

# Chapter 9

## Physico-chemical Characterization of Bioplastics and Biocomposites



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The identification and comparison of different physico-chemical characteristics of materials are particularly important from the commercial point of view to make comparisons between different lots, to assess compliance with the specifications or intended use.

A number of different analytical techniques and approaches are used in this respect. In the following, we will detail the most useful ones.

### 9.1 Morphology. Scanning Electron Microscopy (SEM)

Qualitative information about the physical state, surface and internal structures of bioplastics, and biocomposites can be obtained using microscopic methods. Among them, Scanning Electron Microscopy (SEM) is the most common.

A scanning electron microscope makes use of a focused beam of electrons to produce images of a sample. The surface is scanned by electrons which interact with atoms in the sample specimen. The output signals contain information about the surface morphology and composition. Usually, secondary electrons emitted by atoms excited by the scanning electron beam and back scattered electrons are detected using the Everhart-Thornley detector. The number of secondary electrons depends on specimen topography. This way, a resolution better than 1 nm can be achieved. Anyhow, specimens must be electrically conductive, hence an ultrathin coating of electrically conducting metal (gold and gold/palladium alloy being the most common materials) is usually deposited on non-conducting samples by low-vacuum sputter coating or by high-vacuum evaporation (Álvarez-Chávez et al. 2017; Tiimob et al. 2016; Madera-Santana et al. 2015), prior to scanning.

SEM is usually done in order to analyze the microstructure and morphology of specimens through the analysis of micrographs in different magnifications.

SEM analysis of bioplastics and biocomposites was used for diverse reasons.

Firstly, SEM is a crucial tool to investigate filler adhesion and dispersion in biocomposites (Cecchi et al. 2017; Thunga et al. 2014; Sarki et al. 2011; Koutsomitopoulou et al. 2014; Liu et al. 2009; Quiles-Carrillo et al. 2018; Wu 2015) as illustrated in Chap. 7 (Fig. 7.1) and copolymers (Chłopek et al. 2007; Raza et al. 2019; Quiles-Carrillo et al. 2018). In this respect, the study of the morphology of impact fractured specimens of bioplastics and biocomposites is noteworthy because the microscopic analysis on the fracture surfaces of the samples reveals the failure surface structure and failure behavior induced by tensile test (Johari et al. 2016; Jandas et al. 2012; Liu et al. 2009; Bashir and Manusamy 2015; Tiimob et al. 2016). The interfacial adhesion between the phase of the filler and that of the matrix can be inferred from SEM micrographs of the fractured surface of the biocomposites (Scaffaro et al. 2018). It is usually found that particle size and surface roughness are important for the adhesion of a filler in a polymer matrix, and fatty components of the filler may form a thin film on the filler surface that prevents good adhesion. Actually, samples can also be fractured cryogenically (Álvarez-Chávez et al. 2017; Madera-Santana et al. 2015).

Secondly, SEM analysis can reveal the morphology of fillers used for biocomposites. For example, the morphological analysis of fillers such as cellulose fibers was useful to determine the surface roughness and texture needed to adhere to the surface of the polylactic acid (PLA) matrix. It was concluded that the surface smoothness has a negative effect on adhesion since it precludes physical bonding (Johari et al. 2016). The morphology of various fillers, such as *Posidonia oceanica* dead leaves (Scaffaro et al. 2018), hemp fibers (Song et al. 2013), and olive pit powder in PLA-matrix biocomposites (Koutsomitopoulou et al. 2014) were also studied by SEM imaging.

Thirdly, SEM analysis enabled the investigation of the change in biocomposite surface morphology in studies concerning biodegradability in soil (Wu 2015) or after invasion by bacteria *Burkholderia cepacia* (Jandas et al. 2012). Composting was also studied by SEM: the rate of bioplastics biodegradation at the micro-scale was studied via the comparison of SEM micrographs acquired at different times. SEM analysis highlighted the microbial activity of degradation on the bioplastic: the surface lost its smoothness, and cracks were evident (Adamcová et al. 2018). The presence of the filler increased biodegradation (Wu 2015).

SEM analysis can also be useful for assessing the eventual biphasic morphology of bioplastic blends (Su et al. 2019) that would be witnessed by different discrete domains in the micrographs. SEM imaging was also used to assess the improved filler–matrix interaction when a silane coupling agent (3-aminopropyltriethoxysilane) was used for the preparation of PLA/coconut shell powder biocomposites (Chun et al. 2012).

## 9.2 Crystallinity and Thermal Stability. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

Important characteristics of bioplastics are mechanical, optical, and barrier properties which, in turn, depend on the physical properties (crystallinity, density, phase change temperatures, polarity, etc.).

Polymers may be either semicrystalline or amorphous. Amorphous material has no organization in the solid state. No polymer is organized into a fully crystalline material because imperfections and amorphous areas in semicrystalline polymers may be momentous. The degree of crystallinity usually ranges between 10% and 80%.

Crystallinity is the state which diffracts X-ray and exhibits a first-order transition known as melting that has a discontinuity in the volume-temperature dependence. The heat of transition is called the enthalpy of fusion or melting. Percent crystallinity has a big influence on optical, mechanical, thermal, and chemical properties, such as transparency, hardness, density, and diffusion.

Crystallinity is associated with the partial alignment of molecular chains, which fold together and form ordered regions called lamellae, which, in turn, compose larger spheroidal structures named spherulites or dense, flat regions called crystallites. The amorphous regions give the material certain elasticity and impact resistance, while higher crystallinity increases hardness but also brittleness.

Polymer crystallization usually results from cooling from the melt, mechanical stretching, or solvent evaporation.

The glass transition temperature ( $T_g$ ) is the macro-manifestation of the polymer chain's flexibility and crystallinity. It increases with increasing rigidity of the polymer chain and represents the temperature at which the polymer changes from a hard, glassy, and relatively brittle state to a soft, flexible, rubbery state. This boundary is not only important for the product performance but also for its processing, because below the glass transition temperature, the available energy is insufficient to consent to the molecules' harmonized mobility. Actually, a wide temperature window for thermoplastic processing makes the polymeric material suitable for extrusion, injection molding, thermoforming, and film blowing (Xu and Guo 2010). During heating, the glass transition occurs before melting. Amorphous polymers do not exhibit a melt temperature ( $T_m$ ), they only have a  $T_g$ . On the converse, semicrystalline polymers exhibit both  $T_m$  and  $T_g$  since there are both the amorphous and crystalline regions. The flexibility of amorphous polymers is drastically reduced when they are cooled below the  $T_g$  because a dimensional change in the polymer causes temporary distortions of the strong valence bonds.

Higher  $T_g$  underscores higher degrees of polymerization and better thermal stability of the polymer.

The Flory–Fox equation (Eq. 9.1) relates the number-average molecular weight of the polymer,  $M_n$ , to its glass transition temperature,  $T_g$ , according to the following relationship:

$$T_g = T_{g,\infty} - K / M_n \quad (9.1)$$

where  $T_{g,\infty}$  is the maximum theoretical  $T_g$  at an infinitely high molecular weight and  $K$  is an empirical parameter related to the free volume present in the polymer sample. During heating, cold crystallization at a temperature ( $T_c$ ) above  $T_g$  may occur; it is an intriguing exothermic process in which the polymer chains gain sufficient mobility to fold and arrange themselves into a crystalline structure. Cold crystallization shows if the complete crystallization did not occur during a rapid cooling cycle from the melt and stable nuclei had no time to grow.

Polymers experience major changes in properties during heating or cooling: they either absorb or release heat energy. Heat-induced phase transition behavior of bioplastics and biocomposites can be easily studied by Differential scanning calorimetry (DSC) (Shih and Huang 2011).

DSC is a thermoanalytical technique in which a sample and reference are kept at the same temperature during their heating; the heat required, which depends on the sample and reference heat capacities, is measured as a function of temperature.

In DSC measurements, a certain amount of sample is inserted inside hermetic sample pans and put in the DSC micro-furnace. The reference heat capacity is known over the explored temperature range. From the heating cycle,  $T_g$ ,  $T_m$ , and  $T_c$  can be determined. The  $T_g$  value is obtained from the midpoint of the DSC heating curve deflection from baseline. Enthalpy values can be determined by integrating the area of the cold crystallization and melting peaks (Nisticò et al. 2018). Results may be influenced by the heating rate and sample heat history.

The crystallinity of the sample can be obtained from the comparison of the melting enthalpy obtained for the tested sample with that of a reference sample of the same kind but with 100% crystallinity (Fukushima et al. 2005). The  $T_c$  can be a useful parameter to highlight the internal stress introduced during the bioplastic fabrication and released at that temperature.

For example, DSC results suggested that poly( $\epsilon$ -caprolactone) (PCL) was able to crystallize to a certain extent within PCL/PDLA blends and that PLA was partially miscible with poly(butylene adipate) (Kfoury et al. 2013). Miscibility is often inferred from the fact that a single  $T_g$  is detected in the blend, and its value is between the  $T_g$  of the components (Imre and Pukánszky 2013).

In biocomposites,  $T_c$  and  $T_m$  are not strongly affected by the presence of the filler (Chun et al. 2012); anyhow, when a silane coupling agent (3-aminopropyltriethoxysilane) was used to improve the filler–matrix interaction, the thermal stabilities of the biocomposites increased. For PLA/coconut shell powder biocomposites, the presence of the filler and the use of the silane coupling agent increased the  $T_g$  and crystallinities due to enhanced interfacial bonding. The presence of a peak  $T_c$  indicated that the filler has a nucleating effect (Chun et al. 2012).

Thermogravimetric analysis (TGA) is the technique of choice to study the thermal stability of bioplastics and biocomposites. Both the TGA thermogram and its derivative differential thermo gravimetric (DTG) curves can help in determining the nature and the degree of the sample thermal degradation. The thermogravimeter is an instrument that measures the change in weight of a specimen upon heating. The mass change indicates thermal degradation. Weight loss during heating results from decomposition with the emission of gaseous products and can be recorded as a function of the temperature in thermogravimetric curves. In this respect, the composition of the materials in terms of organic and inorganic components is important.

The thermogravimeter is an extremely accurate balance in which the sample is progressively heated from room temperature up to over 1000 °C with programmable temperature ramps. The results of the thermogravimetry of polymeric materials are usually expressed in terms of percentages of the residual weight of the sample specimen as a function of the temperature.

The TGA analysis method is used to obtain the decomposition onset temperature ( $T_{\text{onset}}$ ), that is, the temperature of initial degradation of the polymeric matrix.

The maximum decomposition temperature ( $T_{\text{max}}$ ) characterized by the maximum weight loss and the decomposition temperature at 50% weight loss ( $T_{50}$ ) are also important parameters to assess the thermal stability of a biomaterial.

The thermal stabilities of coffee ground and bamboo flour PLA biocomposites (Baek et al. 2013), collagen-chitosan biocomposites (Ashokkumar et al. 2012), and dried farm dairy effluent PLA biocomposites were investigated by TGA (Le Guen et al. 2017).

TGA analysis of the coconut shell powder filled PLA biocomposite evidenced the thermal decomposition of hemicellulose at 300 °C, but an increased thermal stability of the biocomposite was inferred from the fact that the total weight loss at 600 °C decreased with filler content, probably because the char may act as a protective barrier (Chun et al. 2012).

In TGA, waste plant fibers, which are potential fillers, usually release absorbed moisture at about 40–140 °C (Shih and Huang 2011), degradation of cellulose and hemicellulose occurs between 250 and 400 °C, while lignin degrades over 400 °C (Baek et al. 2013).

DSC and TGA analyses demonstrated that coconut oil could serve as a nontoxic plasticizer that improves the flexibility of PLA films without affecting their thermal stability or impairing the polymer processing (Bhasney et al. 2017).

TGA and DSC also proved to be useful in biodegradability tests (Alshehrei 2017) and in the study of copolymerization of bioplastics (Xu and Guo 2010).

### 9.3 Nuclear Magnetic Resonance (NMR)

All nuclei that contain an odd number of protons and an odd number of neutrons and nuclei for which the sum of proton and neutron is odd have an intrinsic nuclear magnetic moment and angular momentum (analogous to the classical angular

momentum of a spinning sphere); in other words, they have a nonzero nuclear spin. Common examples are  $^1\text{H}$  and  $^{13}\text{C}$  nuclei. They represent nuclear magnets, and there is no energetic difference for any particular orientation in the space. On the converse, in the presence of an external magnetic field, there is a high-energy state (opposite to the field) and a low-energy state (aligned with the field); in thermal equilibrium, the low-energy orientation is preferred.

If the spin is equal to  $1/2$  (like  $^1\text{H}$ ), there are two possible orientations of the nucleus in a magnetic field.

The energy gap between the levels increases with increasing magnetic field. If the sample is irradiated with electromagnetic radiation of equal energy to the energy difference between the two levels ( $\Delta E$ ), there is a shift in the orientation of the nuclear spin that will rotate from aligned with the field to the opposite direction.

When the nucleus relaxes to its original state, it emits an electromagnetic signal whose energy corresponds to the energy gap between the low and high energy states. The NMR signal of a certain nucleus is displaced into the spectrum at higher or lower frequencies depending on its chemical environment: this happens because the electrons are charged particles. Hence, when they are immersed in a magnetic field, they move and generate a weaker field, which is opposed to the applied one. The greater the electron density, the greater the shielding will be. In this way, the nuclei will feel a lower magnetic field, and therefore the signal will be shifted towards lower frequencies than those of the nuclei with lower electron density.

NMR analysis enables the investigation of the chemical nature of the sample.

$^1\text{H}$ -NMR allows to determine the extent of polymerization because signals from the repetitive units of the polymer are different from those of the corresponding chemical moieties in end groups of the polymeric chain and from their ratio the degree of polymerization (DP), that is, the number of monomeric units in a macromolecule can be calculated.

The number average molecular weight ( $M_n$ ) is the average molecular weight of all the polymer chains in the sample and is defined by:

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad (9.2)$$

where  $M_i$  represents the molecular weight of a specific chain and  $N_i$  is the number of chains of that molecular weight. It follows that  $M_n$  is the the ratio of the total weight of polymer to the total number of molecules.

$M_n$  is obtained by multiplying the mass of each repeating unit by the DP.

Actually,  $^1\text{H}$ -NMR allows determining  $M_n$  until 5000 Da. Above this value, the signals of the end-groups are difficult to measure.  $^1\text{H}$ -NMR enabled the determination of DP and  $M_n$  of the prepolymer used to synthesize PLLA for biomedical applications via safe multimetallic cerium complexes and  $^{13}\text{C}$ -NMR confirmed the PLLA configuration; results were compared with the absolute molecular mass obtained from gel permeation chromatography, another important analytical strategy that is also able to shed light on polymers chain linearity (Pastore et al. 2021).

NMR analyses are also convenient for following the polymerization reaction (Xie et al. 1999), for the evaluation of the bioplastic purity or the eventual presence

of side products (Li et al. 2005), for the determination of a specific copolymer content (Xu and Guo 2010), for the characterization of a potential natural plasticizer for bioplastics (coconut oil) (Bhasney et al. 2017), for the assessment of the influence of mechanical processing of PLA (injection and extrusion/injection) on PLA chains (Kfoury et al. 2013; Farah et al. 2016), to evaluate the content of cellulose in different fillers (Le Guen et al. 2017), in biodegradability tests (Alshehrei 2017), for the study of blends (Yu et al. 2006) and compatibilization in bioplastic blends (Imre and Pukánszky 2013).

Both proton and carbon-13 NMR are expedient for the determination of tacticity (Kapelski 2013), (Pastore et al. 2021), which represents the relative stereochemistry of adjacent chiral centers within a macromolecule.

## 9.4 Barrier and Permeation Properties, Transmission Rate Measurement

Polymers are permeable to gases, and their barrier or permeation properties may impair their suitability for a specific application. These properties are very important factors in determining the suitability of polymer for a wide range of applications in the packaging, medical, cosmetics, or food sectors.

In packaging, for example, ineffective barrier properties may reduce the shelf life of the enclosed product that becomes vulnerable to surrounding environmental factors.

Barrier and permeation properties depend on material characteristics, morphology, orientation, crystallinity, thickness, temperature, and additives. They are crucial for product development, manufacture, and marketing.

Barrier and permeation properties are evaluated by measurement of transmission rate for gases (quantity of gas that is able to pass through a specific area of the plastic material in the unit time). The main gases that affect the stability of most products are water vapor and oxygen.

The water vapor transmission rate is calculated according to ASTM D1653, for organic coating films (ASTM International 2013), ASTM E96 for materials (ASTM International 2016), and ASTM F1249 for plastic film and sheeting using a modulated infrared sensor (ASTM International 2020a).

The water vapor transmission rate is particularly important in packaging because some products need protection from outside air moisture, others require that the moisture contained should not be allowed to evaporate through the package.

The oxygen transmission Rate is measured via ASTM D3985, for flexible barrier materials using a coulometric sensor (ASTM International 2017a): at selected temperature and humidity conditions that particularly influence the measure, a barrier film (typical test area: 50 cm<sup>2</sup>) is sealed between a chamber containing oxygen and a chamber void of oxygen and a coulometric sensor quantifies the oxygen that is transmitted through the material in mol/(m<sup>2</sup>s).

Customized tests study how other gases and vapors – such as hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), Argon (Ar), carbon dioxide (CO<sub>2</sub>), and water (H<sub>2</sub>O) – move across a material.

In Sect. 6.8 the strategies used to improve barrier properties, crucial for food packaging, and to bridge the gap to conventional plastics are discussed.

## 9.5 Biodegradation and Composting

The end of life scenarios of bioplastics is an emerging field of research.

In our “disposable” culture, biodegradable and compostable packaging materials are two of the new green living trends.

Anyhow only a few people are aware of the difference between these two terms, which are not equivalent and should not be used interchangeably to avoid confusion in the marketplace.

Unsubstantiated claims to biodegradability and compostability were common in the past as a consequence of the lack of well-identified testing methods and environmental requirements.

Three international standards (the European Standard EN 13432:2000, ISO 17088:2012, and the US Standard ASTM D6400, see references in Table 9.1) outline the same test schemes and lay down criteria for what can or cannot be described as compostable as regards plastics and products made from plastics under an aerobic and thermophilic environment, in municipal and industrial aerobic composting facilities. Logos and certificates issued by certification bodies allow demonstrating the conformity of a product with the standard compostability norms. False and misleading environmental claims are being pursued.

These standards are intended to ensure that the materials will break down in industrial composting conditions.

A compostable material must

1. be biodegradable, and this means that at least 90% of the materials have to be broken down biochemically within 6 months, into CO<sub>2</sub>, water, and minerals with the eventual production of biomass with the help of microorganisms. Biodegradability is determined by measuring the CO<sub>2</sub> produced by the sample under controlled composting conditions according to ISO 14855-1:2012 and ISO 14855-2:2018;
2. be disintegrable, and this involves the physical decomposition of a product into tiny pieces. After 12 weeks, at least 90% of the product should undergo a physical decomposition into tiny pieces and should be able to pass through 2 × 2 mm mesh; disintegration is evaluated at pilot-scale by simulating an authentic composting environment according to ISO 16929:2019;
3. have a chemical composition characterized by low levels of heavy metals (less than specified values for certain elements such as Zn, Cu, Ni, Cd, Pb, Hg, Cr, Mo, Se, As, Co) and of hazardous substances to the environment (such as F)
4. not be ecotoxic, which involves the absence of negative effects of the final compost in the environment.



**Table 9.1** Extract of latest standards in respect of biodegradability, disintegration, compostability

Standard	Title
ISO 14855-1:2012 (ISO 2012a)	Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions—Method by analysis of evolved carbon dioxide—Part 1: General method
ISO 14855-2:2018 (ISO 2018)	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
ISO 16929:2019 (ISO 2019a)	Plastics—Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test
ISO 20200:2015 (ISO 2015)	Plastics—Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test
ISO 14851:2019 (ISO 2019)	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—Method by measuring the oxygen demand in a closed respirometer
ISO 14852:2018 (ISO 2018)	Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium—Method by analysis of evolved carbon dioxide
ISO 17556:2019 (ISO 2019b)	Plastics—Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved
ISO 16221:2001 (ISO 2001)	Water quality—Guidance for determination of biodegradability in the marine environment
ISO 17088:2012 (ISO 2012b)	Specifications for compostable plastics
ISO 18606:2013 (ISO 2013)	Packaging and the environment—Organic recycling
EN 17033:2018 (CEN 2018)	Plastics—Biodegradable mulch films for use in agriculture and horticulture—Requirements and test methods
EN 14995:2006 (CEN 2006)	Plastics—Evaluation of compostability—Test scheme and specifications
EN 13432:2000 (CEN 2000)	Packaging—Requirements for packaging recoverable through composting and biodegradation—Test scheme and evaluation criteria for the final acceptance of packaging
ASTM D6400 – 19 (ASTM International 2019a)	Standard specification for labeling of plastics designed to be aerobically composted in municipal or industrial facilities
ASTM D5988-18 (ASTM International 2018a)	Standard test method for determining aerobic biodegradation of plastic materials in soil
ASTM D5929-18 (ASTM International 2018b)	Standard test method for determining biodegradability of materials exposed to source-separated organic municipal solid waste mesophilic composting conditions by respirometry
ASTM D6954-18 (ASTM International 2018c)	Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation

(continued)

**Table 9.1** (continued)

Standard	Title
ASTM D6691-17 (ASTM International 2017b)	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 D7991-15 (ASTM International 2015a)	Standard test method for determining aerobic biodegradation of plastics buried in sandy marine sediment under controlled laboratory conditions
ASTM D7475-20 (ASTM International 2020b)	Standard test method for determining the aerobic degradation and anaerobic biodegradation of plastic materials under accelerated bioreactor landfill conditions
ASTM D5526-18 (ASTM International 2018d)	Standard test method for determining anaerobic biodegradation of plastic materials under accelerated landfill conditions
ASTM D5511-18 (ASTM International 2018e)	Standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic-digestion conditions
ASTM D7473-12 (ASTM International 2012)	Standard test method for weight attrition of plastic materials in the marine environment by open system aquarium incubations
ASTM D5338-15 (ASTM International 2015b)	Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures

It is clear that for compostable materials, a high degree of biodegradation and disintegration is needed on specified limited time-scales, without any harmful effect of the compost quality on the environment (Imre and Pukánszky 2013). Actually, during biodegradation, it is important to focus on the fate of additives, including catalysts, fillers, and colorants, among others, used to optimize the technical properties of biodegradable plastics. They can be released via migration, leaching, emission, degradation, or fragmentation. Nevertheless, a comprehensive chemical analysis of heavy metals and any toxic chemicals embedded in such a complex matrix is difficult and expensive to achieve. Thus, the final compost might contain a mixture of plastic-derived chemicals.

It is clear that a biodegradable material may not be compostable, while every compostable material is at least biodegradable.

Biodegradation is possible only if monomers or specific additives are susceptible to a microbial attack via specific enzymatic processes. Biodegradation is linked to a significant change in the chemical structure of a material caused by biochemical (enzymatic and non-enzymatic) activity, while disintegration is the material breakdown into very small fragments (Su et al. 2019). The biodegradability is, in the first place, influenced by the chemical structure of the polymers; in particular, microorganisms cannot easily attack polymers with a C–C backbone (i.e., polyolefins). Polyesters are biodegradable, but the material structure (crystallinity, orientation, morphology, and shape) influences biodegradation and disintegration (Kim and Park 1999): for example, it is clear that amorphous or less-ordered regions degrade

more easily than crystalline regions. Under controlled conditions, the biodegradability of polymers can be tailored by the optimization of parameters, such as temperature, oxygen, and water content and the presence of specific microorganisms (EU 2018). The process is favored by darkness, high humidity, adequate minerals, and other nutrients. Biodegradation does not necessarily occur under all conditions. For example, anaerobic conditions in landfills usually prevent many biological processes necessary for mineralization. Enzymatic degradation starts from the polymers' surface because enzymes cannot penetrate the polymer, and degradation products with low molecular weights easily dissolve in the surrounding aqueous medium (Mochizuki and Hirami 1997). Actually, there are diverse environments for biodegradation, such as soil, water environments, digester plants, household composting units, and industrial composting facilities.

Polymers can also be degraded by photodegradation and thermal degradation. These different processes, along with biodegradation, can act either independently or in combination. Photodegradation is initiated by the absorption of light energy by reactive groups of the polymer, leading to smaller fragments. Similarly, heating of the polymer in the presence of oxygen results in thermo-oxidative degradation: bonds are broken down with the formation of radicals and volatiles.

While industrial composting conditions are characterized by elevated temperatures (55–60 °C) combined with high relative humidity, the presence of oxygen, and periodical mixing under standardized conditions, home-composting is an uncontrolled process strongly dependent on the geographical and climatological parameters as well as on individual actions taken by households and plastics claimed to be compostable may not be suitable for home composting (EU 2018). For this reason, there is no general standard for the biodegradability of plastics in these uncontrolled environments. For example, neat PLA needs industrial composting conditions at high temperatures for quick biodegradation and is not eligible for home composting or biodegradation in soil in a reasonable time frame. On the converse, PBS has the ability to biodegrade at ambient temperatures (<35 °C) (Nova-Institute 2019).

Worldwide, standards and draft standards for biodegradability, disintegration, and compostability of plastics under controlled parameters have been recently released and are illustrated in Table 9.1.

Biodegradable bioplastics were indicated in Fig. 6.1 of Chap. 6. It is clear that not all biobased products are biodegradable and compostable, and not all fossilbased plastics will not biodegrade or compost.

As regards polylactic acid, it can be recycled to its monomer by thermal depolymerization or hydrolysis; since it is a thermoplastic aliphatic polyester, it undergoes simple hydrolytic cleavage of the ester moieties of the polymer backbone with only a little or even no assistance from enzymes resulting in the formation of non-harmful and not toxic monomers (Pawar et al. 2014) but it can also be attacked by microorganisms. Heterogeneous PLA composting with small amounts (<30% by weight) of pre-composted yard waste was effective (Ghorpade et al. 2001). However, it has been emphasized that PLA does not biodegrade as fast as other organic wastes during composting, worsening its acceptance in industrial composting facilities; to enable its biodegradation in comparable time frames with other organic materials,

bioaugmentation, that is, the addition of specific microbial strains such as *Geobacillus thermoleovorans*, proved to be a promising technique to accelerate the biodegradation of compostable plastics (Castro-Aguirre et al. 2018). PLA composite and blends were also explored to increase PLA biodegradability. PLA/PHA blends (Zembouai et al. 2014) were investigated with the aim of obtaining a wide range of physical properties and improved processibility (Ohkoshi et al. 2000), but, above all, to increase both the biocompatibility and biodegradability of neat PLA and the thermal stability of neat PHA. The compatibility of PLA/PHBH blends was enhanced using a reactive epoxy as a bifunctional compatibilizer (Zhou et al. 2015), but the poor toughness is still the major drawback. The hydrophobicity of PLA partly impairs its biodegradability. PLA was blended with more hydrophilic polymers, such as starch, chitosan, and cellulose to enhance biodegradability. Contrasting results as regards the PHA/PLA blends were reported, while faster degradation in soil was noticed for PLA/PBS blends (Hubbe et al. 2021).

Polybutylene succinate (PBS) is a bioplastic that biodegrades into water and carbon dioxide with the microorganism under the soil. It was found that *Amycolatopsis* sp. HT-6 and *Penicillium* sp. strain 14-3 are able to degrade PBS. Several thermophilic actinomycetes such as *Microbispora rosea*, *Excellospora japonica* and *E. viridilutea* can degrade samples of emulsified PBS (Tokawa et al. 2009). The biodegradability of PHA and of various blends of different types of PHA makes them good candidates in the packaging and biomedical sectors (Koller 2018).

Polyglycolic acid (PGA) biodegradability into nontoxic compounds is particularly appreciated in biomedical applications even if removal of the tin (II) based catalyst is needed since it is known to be toxic (Budak et al. 2020).

Actually, in various circumstances, composite production aimed at obtaining a material with improved biodegradability; for example, dried distillers grains with solubles, a major co-product of the bioethanol industry, have been used for the production of “green” composites with enhanced biodegradability, using biodegradable poly(butylene adipate-co-terephthalate) (PBAT) and PHAs as polymer matrices (Muniyasamy et al. 2013; Madbouly et al. 2014). A fully biodegradable PLA/PBS composite reinforced with wood flour (Ludwiczak et al. 2019) is another example of this largely used strategy.

## 9.6 Determination of the Biobased Carbon Content

The market chain is strongly interested in showing that the material is indeed based on recently living organic matter. A renewable resource is something that is replenish to replace the portion depleted at a rate that exceeds depletion according to ASTM E2114 (ASTM International 2019b). A biobased material is an organic substance in which carbon derives from carbon dioxide recently fixed via photosynthesis in a renewable resource. Biobased materials can be both plant-based and animal-based. The quantification of the biobased carbon content of a product is crucial in assessing the renewability of the naturally replenished supply used to

produce it. This is essential because a specific building block may be fossilbased or biobased, as in the case of drop-in platform molecules.

The determination of the biobased carbon content can be accomplished, taking into account that  $^{14}\text{C}$  is only found in biobased materials: renewable carbon was directly in equilibrium with  $\text{CO}_2$  in the atmosphere at the time of harvesting of a crop. On the converse,  $^{14}\text{C}$  can not be found in fossil fuels because it has a half-life of about 5700 years. It follows that the relative  $^{14}\text{C}$  levels are proportional to the biomass content of the material. Standard Test Methods for discriminating between carbon resulting from contemporary input and that derived from fossilbased input are described in ASTM D6866 (ASTM International 2021). These test methods apply to any product that can be combusted in the presence of oxygen to produce  $\text{CO}_2$  gas. Radioactive-isotope analysis can determine the proportion of carbon in a material's organic compounds that comes from recently living, non-petroleum sources, even if the original biobased material has been chemically, thermally, or physically modified.

## 9.7 Chemical Compatibility

Both packaging and recent high-profile uses of bioplastics formulated into durable automotive, electronics, and consumer goods necessitate chemical compatibility of the material with the intended environment. Testing related to chemical compatibility is crucial. A current test used for plastics, such as ASTM D543 (ASTM International 2020c), is usually adopted for evaluating the resistance to chemical reagents. Prediction of the actual performance on the basis of test results depends upon the similarity between the testing and the end-use conditions. The effect of chemical reagents on sample properties shall be established by making measurements on standard specimens suitable for the described tests before and after immersion or stress, or both. Fluids can affect plastics by attacking chemically or absorbing into critical zones. Chemically reactive fluids can cause chain scission, chemical modification, and cross-linking by hydrolysis and oxidation. Adsorption of chemicals into micro-yielded or stress-dilated zones weakens mechanical strength (Wright 1996). Crystallinity obviously improves chemical resistance. The selection of test conditions (manner and duration of contact with reagents, temperature of the system, applied stress, and other factors) should mimic those encountered in the particular application. Unfortunately, while chemical compatibility charts are available for fossilbased plastics, literature data are very scarce as regards bioplastics (Heikkinen et al. 2018); the chemical resistance of PBS, biobased polyamides, and biobased polyethylene terephthalate was graded good as that of petroleum-based plastic, while that of PLA, PHA, and thermoplastic starch was rated poor (Zhao et al. 2020).

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