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Review

Polymer biodegradation: Mechanisms and estimation techniques

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ABSTRACT

Within the frame of the sustainable development, new materials are being conceived in order to increase their biodegradability properties. Biodegradation is considered to take place throughout three stages: biodeterioration, biofragmentation and assimilation, without neglect the participation of abiotic factors. However, most of the techniques used by researchers in this area are inadequate to provide evidence of the final stage: assimilation. In this review, we describe the different stages of biodegradation and we state several techniques used by some authors working in this domain. Validate assimilation (including mineralisation) is an important aspect to guarantee the real biodegradability of items of consumption (in particular friendly environmental new materials). The aim of this review is to emphasise the importance of measure as well as possible, the last stage of the biodegradation, in order to certify the integration of new materials into the biogeochemical cycles. Finally, we give a perspective to use the natural labelling of stable isotopes in the environment, by means of a new methodology based on the isotopic fractionation to validate assimilation by microorganisms.

Contents

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1. Introduction

The respect of the environment is a capital point in a sustainable development context. We should act in this way to preserve fossil resources and reduce the pollution of the Earth. The fabrication of industrial products must consume less energy and the raw materials must be in priority renewable resources, in particular from agricultural origins.

Currently, two approaches are explored to minimise the impact of the usage of polymers on the environment:

- The design of polymeric materials for long duration (e.g. aeronautic devices, construction materials, coatings and containers), these materials must combine unalterability and be fashioned preferentially from renewable resources (e.g. plant oil in thermoset, wood fiber in composites materials) (Wuambua et al., 2003; Mougin, 2006; Sudin and Swamy, 2006; Ashori, 2008). This kind of materials of industrial interest and low environmental impact is not within the aim of this review due to a minor biodegradability.
- Technological innovations designed for the production of polymers for short duration (e.g. disposable packages, agricultural mulches, horticultural pots, etc.) (Bastioli, 1998; Chandra and Rustgi, 1998; Lörcks, 1998; Lunt, 1998; Averous and Le Digabel, 2006) must have the intention of fast biodegradability. Most biodegradable polymers belong to thermoplastics (e.g. poly(lactic acid), poly(hydroxyalkanoate), poly(vinyl alcohol)) or plants polymers (e.g. cellulose and starch). Thermoplastics from polyolefins are not biodegradable, even if some of them have prooxidant additives making them photo and/or thermodegradable, the assimilation of oligomers or monomers by microorganims is not yet totally proved.

This dichotomy between durable and biodegradable polymers is not obvious. In recent years, innovating experiments are realised to combine both approaches, the results are the production of polymeric materials with controlled life spans. The designed materials must be resistant during their use and must have biodegradable properties at the end of their useful life. A possibility to obtain interesting results is to co-extrude natural and artificial polymers, in order to combine the properties of each macromolecule to obtain the desired properties (Muller et al., 2001; Shibata et al., 2006). Today, a fast-growing industrial competition is established for the production of a great variety of controlled life span materials. It is important to develop new comparative tests to estimate their biodegradability. Actually, it seems to have confusion in the interpretation of biodegradation, biofragmentation and biodeterioration. Hereafter, we are giving attention to the meaning of polymer biodegradation.

Earlier, biodegradation was defined as a decomposition of substances by the action of microorganisms. This action leads to the recycle of carbon, the mineralisation (CO_2, H_2O and salts) of organic compounds and the generation of new biomass (Dommergues and Mangenot, 1972). At present, the complexity of biodegradation is better understood and cannot be easily summarised (Grima, 2002; Belal, 2003). The biodegradation of polymeric materials includes several steps and the process can stop at each stage (Pelmont, 1995) (Fig. 1)

- The combined action of microbial communities, other decomposer organisms or/and abiotic factors fragment the biodegradable materials into tiny fractions. This step is called biodeterioration (Eggins and Oxley, 2001; Walsh, 2001).
- Microorganisms secrete catalytic agents (i.e. enzymes and free radicals) able to cleave polymeric molecules reducing progressively their molecular weight. This process generates oligomers, dimers and monomers. This step is called depolymerisation.
- Some molecules are recognised by receptors of microbial cells and can go across the plasmic membrane. The other molecules stay in the extracellular surroundings and can be the object of different modifications.
- In the cytoplasm, transported molecules integrate the microbial metabolism to produce energy, new biomass, storage vesicles and numerous primary and secondary metabolites. This step is called assimilation.
- Concomitantly, some simple and complex metabolites may be excreted and reach the extracellular surroundings (e.g. organic acids, aldehydes, terpens, antibiotics, etc.). Simple molecules as CO_2, N_2, CH_4, H_2O and different salts from intracellular metabolites that are completely oxidised are released in the environment. This stage is called mineralisation.

The term "biodegradation" indicates the predominance of biological activity in this phenomenon. However, in nature, biotic and abiotic factors act synergistically to decompose organic matter. Several studies about biodegradation of some polymers show that the abiotic degradation precedes microbial assimilation

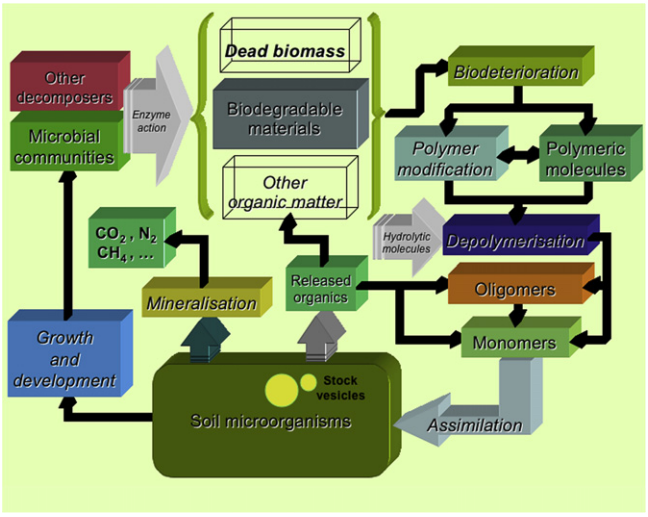

Fig. 1. Polymer biodegradation scheme.

(Kister et al., 2000; Proikakis et al., 2006). Consequently, the abiotic degradation must not be neglected.

Herein, we describe the different degrees of the biodegradation process: biodeterioration, biofragmentation and assimilation including the abiotic involvement. Each mechanism is illustrated by an example. Furthermore, we suggest the technical estimation adapted to each level of biodegradation.

2. Abiotic involvement

Polymeric materials that are exposed to outdoor conditions (i.e. weather, ageing and burying) can undergo transformations (mechanical, light, thermal, and chemical) more or less important. This exposure changes the ability of the polymeric materials to be biodegraded. In most cases, abiotic parameters contribute to weaken the polymeric structure, and in this way favour undesirable alterations (Helbling et al., 2006; Ipekoglu et al., 2007). Sometimes, these abiotic parameters are useful either as a synergistic factor, or to initiate the biodegradation process (Jakubowicz et al., 2006). It is necessary to study the involvement of the abiotic conditions for a better estimation of the durability of polymeric materials.

2.1. Mechanical degradation

Mechanical degradation can take place due to compression, tension and/or shear forces. The causes of these forces are numerous, e.g. a range of constraints during material installation, ageing due to load, air and water turbulences, snow pressure and bird damages. So, thermoplastic films can undergo several mechanical degradations under field conditions (e.g. low-tunnel films, mulches, etc.) (Briassoulis, 2004,2006,2007).

Frequently, at the macroscopic level, damages are not visible immediately (Duval, 2004), but at the molecular level degradation could started.

Mechanical factors are not predominant during biodegradation process, but mechanical damages can activate it or accelerate it (Briassoulis, 2005). In field conditions, mechanical stresses act in synergy with the other abiotic parameters (temperature, solar radiations and chemicals).

2.2. Light degradation

Several materials are photosensitive. The energy carried by photons can create unstable states in various molecules. Energy transfer can be accomplished by photoionisation, luminescence, fluorescence, thermal radiation. Sometimes, involuntarily, the resistance of the material can be affected by impurities that are present in manufactured products. In other cases, photosensitive molecular structures are added intentionally (i.e. by simple addition or copolymerisation) into the polymer framework to induce a macromolecular degradation by light (e.g. prooxidants agents that can be activated depending on the light intensity and time exposure) (Kounty et al., 2006; Wiles and Scott, 2006). This strategy is used by polyolefin manufacturers to enhance degradability of plastic bags, packaging, agricultural films, etc. (Weiland et al., 1995; Schyichuk et al., 2001).

In abiotic degradation, the action of light radiation is one of the most important parameters. The Norrish reactions express photodegradation that transform the polymers by photoionisation (Norrish I) and chain scission (Norrish II). Photodegradation can conduce to Norrish reactions, and/or crosslinking reactions, or oxidative processes (Nakamura et al., 2006). Norrish II reaction has been recently described during photodegradation of PLA (poly[lactic acid]) and PCL (poly[caprolactone]) (Tsuji et al., 2006). Kijchavengkul et al. (2008) have found crosslinking reactions that are responsible of the brittleness of PBAT (poly[butylene adipate terephtalate]).

2.3. Thermal degradation

Thermal degradation of thermoplastic polymers occurs at the melting temperature when the polymer is transformed from solid to liquid (e.g. 159–178 °C for L-PLA depending on its molecular weight, 137–169 °C for P(HB/HV) (poly[hydroxybutyrate-*co*-hydroxyvalerate]) depending on the percentage of hydroxyvalerate, 175 °C for PHB (poly[hydroxybutyrate]) (Ojumu et al., 2004). Generally, the environmental temperature is lower than the melting point of thermoplastic polymers. However, some thermoplastic polymers as PCL ($t_m \approx 60$ °C) or composite materials as MaterBi® ($t_m \approx 64$ °C) exhibit melting temperatures near to environmental conditions. This is the case for the thermophile stage of composting.

Otherwise, temperature may influence the organisation of the macromolecular framework. Biodegradable polymers such as L-PLA, PCL, PBA (poly[butylene adipate]) or cellulose are semicrystalline polymers, they possess amorphous and crystalline regions (Wyart, 2007). Structural changes take place at their glass transition temperature (T_g) (e.g. 50 °C for L-PLA, 25 °C for PBT (poly[butylene terephtalate]), 5 °C for PHB, −10 to −45 °C for PBS (poly[butylene succinate])), the mobility and the volume of the polymeric chains are modified. Above T_g (rubbery state), the desorganisation of chains facilitate the accessibility to chemical and biological degradations (Iovino et al., 2008). Under T_g (glassy state), the formation of spherulites may take place, generating interspherulitic cracks and the brittleness of the thermoplastics polymers (El-Hadi et al., 2002).

Industrial thermoplastics have different properties depending on the nature and percentage of monomers that produce the final copolymeric material. Within the crystalline regions, there exist a polymorphism of crystals that can influence the biodegradation (Zhao and Gan, 2006). For instance, PBA contain two forms of crystals, α and β, a temperature above 32 °C favours the α-form, a temperature below 27 °C favours the β-form and between 27 °C and 32 °C, α and β crystals are mixed (Zhao et al., 2007). α crystals show a faster hydrolysis by the action of lipase from *Pseudomonas* sp. (Gan et al., 2005).

Some authors (Bikiaris et al., 1997a,b) assert that LDPE thermoplastics show a thermooxidative biodegradability by adding prooxidants (soaps of transition metals such as Zn, Cu, Ag, Co, Ni, Fe, Mn, Cr and V).

Also, the same research group (Bikiaris and Karayannidis, 1999) reports the acceleration of the formation of free radicals due to the presence of carboxylic end groups within copolymeric thermoplastics (PET (poly[ethylene terephtalate]) and PBT), these free radicals favour the thermochemical degradability of these plastics.

2.4. Chemical degradation

Chemical transformation is the other most important parameter in the abiotic degradation. Atmospheric pollutants and agrochemicals may interact with polymers changing the macromolecule properties (Briassoulis, 2005). Among the chemicals provoking the degradation of materials, oxygen is the most powerful. The atmospheric form of oxygen (i.e. O_2 or O_3) attacks covalent bonds producing free radicals. The oxidative degradation depends on the polymer structure (e.g. unsaturated links and branched chains) (Duval, 2004). These oxidations can be concomitant or synergic to light degradation to produce free radicals. Like the products of Norrish reactions, peroxyl radicals resulting of the oxidative degradation can lead to crosslinking reactions and/or chain scissions.

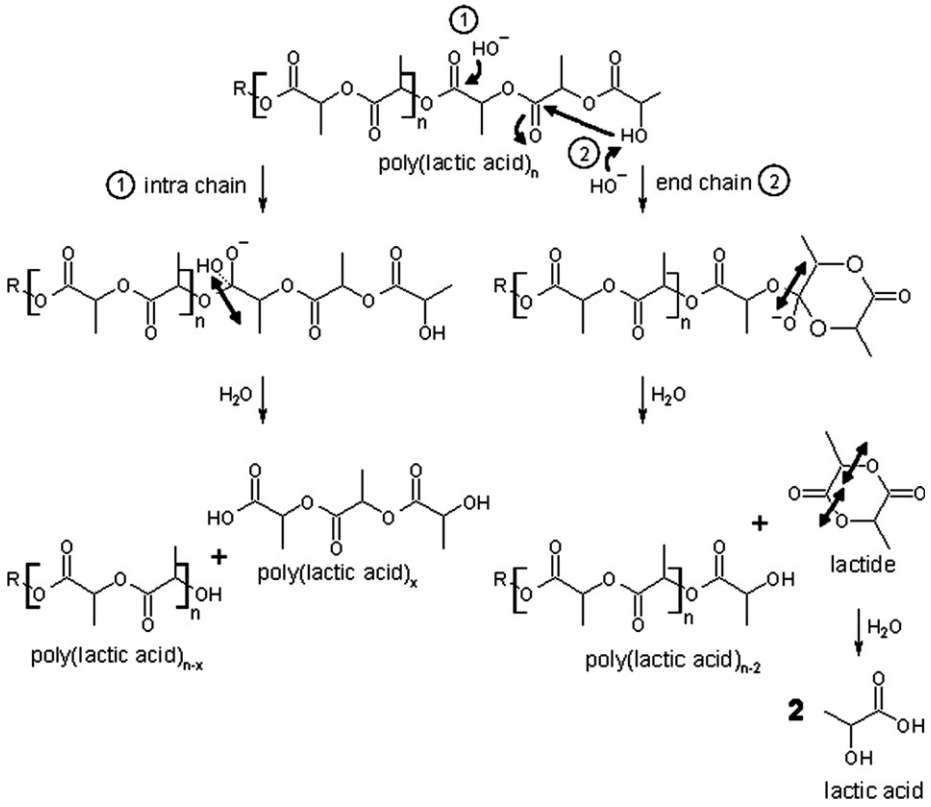

Fig. 2. PLA hydrolysis in alkaline conditions.

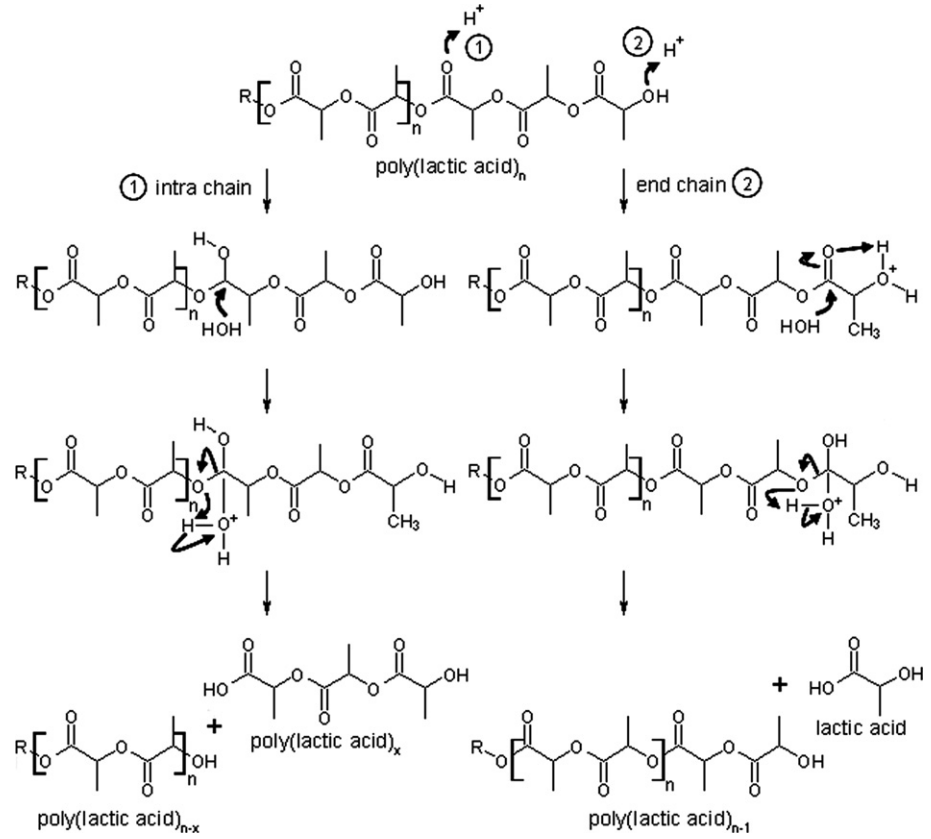

Fig. 3. PLA hydrolysis in acidic conditions.

Table 1
(Bio)degradability tests summary

Tests	Norms	Characteristics		Estimating			
		Difficulty	Reality	AB[a]	BD[b]	BF[c]	A[d]
Out-door exposure		+	++++	X	X		
UV exposure	ISO 4582	+	++	X			
Suntest	ISO 4892 series	+	++	X			
Accelerated weathering chamber		++	+++	X			
Differential scanning calorimetry		++	+	X			
Thermogravimetric analysis		++	+	X			
Pyrolysis		++	+	X			
Microorganisms surface colonisation	ISO 846 ISO 11266 NF X41-513 NF X41-514 ASTM G22-76 ASTM G21-70 ASTM G21-90	+++	+++		X	X	
Weight loss	ISO 14852 ISO 14855 NF EN ISO 13432	+	+	X	X	X	
Significant enzymes in batch		++	++		X	X	
Clear zone test		+++	+++		X	X	
Respirometry	OECD series, ISO 14852, ISO 14855 ASTM D 5209	++	++				X

[a] Abiotic degradation.
[b] Biodeterioration.
[c] Biofragmentation.
[d] Assimilation.

Hydrolysis is another way by which polymers can undergo chemical degradation (Muller et al., 1998; Tsuji and Ikada, 2000; Yi et al., 2004). To be split by H_2O, the polymer must contain hydrolysable covalent bonds as in groups ester, ether, anhydride, amide, carbamide (urea), ester amide (urethane) and so forth. Hydrolysis is dependent on parameters as water activity, temperature, pH and time. The design of materials with controlled life span needs the choice of specific monomers to obtain a copolymer with the wanted hydrophilic characteristics (Le Digabel and Averous, 2006; Yew et al., 2006).

Well organised molecular frameworks (crystalline domains) prevent the diffusion of O_2 and H_2O, limiting in this way the chemical degradation. Oxidative and hydrolytic degradations on a given material are more easily performed within desorganised molecular regions (amorphous domains).

2.4.1. PLA hydrolysis is a good illustration to explain the mechanism of an abiotic chemical degradation

PLA degradation occurs in the presence of water provoking a hydrolysis of the ester bonds. PLA, as well as, PCL or PPC (poly[propylene carbonate]) have a slow degradability in neutral conditions and they show a higher degradability in basic conditions than acidic ones (Jung et al., 2006).

De Jong et al. (2001) observed PLA depolymerisation by a progressive release of dimers in alkaline conditions (Fig. 2). The end-chain degradation may be explained by an intramolecular transesterification. An electrophilic attack, catalysed by a base, of the hydroxyl end-group on the second carbonyl group leads to a ring formation. The polymer is shortened by the hydrolysis of the resulting lactide. In a second step, the free lactide is hydrolysed into two molecules of lactic acid. The intramolecular degradation occurs by a random alkaline attack on the carbon of the ester group, followed by the hydrolysis of the ester link. Thus, new molecules with low molecular weight are produced.

In acidic conditions (Fig. 3), the protonation of the hydroxyl end-group forms an intramolecular hydrogen bond. The hydrolysis of the ester group allows the release of a lactic acid molecule leading to the decrease of the degree of polymerisation of the PLA. An intramolecular random protonation of carbon of the ester group conduces also to the hydrolysis of ester linkages. This hydrolysis gives different fragments of lower molecular weights.

2.5. How can we estimate the abiotic degradation?

2.5.1. Photodegradation

Photodegradation is the most efficient abiotic degradation occurring on the environment. Different experiments are used to test the effects of the polymer exposure to sunlight (Table 1). The less expensive, easier to realise and closer to the real conditions is an outdoor exposure (Abd El-Rehim et al., 2004). Photodegradation experiments, easy to carry out and not expensive, can be also realised under laboratory UV exposure (ISO 4582; ASTM D5208-01; Krzan et al., 2006). Shyichuk et al. (2004) have introduced a model, the Molecular Weight Distribution Computer Analysis (MWDCA), based on the ISO 4582 test. A device named "suntest" (ISO 4892 series; ASTM D5071-99; Krxan et al., 2006) exists: the most used version involves the irradiation of polymer materials by a xenon lamp (Briassoulis, 2005; Nagai et al., 2005; Morancho et al., 2006; Luengo et al., 2006). The most expensive test is "The Accelerated Weathering Chamber" that exposes the polymer materials to accelerated atmospheric conditions. With this aim, cyclic programs can control parameters (i.e. irradiation, temperature and humidity) to simulate real conditions (Tsuji et al., 2006).

Table 2
(Bio)degradability estimation: analytical techniques

Analytical techniques	Norms	Characteristics		Estimating			
		Cost	Difficulty	AB	BD	BF	A
Morphological							
Yellowness	ASTM D 1925	+	+	X			
Photonic microscopy		++	++	X	X		
Electronic microscopy		++++	++++	X	X		
Polarization microscopy		+++	++	X	X		
Rheological							
Tensile	ISO 527-3	++	+	X	X	X	
X-ray diffraction		++++	+++	X	X	X	
Differential scanning calorimetry		++++	++	X	X	X	
Thermogravimetric analysis		++++	++	X	X	X	
Gravimetric		+	+	X	X	X	
Spectroscopic							
Fluorescence		++	++	X	X	X	
UV–visible		+	+	X	X	X	
FTIR		++	++	X	X	X	
RMN		++++	++	X	X	X	
Mass spectrometry		++++	+++	X	X	X	
Chromatographic							
Gel permeation chromatography		+++	++	X	X	X	
Hight performance Liquid chromatography		+++	++	X	X	X	
Gas phase chromatography		+++	++	X	X	X	

Complementary analytical techniques (Table 2) are necessary to evaluate photodegradation. Colour modifications of the polymer surface may be estimated by the yellowness index (ASTM D 1925, 1988). Tensile tests (strength, elongation at break) are used to investigate mechanical changes during the degradation (ISO 527-3, ASTM D 882, 2002). The crystallinity degree may be estimated by X-ray diffraction. Thermal properties as glass transition, cold crystallisation and/or melting point are estimated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Since UV radiation produces polymer fragments, the molecular weight of the released fragments are revealed by gel permeation chromatography (GPC). Spectroscopic analysis (Fourier transform infra-red (FTIR), fluorescence, nuclear magnetic resonance (NMR), mass spectrometry (MS)) are regularly used to reveal chemical modifications of the polymer structure. Gravimetric measures are frequently used, but loss of weight is often insignificant, so, they are associated to the techniques described above.

2.5.2. Thermodegradation

Differential scanning calorimetry (DSC) is used to study the thermal transitions of polymers. These changes take place when a polymer is heated. The melting and glass transition temperatures of a polymer are examples of thermal transitions. These transitions up to complete pyrolysis (Table 1) using GC–MS have been observed by Kim et al. (2006a) and Bikiaris et al. (2007), they have shown that the thermal degradation of aliphatic polyesters is a mechanism of α or β hydrogen bond scission. The different steps of pyrolysis are better followed by TGA (Fan et al., 2004).

Actually, the analytical techniques used to estimate the thermodegradation are very similar to those that are used for the estimation of photodegradation (i.e. tensile tests, TGA, GPC, FTIR, NMR and GC–MS) (Bikiaris et al., 1997a,b; Bikiaris and Karayannidis, 1999; Zaharescu, 2001; Fan et al., 2004; Chrissafis et al., 2005, 2006a; Averous and Le Digabel, 2006; Kim et al., 2006a).

2.5.3. Chemodegradation

The abiotic hydrolysis is performed in acidic (HCl and H_2SO_4) or alkaline (NaOH) media (Yu et al., 2005; Jung et al., 2006). The analysis of the residual monomers and released fragments is realised by the same techniques mentioned previously (i.e. GPC, weight loss, DSC, TGA, FTIR and NMR). Otherwise, aqueous media give the possibility to investigate the presence of different oligomers by HPLC or by GPC.

Scaffaro et al. (2008) have developed and patented a new equipment that is able to perform gradual tests of the behaviour of polymers by combining the effects of loads, UV exposure, temperature and humidity. These parameters can be varied in order to reproduce and simulate different environmental conditions.

All these varied techniques may estimate the transformations of a given polymeric material, but they cannot demonstrate the assimilation of the modified polymer by microorganisms.

3. Biodeterioration

Deterioration is a superficial degradation that modifies mechanical, physical and chemical properties of a given material. Abiotic effects provoking deterioration are described above. This section focuses on the biological aspects of deterioration.

The biodeterioration is mainly the result of the activity of microorganisms growing on the surface or/and inside a given material (Hueck, 2001; Walsh, 2001). Microorganisms act by mechanical, chemical and/or enzymatic means (Gu, 2003).

Microbial development depends on the constitution and the properties of polymer materials. The specific environmental conditions (e.g. humidity, weather and atmospheric pollutants) are also important parameters (Lugauskas et al., 2003). Microorganisms involved in biodeterioration are very diverse and belong to bacteria, protozoa, algae, fungi and lichenaceae groups (Wallström et al., 2005). They can form consortia with a structured organisation called biofilms (Gu, 2003). This microbial mat, that works in synergy, provokes serious damages on different materials (Gu et al., 1996a,b, 1997, 1998a,b, 2007; Flemming, 1998). The development of different microbial species, in a specific order, increases the biodeterioration facilitating in this way the production of simple molecules. All these substances act as carbon and nitrogen sources, as well as growth factors for microorganisms (Crispim and Gaylarde, 2005). Recent studies show that atmospheric pollutants are potential sources of nutrients for some microorganisms (Zanardini et al., 2000; Nuhoglu et al., 2006). Mitchell and Gu (2000) report the deposition of sulphur dioxide, aliphatic and aromatic hydrocarbons from the urban air on several polymer materials. These adsorbed pollutants may also favour the material colonisation by other microbial species. Organic dyes are also potential nutrients for these microorganisms (Tharanathan, 2003; Faÿ et al., 2007).

3.1. Physical way

Microbial species can adhere to material surfaces due to the secretion of a kind of glue (Capitelli et al., 2006). This substance is a complex matrix made of polymers (e.g. polysaccharides and proteins). This slime matter infiltrates porous structures and alters the size and the distribution of pores and changes moisture degrees and thermal transfers. The function of the slime matrix is to protect microorganisms against unfavourable conditions (e.g. desiccation and UV radiations). Filamentous microorganisms develop their mycelia framework within the materials. The mechanical action of apices penetrating the materials increases the size of pores and provokes cracks. Thus, the resistance and durability of the material is weakened (Bonhomme et al., 2003).

3.2. Chemical way

The extracellular polymers produced by microorganisms can act as surfactants that facilitate the exchanges between hydrophilic and hydrophobic phases. These interactions favour the penetration rate of microbial species. Moreover, according to Warscheid and Braams (2000), the presence of slime increases the accumulation of atmospheric pollutants, this accumulation favour the development of microorganisms and accelerate the biodeterioration (Zanardini et al., 2000).

Each kind of microbial flora developing successively into the materials contributes to the chemical biodeterioration. Chemolithotrophic bacteria use inorganic compounds (e.g., ammonia, nitrites, hydrogen sulphide, thiosulphates and elementary sulphur) as energy and electron sources (Regnault, 1990). They can release active chemicals as nitrous acid (e.g. *Nitrosomonas* spp.), nitric acid (e.g. *Nitrobacter* spp.) or sulphuric acid (e.g. *Thiobacillus* spp.) (Warscheid and Braams, 2000; Roberts et al., 2002; Crispim and Gaylarde, 2005; Rubio et al., 2006). Chemoorganotrophic microorganisms use organic substrates as carbon, energy and electron sources (Alcamo, 1998; Pelmont, 2005). They release organic acids as oxalic, citric, gluconic, glutaric, glyoxalic, oxaloacetic and fumaric acids (Jenings and Lysek, 1996).

Succinic acid, adipic acid, lactic acid and others, as well as, butanediol are released by abiotic and/or biotic hydrolysis of several polymers (e.g. PBS, PBA and PLA) (Göpferich, 1996; Lindström et al., 2004b; Trinh Tan et al., 2008). Water enters in the polymer matrix, which might be accompanied by swelling. The intrusion of water initiates the hydrolysis of the polymer, leading to the creation of oligomers and monomers. Progressive degradation changes the microstructure of the matrix due to the formation of pores, then oligomers and monomers are released. Concomitantly,

the pH inside pores is modified by the degradation products, which normally have some acid–base characteristics (Göpferich, 1996).

These acids have various ways of action. Some can react with components of the material and increase the erosion of the surface (Lugauskas et al., 2003). Other can sequestrate cations present into the matrix (e.g. Ca^{2+}, Al^{3+}, Si^{4+}, Fe^{2+}, Mn^{2+} and Mg^{2+}) to form stable complexes. Organic acids are more efficient than mineral acids to fix cations. They are considered as one of the main causes of biodeterioration (Warscheid and Braams, 2000). Also, some microorganisms as filamentous bacteria and fungi are able to use these organic acids as carbon sources to extend their mycelia framework (cf. § physical way) (Hakkarainen et al., 2000).

Chemical biodeterioration may also be the result of oxidation processes. Some chemolithotrophic bacteria and some fungi can uptake iron and/or manganese cations from the matrix by oxidation reactions. They use specific proteins located into cellular membranes that trap siderophores (i.e. iron chelating compounds secreted by other microorganisms) to recover iron atoms (Pelmont, 2005). Redox reactions can take place with siderophores in the presence of oxygen within photosynthetic structures. Some extracellular enzymes, in particular the peroxidases, are able to couple the oxidation of cations and the catalytic degradation of hydrocarbons (Enoki et al., 1997; Zapanta and Tien, 1997; Hofrichter, 2002; Otsuka et al., 2003).

3.3. Enzymatic way

Some materials considered as recalcitrant polymers (e.g. polyurethane, polyvinylchloride and polyamide) are nevertheless subject to microbial biodeterioration (Shimao, 2001; Howard, 2002; Szostak-Kotowa, 2004; Shah et al., 2008). The microbial vulnerability of these polymers is attributed to the biosynthesis of lipases, esterases, ureases and proteases (Flemming, 1998; Lugauskas et al., 2003). Enzymes involved in biodeterioration require the presence of cofactors (i.e. cations present into the material matrix and coenzymes synthesised by microorganisms) for the breakdown of specific bonds (Pelmont, 2005).

The biodeterioration of thermoplastic polymers could proceed by two different mechanisms, i.e., bulk and surface erosion (von Burkersroda et al., 2002; Pepic et al., 2008). In the case of bulk erosion, fragments are lost from the entire polymer mass and the molecular weight changes due to bond cleavage. This lysis is provoked by chemicals (e.g. H_2O, acids, bases, transition metals and radicals) or by radiations but not by enzymes. They are too large to penetrate throughout the matrix framework. While in surface erosion, matter is lost but there is not change in the molecular weight of polymers of the matrix. If the diffusion of chemicals throughout the material is faster than the cleavage of polymer bonds, the polymer undergoes bulk erosion. If the cleavage of bonds is faster than the diffusion of chemicals, the process occurs mainly at the surface of the matrix (von Burkersroda et al., 2002; Pepic et al., 2008). Some authors describe erosion mechanisms of polymers: surface erosion for aliphatic–aromatic copolyesters (Muller, 2006), PHB (Tsuji and Suzuyoshi, 2002) and polyanhydrides (Göpferich and Tessmar, 2002); and bulk erosion for PLA and PLGA (Siepmann and Göpferich, 2001).

3.4. How can we estimate polymer biodeterioration?

Several methods can be used

(a) The evaluation of macroscopic modifications in the materials, i.e. roughening of the surface, formation of holes and cracks, changes in colour, development of microorganisms over the surface, etc. (Lugauskas et al., 2003; Rosa et al., 2004; Bikiaris et al., 2006; Kim et al., 2006b). There exist normalised tests to estimate the biodeterioration by the colonisation of microorganisms on Petri dishes (ASTM G21-70, ASTM G22–76, ISO 846, NF X41-514, NF X41-513, ISO 11266; Krzan et al., 2006). A positive result of the test is considered as an argument indicating the consumption of the polymer by the microbial species. Notwithstanding, since microorganisms are able to use reserve substances and other molecules as impurities; this result cannot be accepted as an irrefutable conclusion. In this way, different microscopic techniques are used to refine the analysis: photonic microscopy (Tchmutin et al., 2004), electronic microscopy (Hakkarainen et al., 2000; Peltola et al., 2000; Ki and Park, 2001; Preeti et al., 2003; Zhao et al., 2005; Kim et al., 2006b; Marqués-Calvo et al., 2006; Tserki et al., 2006) and/or polarisation microscopy (Tsuji et al., 2006). Atomic force microscopy can be used to observe the surface topology of the polymer (Chanprateep et al., 2006).

(b) The measure of the weight loss is frequently used for the estimation of biodegradability. This method is standardised for in situ biodegradability tests (NF EN ISO 13432, ISO 14852; Krzan et al., 2006, ISO 14855 Krzan et al., 2006). Actually, the measure of the weight loss of samples even from buried materials is not really representative of a material biodegradability, since this loss of weight can be due to the vanishing of volatile and soluble impurities.

(c) Internal biodeterioration can be evaluated by change of rheological properties (Van de Velde and Kiekens, 2002). Tensile strength is measured with a tensile tester (Ratto et al., 1999; Kim et al., 2006b; Tsuji et al., 2006), elongation at break by a mechanical tester (Tserki et al., 2006), elongation percentage and elasticity by dynamic mechanical thermal analysis (Domenek et al., 2004). Most studies on polymer biodegradation describe the thermal evolution by using the differential scanning calorimeter that gives the glass transition temperature (T_g), cold crystallisation temperature (T_{cc}) and/or melting temperature (T_m), (Weiland et al., 1995; Ratto et al., 1999; Hakkarainen et al., 2000; Ki and Park, 2001; Abd El-Rehim et al., 2004; Rizzarelli et al., 2004; Marten et al., 2005; Zhao et al., 2005; Bikiaris et al., 2006; Kim et al., 2006b; Morancho et al., 2006; Tserki et al., 2006; Tsuji et al., 2006). Crystallinity is determined by X-ray diffraction (Ki and Park, 2001; Abd El-Rehim et al., 2004; Gan et al., 2004; Rizzarelli et al., 2004; Bikiaris et al., 2006; Tserki et al., 2006) (Table 2).

(d) Product formation can also be used as an indicator of biodeterioration. For instance the production of glucose can be followed to assert the degradation of polymeric materials containing cellulose (Aburto et al., 1999). In addition, Lindström et al. (2004) have measured the biodeterioration of PBA and PBS by the quantification of the production of adipic acid, succinic acid and 1,4-butanediol.

4. Biofragmentation

Fragmentation is a lytic phenomenon necessary for the subsequent event called assimilation (cf. § Assimilation). A polymer is a molecule with a high molecular weight, unable to cross the cell wall and/or cytoplasmic membrane. It is indispensable to cleave several bonds to obtain a mixture of oligomers and/or monomers. The energy to accomplish scissions may be of different origins: thermal, light, mechanical, chemical and/or biological. The abiotic involvement was described previously. This section focuses on the biological aspect of fragmentation. Microorganisms use different *modi operandi* to cleave polymers. They secrete specific enzymes or generate free radicals.

Enzymes are catalytic proteins that decrease the level of activation energy of molecules favouring chemical reactions. These proteins have a wide diversity and a remarkable specificity, but they are easily denatured by heat, radiations, surfactants, and so forth (Weil, 1994). Endopeptidase, endoesterases accomplish their catalytic action along the polymer chain whereas exoenzymes catalyse reactions principally at the edges. Constitutive enzymes are synthesised during all the cellular life, independently of the presence of specific substrates. Inducible enzymes are produced when a molecular signal due to the presence of a specific substrate is recognised by the cell. In this case, enzymes are not synthesised instantaneously but a latent period is necessary to establish the cell machinery. The concentration of inducible enzymes increases as a function of time and stops at substrate exhaustion. When released into the extracellular environment, enzymes can be found as free catalysts (i.e. soluble within aqueous or lipophilic media) or fixed on particles (e.g. soil organic matter, clays and sand). Fixed enzymes are stabilised and their catalytic activity is often increased. Moreover, they are also protected against autocatalytic denaturation (in particular proteases) (Mateo et al., 2007). The activity of secreted enzymes can continue even if the producer cells are dead.

Enzymes are named and numbered (EC number) according to rules adopted by the Enzyme Commission of the International Union of a Pure and Applied Chemistry (IUPAC). The first number informs on the class of enzymes catalysing a given chemical reaction: (1) oxidoreductases; (2) transferases; (3) hydrolases; (4) lyases; (5) isomerases; (6) ligases (Weil, 1994).

4.1. Enzymatic hydrolysis

Biofragmentation is mainly concerned by enzymes that belong to oxidoreductases and hydrolases. Cellulases, amylases and cutinases are hydrolases readily synthesised by soil microorganisms to hydrolyse natural abundant polymers (e.g. cellulose, starch and cutin). These polymers are, in some industrial composites, co-extruded with polyesters to increase the biodegradability (Chandra and Rustgi, 1998; Ratto et al., 1999). Some enzymes with an activity of depolymerisation of (co)polyesters have been identified (Walter et al., 1995; Marten et al., 2003; Gebauer and Jendrossek, 2006; Muller, 2006). They are lipases and esterases when they attack specifically carboxylic linkages and they are endopeptidases if the cleaved bond is an amide group.

4.1.1. The mechanism described underneath is an illustration of a biofragmentation by hydrolytic enzymes: polyester depolymerisation

Studies on the biodegradation of bacterial polymers show that microorganisms secrete extracellular depolymerases. The first discovery on the hydrolytic cleavage of a microbial polymer by specific enzymes was made on poly(hydroxybutyrate) (PHB). The name of these enzymes (PHB depolymerases) was conserved even if these enzymes were found to be effective on the hydrolytic catalysis of other polyesters: poly(propriolactone), poly(ethylene adipate), poly(hydroxyacetate), poly(hydroxyvalerate), etc. (Scherer et al., 1999). However, in several studies on polyester biodegradation, some authors adopt another nomenclature, they use the abbreviated name of the polyester followed by "depolymerase"; for instance, PBSA depolymerase (Zhao et al., 2005), enzyme fragmenting the poly(butylene succinate-*co*-butylene adipate); PCL depolymerase (Murphy et al., 1996; Jendrossek, 1998), enzyme fragmenting the poly(caprolactone).

A very common feature of hydrolases (e.g. depolymerases) is a reaction mechanism that uses three aminoacids residues: aspartate, histidine and serine (Fig. 4). Aspartate interacts with the histidine ring to form a hydrogen bond. The ring of histidine is thus oriented to interact with serine. Histidine acts as a base, deprotonating the serine to generate a very nucleophilic alkoxide group ($-O^-$). Actually, it is this group that attacks the ester bond (the alkoxide group is a stronger nucleophile than an alcohol group) leading to the formation of an alcohol end group and an acyl-enzyme complex. Subsequently, water attacks the acyl-enzyme bond to produce a carboxyl end group and the free enzyme. This arrangement of serine, histidine and aspartate is termed as catalytic triad (Abou Zeid, 2001; Belal, 2003).

According to the microbial species, low molecular weight fragments can be metabolised or not. For instance, actinomycetes have a high potential for the depolymerisation of polyesters, but they are not able to metabolise the formed products (Kleeberg et al., 1998; Witt et al., 2001). A complete polyester biodegradation would be the result of a microbial synergy.

4.2. Enzymatic oxidation

When the scission reactions by specific enzymes are difficult (i.e. crystalline area, hydrophobic zones and steric hindrances), other enzymes are implicated in the transformation of the molecular edifices. For instance, mono-oxygenases and di-oxygenases (i.e. oxidoreductases) incorporate, respectively, one and two oxygen atoms, forming alcohol or peroxyl groups that are more easily fragmentable. Other transformations are catalysed by peroxidases leading to smaller molecules. They are hemoproteins, enzymes containing a prosthetic group with an iron atom that can be electron donor or acceptor (i.e. reduced or oxidative form). Peroxidases catalyse reactions between a peroxyl molecule (e.g. H_2O_2 and organic peroxide) and an electron acceptor group as phenol, phenyl, amino, carboxyl, thiol or aliphatic unsaturation (Hofrichter, 2002). A third group of oxidoreductases, named oxidases, are metalloproteins containing copper atoms. They are produced by most lignolytic microorganisms. Two types of oxidases are well studied: one type catalyses hydroxylation reactions and the other one is involved in oxidation reactions (Chiellini et al., 2003, 2006; Pelmont, 2005).

Lignins are considered as three-dimensional natural polymers. Lignins are intemely associated to cellulose and hemicelluloses. This association gives a major role to lignin in the case on new materials using lignocellulosic sources, because lignin is a macromolecular framework difficult to degrade even by microorganisms, only lignolytic microorganisms can do it.

4.2.1. To illustrate biofragmentation by oxidative enzymes, the lignin depolymerisation is described below

Lignolytic microorganisms synthesise enzymes able to cleave the complex macromolecular lignin network. Three main enzymes may be excreted: lignin peroxidase, manganese peroxidase and laccase (Leonowicz et al., 1999). They can act alone or synergistically (Tuor et al., 1995), with different cofactors (e.g. iron, manganese and copper). They can interact with low molecular weight molecules (Call and Mücke, 1997; Zapanta and Tien, 1997; Hammel et al., 2002; Hofrichter, 2002), that could lead to the formation of free radicals and consequently to oxidise and to cleave of polylignols bonds (Otsuka et al., 2003).

4.3. Radicalar oxidation

The addition of a hydroxyl function, the formation of carbonyl or carboxyl groups increases the polarity of the molecule. The augmentation of the hygroscopic character of the compound favours biological attack. Moreover, some oxidation reactions catalysed by various enzymes produce free radicals conducing to chain reactions that accelerate polymer transformations. However, crystalline structures and highly organised molecular networks (Muller et al., 1998) are not favourable to the enzymatic attack, since the

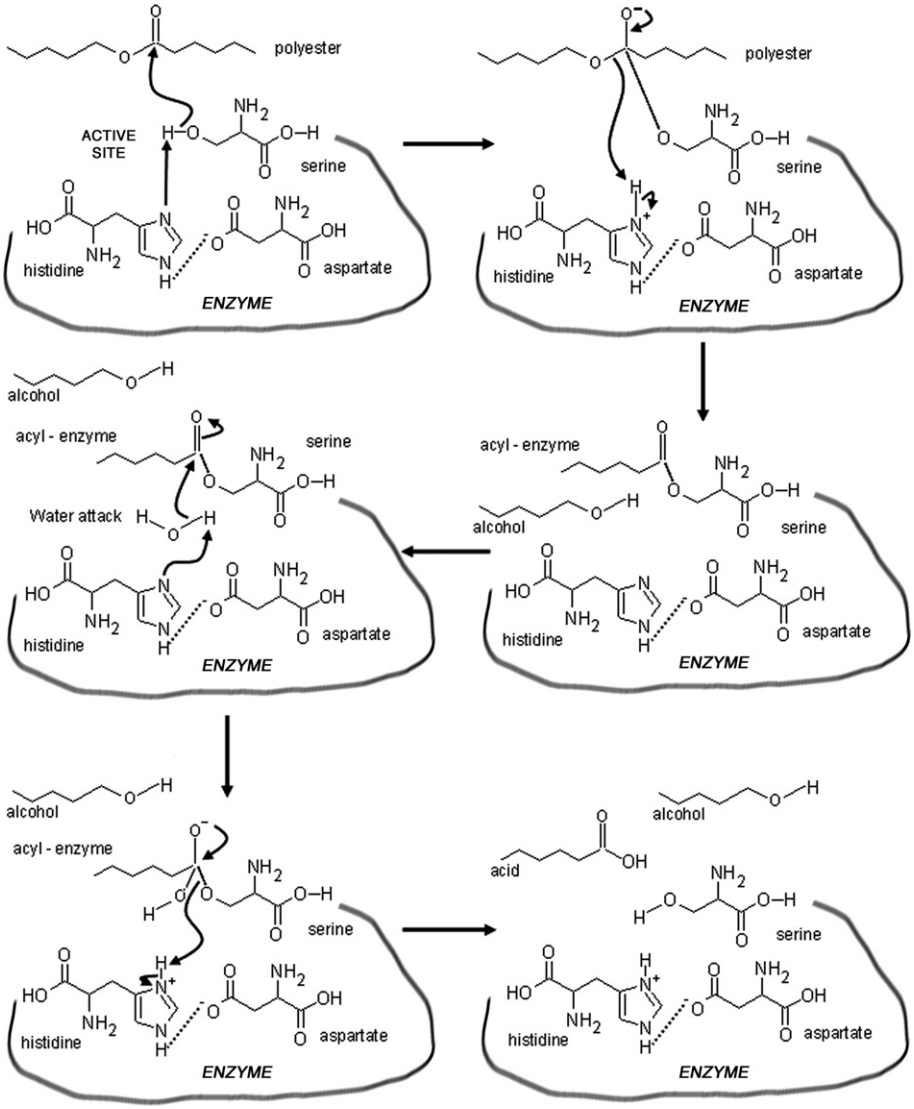

Fig. 4. Representation of the catalytic site of depolymerase and the mechanism of action.

access to the internal part of these structures is extremely constrictive. Several soil decomposers, particularly brown-rot fungi, are able to produce H_2O_2 (Green III and Highley, 1997) that is an oxidative molecule very reactive allowing the enzymatic biodegradation of cellulose molecules.

4.3.1. The biofragmentation of cellulose by radicals is illustrated below

Hydrogen peroxide produced by rot fungi reacts with ferrous atoms to perform the Fenton reaction (Green III and Highley, 1997)

$$H_2O_2 + Fe^{2+} + H^+ \rightarrow H_2O + Fe^{3+} + OH^{\cdot}$$

The free radical $OH^{\cdot}$ is extremely reactive but non-specific. Fungi protect themselves against free radicals by the production of low molecular weight molecules that have a high affinity for these radicals. At present, this mechanism is not well understood; but these molecules seem to act as free radicals transporters. They easily diffuse throughout the matrix where these radicals are reactivated to provoke polymer fragmentation. Kremer et al. (1993) have found that brown-rot fungi produce oxalate molecules able to diffuse within the cellulose fibres and chelate ferrous atoms. Hammel et al. (2002) have specified the involvement of a flavoprotein (cellobiose deshydrogenase) with a heme prosthetic group. Enoki et al. (1992) have isolated and purified an extracellular substance in *Gloeophyllum trabeum* cultures. This substance is a polypeptide named Gt factor, with oxidoreduction capacities and iron ions affinity (Enoki et al., 1997; Wang and Gao, 2003). If the mechanism of formation of free radicals is not well known, on the contrary, the mechanism of cellulose degradation by free radicals has been described by Hammel et al. (2002).

4.4. How can we know if a polymer is biofragmented?

A polymer is considered as fragmented when low molecular weight molecules are found within the media. The most used analytical technique to separate oligomers with different molecular weight is the GPC, also called size exclusion chromatography (SEC) (Ratto et al., 1999; Hakkarainen et al., 2000; Ki and Park, 2001; Preeti et al., 2003; Kawai et al., 2004; Rizzarelli et al., 2004; Marten et al., 2005; Bikiaris et al., 2006; Marqués-Calvo et al., 2006). HPLC and GC are usually used to identify monomers and oligomers in a liquid (Gattin et al., 2002; Araujo et al., 2004) or in a gaseous phase (Witt et al., 2001). After purification, intermediates molecules can be identified by MS (Witt et al., 2001). Monomer structures may be determined by NMR (Marten et al.,

2005; Zhao et al., 2005), functional chemical changes are easily detected by FTIR (Nagai et al., 2005; Kim et al., 2006b) (Table 2).

Some authors use enzymatic tests to estimate propensity for depolymerising a given substrate (Cerda-Cuellar et al., 2004; Rizzarelli et al., 2004; Marten et al., 2005; Bikiaris et al., 2006). A simple method consists in mixing the polymer and an enzyme of specific activity within a liquid medium. The estimation of hydrolysis is determined by the appropriated techniques cited above. The so called "clear zone test" is a common method used to screen the microbial ability to hydrolyse a specific polymer. Very fine particles of a polymer and agar are dispersed within a hot synthetic medium. After cooling into Petri dishes, solid agar presents an opaque appearance. Subsequently, a microbial strain is inoculated and, after incubation, the formation of a clear halo around the microbial colony indicates the biosynthesis and the excretion of depolymerases (Abou Zeid, 2001; Belal, 2003) (Table 1).

5. Assimilation

The assimilation is the unique event in which there is a real integration of atoms from fragments of polymeric materials inside microbial cells. This integration brings to microorganisms the necessary sources of energy, electrons and elements (i.e. carbon, nitrogen, oxygen, phosphorus, sulphur and so forth) for the formation of the cell structure. Assimilation allows microorganisms to growth and to reproduce while consuming nutrient substrate (e.g. polymeric materials) from the environment. Naturally, assimilated molecules may be the result of previous (bio)deterioration and/or (bio)fragmentation. Monomers surrounding the microbial cells must go through the cellular membranes to be assimilated. Some monomers are easily brought inside the cell thanks to specific membrane carriers. Other molecules to which membranes are impermeable are not assimilated, but they can undergo biotransformation reactions giving products that can be assimilated or not. Inside cells, transported molecules are oxidised through catabolic pathways conducing to the production of adenosine triphosphate (ATP) and constitutive elements of cells structure.

Depending on the microbial abilities to grow in aerobic or anaerobic conditions, there exist three essential catabolic pathways to produce the energy to maintain cellular activity, structure and reproduction: aerobic respiration, anaerobic respiration and fermentation.

Aerobic respiration: numerous microorganisms are able to use oxygen as the final electron acceptor. These microorganisms need substrates that are oxidised into the cell. Firstly, basic catabolic pathways (e.g. glycolysis, β-oxidation, aminoacids catabolic reactions, purine and pyrimidine catabolism) produce a limited quantity of energy. Secondly, more energy is then produced by the oxidative phosphorylations realised by electron transport systems that reduce oxygen to water (Moussard, 2006).

Anaerobic respiration: several microorganisms are unable to use oxygen as the final electron acceptor. However, they can realise complete oxidation by adapted electron transport in membrane systems. They use final electron acceptors other than oxygen (e.g. NO_3^-, SO_4^{2-}, S, CO_2, Fe^{3+} and fumarate) (Brock and Madigan, 1991). The result is also the synthesis of larger quantities of ATP molecules than in an incomplete oxidation.

Fermentation: some microorganisms lack of electron transport systems. They are inapt to use oxygen or other exogenous mineral molecules as final electron acceptors. Fermentation, an incomplete oxidation pathway, is their sole possibility to produce energy. Endogenous organic molecules synthesised by the cell itself are used as final electron acceptors. The products of fermentation can be mineral and/or organic molecules excreted into the environment (e.g. CO_2, ethanol, lactate, acetate and butanediol) (Regnault, 1990; Brock and Madigan, 1991; Alcamo, 1998). Frequently, these molecules can be used as carbon sources by other organisms, since they have still a reduction power.

Generally, mineral molecules released by microorganisms do not represent ecotoxicity risk, since they follow the biogeochemical cycles. On the contrary, microbial organic molecules excreted or transformed could present ecotoxic hazards in some conditions and at different levels.

5.1. How evaluate the assimilation?

Assimilation is generally estimated by standardised respirometric methods (ISO 14852; Krzan et al., 2006) (Table 1). It consists in measuring the consumption of oxygen or the evolution of carbon dioxide (Pagga, 1997). The decrease of oxygen is detected by the diminution of the pressure (Massardier-Nageotte et al., 2006) and may be fully automated (Oxitop®). The experiment can be conduced with oxygen limitation or not. In anaerobic conditions, gases are released and the augmentation of the pressure is then measured. The identification of the evolved gases is realised by GC. This technique is also used to estimate the evolution of carbon dioxide, but in most cases, FTIR is preferred (Itavaara and Vikman, 1995; Lefaux et al., 2004). The quantity of carbon dioxide may be also determined by titrimetry. Carbon dioxide is trapped in an alkaline solution to form a precipitate. The excess of hydroxide is titrated by an acid solution with a colour indicator (Calmon et al., 2000; Peltola et al., 2000).

Few biodegradability tests using complex media (e.g. soils, compost and sand) give information to assert assimilation of molecules from polymers by microbial cells. As long as we know, the only method to prove the assimilation in complex media is the use of a radiolabelled polymer to perform $^{14}CO_2$ respirometry (Reid et al., 2001; Rasmussen et al., 2004). However, this hazardous and expensive test requires particular lab room, specific equipment, training technicians and is time consuming.

6. Conclusion

The biodegradation is a natural complex phenomenon. Nature-like experiments are difficult to realise in laboratory due to the great number of parameters occurring during the biogeochemical recycling. Actually, all these parameters cannot be entirely reproduced and controlled *in vitro*. Particularly, the diversity and efficiency of microbial communities (e.g. the complex structure of microbial biofilm) and catalytic abilities to use and to transform a variety of nutrients cannot be anticipated.

Nevertheless, biodegradability tests are necessary to estimate the environmental impact of industrial materials and to find solutions to avoid the disturbing accumulation of polymers. The augmentation of derived biodegradability tests, developed by different research groups (Pagga et al., 2001; Rizzarelli et al., 2004; Wang et al., 2004; Kim et al., 2006b), has conduced to confused interpretations about biodegradation mechanisms. To compensate for this problem, it is necessary to explain the different phenomena involved in biodegradation (i.e. biodeterioration, biofragmentation and assimilation). In addition, each biodegradation stage must be associated with the adapted estimation technique. For instance, abiotic degradation and biodeterioration are mainly associated to physical tests (e.g. thermal transitions and tensile changes). Biofragmentation is revealed by the identification of fragments of lower molecular weight (i.e. using chromatographic methods). Assimilation is estimated by the production of metabolites (e.g. respirometric methods) or the development of microbial biomass (e.g. macroscopic and microscopic observations).

The unique proof that a polymer is consumed by microorganisms is the release of carbon dioxide. Naturally, this method is suit-

able if the polymer is the sole carbon source into the media. However, in soil, in compost or any other complex matrix, this test is unsuitable because the released carbon dioxide may come either from the polymer, or from the matrix, or from both. How to make the difference? One solution consists in labelling the initial polymer with a fluorochrome, a radioelement or a stable isotope. But, these methods are expensive because of specific chemicals, analytical equipment and qualified technicians.

Our research group suggests another labelling procedure. Instead of labelling the polymeric substrates, it is possible to label the microbial biomass itself. In nature, there exist different photosynthetic pathways that produce isotopic differences between the constitutive molecules of diverse plants. These plants are called "C3 plants" (CO_2 is incorporated into a 3-carbon compound), "C4 plants" (CO_2 is incorporated into a 4-carbon compound) and "CAM plants" (crassulacean acid metabolism, CO_2 is stored in the form of an acid before incorporation). A microbial assimilation of molecules from a C3 plant generates a "C3-labelled" biomass. After "C3-labelling", any other nutrient assimilation leads to an isotopic modification of the developing microbial biomass. Applying this procedure to the biodegradation of industrial materials, a change of the isotopic content confirms unquestionably the assimilation of the polymeric material used as substrate (Lucas, 2007).

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