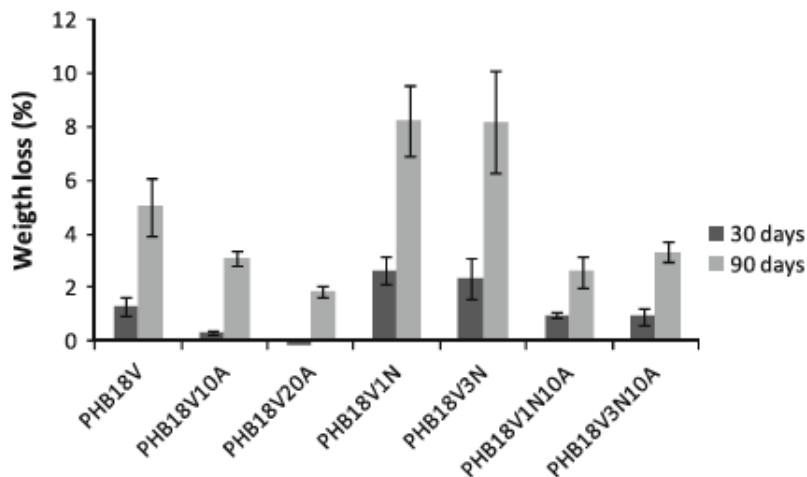sponge effect of nanoclays that trap the water molecules, promoting biotic and abiotic PHBV degradation [56].

Figure 14. Samples weight losse recorded after 30 and 90 days of biodegradation, for various PHB18V-based systems (from Corrêa [109]).

CONCLUSION

In the last decade, bionanocomposites have been subject of intense research in different fields, going from the regenerative medicine to food packaging. Even thought, the production cost still superior than conventional material, the properties, as biocompatibility, biodegradability, great abundance in nature and diversity make these materials adequate for a wide range of applications. The use of bionanocomposites has been driven by the requirement of replacing the commonly employed petroleum-derived polymers and by warned societies that required more sustainable materials. Nevertheless, governments and companies have to continue to found and stimulated the research on bio-nanocomposites field in order to develop new materials with improved properties, exploiting them in direction to a more sustainable future.

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