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Biodegradability of Poly(vinyl acetate) and Related Polymers

Manfred Amann and Oliver Minge

Abstract This chapter deals with the biodegradability of vinyl ester-based polymers with a special emphasis on poly(vinyl acetate) and poly(vinyl alcohol). A proper discussion of the importance of the biodegradability of a certain polymer class cannot be made without understanding the impact that polymer class has on the environment. Therefore, apart from discussing the actual biodegradation mechanisms, other issues will be addressed. These include, but are not limited to, how long the class of vinyl ester-based polymers has been known and produced on an industrial scale, what quantities are produced and released into the environment each year, and what applications are addressed with this polymer class. We will also look at the general physical and chemical properties of this polymer class and how these properties can influence biodegradability. After a discussion of what "biodegradability" actually means – and what not – the mechanisms for the biodegradation of poly(vinyl ester)s will be discussed in more detail and a summary given of the biological systems able to process poly(vinyl ester)s.

Keywords Biodegradation · Poly(vinyl acetate) · Poly(vinyl alcohol)

Contents

M. Amann (✉) and O. Minge
WACKER Consortium für elektrochemische Industrie, Zielstattstrasse 20, 81379 Munich, Germany
e-mail: manfred.amann@wacker.com; oliver.minge@wacker.com

1 Introduction to Poly(vinyl ester)s

1.1 History

Poly(vinyl acetate) (PVAc) and its corresponding polymers poly(vinyl alcohol) (PVA) and poly(vinyl butyral) (PVB) have long been known and their histories of discovery and development are as closely linked as their chemistries, which are characterised by an all-carbon polymer backbone and by 1,3-diol structures or their derivatives (see Fig. 1).

In fact, the first description of a polymeric vinyl ester dates back to 1912 when Klatte [1] managed to polymerise vinyl chloroacetate to obtain a solid resin. However, the potential of these materials was not seen at that time [2]. Additionally the polymerisation reaction faced severe practical problems leading to products

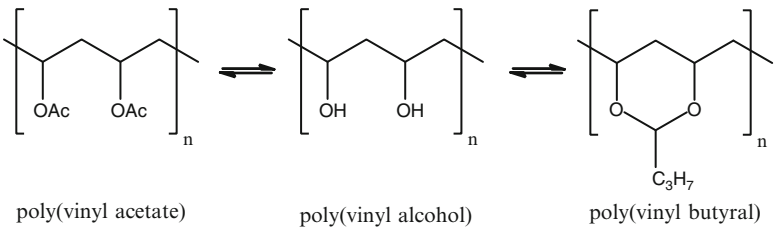

Fig. 1 Repeating units of poly(vinyl acetate), poly(vinyl alcohol) and poly(vinyl butyral)

with low molecular masses and mediocre physical properties (please note that the concepts of polymerisation and macromolecules were not introduced before 1917 by Staudinger [3, 4]).

Soon afterwards, however, Wacker Chemie developed methods for the large scale production of vinyl acetate monomer (VAM) and also overcame synthetic limitations in the production of PVAc from VAM [5, 6]. The resulting polymer PVAc was soon found to be suitable for use both as a binder and as a major component in adhesives.

The chemistry of PVAc was explored further in the following years: In 1924, PVA, the hydrolysis product of PVAc, was discovered by Hermann and Haehnel at Wacker Chemie in Germany [7, 8]. At the same time Staudinger independently discovered PVA [9]. After the saponification process for PVAc had been optimised, PVA was *inter alia* the material to be processed into the first fully synthetic fibre (Synthofil, 1931) [10]. PVA also was the first fully synthetic stabiliser for colloidal systems [11].

In 1928, PVB, an polyacetal of PVA and butyric aldehyde, was shown to be suitable for the production of laminated safety glasses [12], for which it is still used today.

In the following decades, homo-, co- and terpolymers of VAM with other vinyl esters, (meth)acrylates, and ethylene were developed to give thermoplastic materials with tailored properties that are nowadays produced as solid resins, aqueous dispersions and dispersible powders.

As one can see, PVAc and its related polymers are nothing new and the materials have been around for almost 100 years. Practical applications of polymers based on VAM have been known for over 80 years and products containing VAc-based polymers have been spreading into the environment for just as long.

2 Basic Materials, Production and Producers

2.1 Raw Materials

The synthesis route to vinyl ester-based polymers starting from ethylene is shown in Fig. 2. The basic monomer for PVAc and its related polymers is VAM. The worldwide production capacity for VAM was estimated to be close to 5,900 ktons in 2009 with an actual production of around 5,500 ktons [13]. About 50% of the VAM is converted to PVAc and VAc-containing polymers, and around 30% is converted to PVA. The remaining 20% is converted in other ways, including the production of PVB [13]. As can be seen from Fig. 2, basically only ethylene and air are needed for the production of PVAc and its polymer analogous products PVA and PVB.

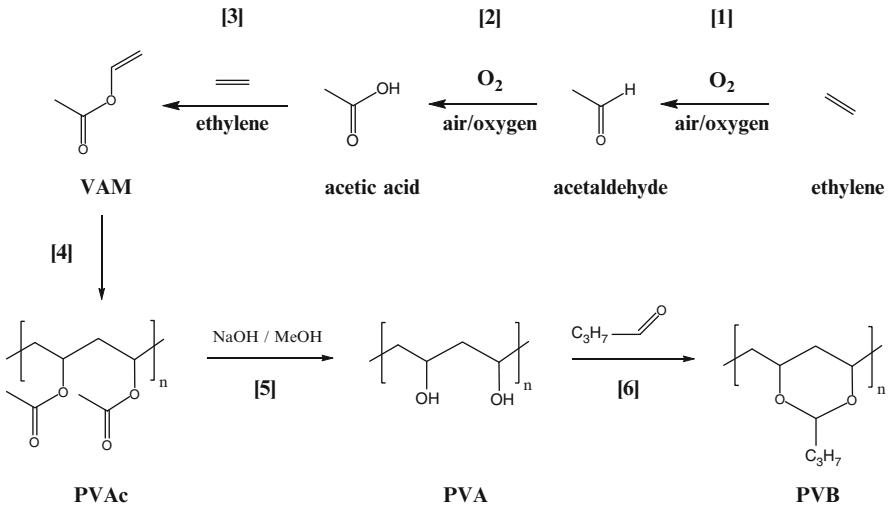

Fig. 2 Pathway to vinyl ester-based polymers starting from ethylene

VAM can be produced starting from ethylene, which is converted to acetic acid via acetaldehyde by two sequential oxidation steps (reactions 1 and 2 in Fig. 2), the first step being the famous Wacker process (reaction 1 in Fig. 2) [14].

Another way to produce acetic acid is based on a carbonylation of methanol in the so called Monsanto process, which is the dominant technology for the production of acetic acid today [15]. Acetic acid then is converted to VAM by addition of ethylene to acetic acid in the gas phase using heterogeneous catalysts usually based on palladium, cadmium, gold and its alloys (vinylation reaction 3 in Fig. 2) [16] supported on silica structures.

It should be pointed out that the raw materials for VAM and its related polymers (i.e. ethylene and acetic acid) are produced from fossil resources, mainly crude oil. It is possible to completely substitute the feedstock for these raw materials and switch to ethanol, which can be produced from renewable resources like sugar cane, corn, or preferably straw and other non-food parts of plants. Having that in mind, the whole production of PVAc, that nowadays is based on traditional fossil resources, could be switched to a renewable, sustainable and CO_2-neutral production process based on bioethanol, as shown in Fig. 3. If the "vinyl acetate" circle can be closed by the important steps of biodegradation or hydrolysis and biodegradation of vinyl ester-based polymers back to carbon dioxide, then a truly sustainable material circle can be established.

2.2 Polymer Production

The polymerisation of VAM (reaction 4 in Fig. 2) can be carried out using different kinds of standard polymerisation techniques, the technically most important of

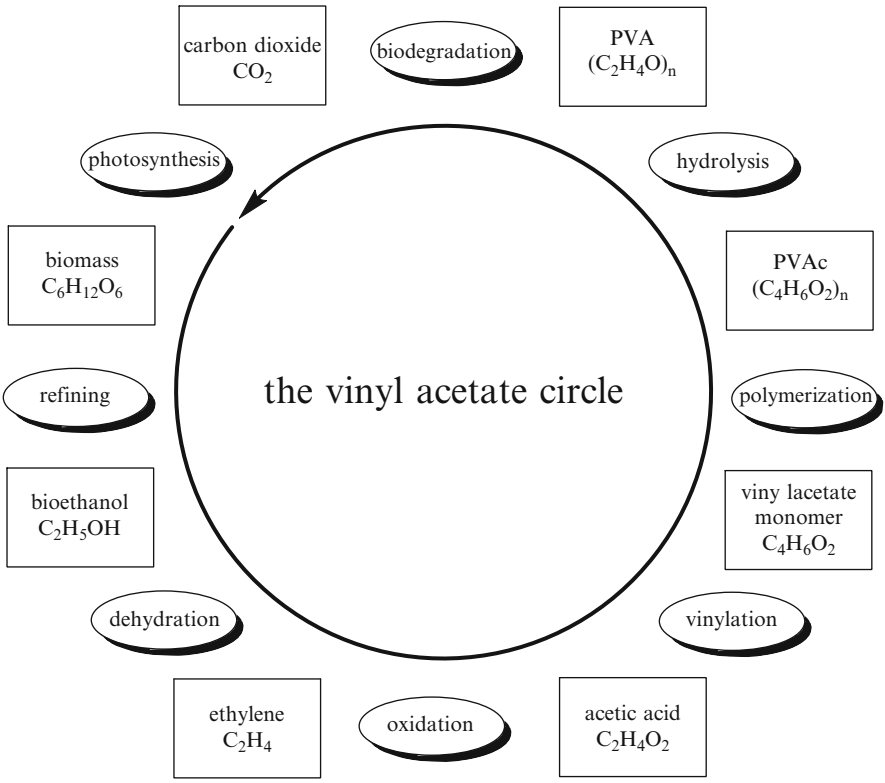

Fig. 3 Vision of the "vinyl acetate circle" wholly based on ethanol as a raw material source

them being emulsion-, suspension- and solution-polymerisation yielding either aqueous dispersions or solid resins [17]. Depending on the polymerisation method employed, the PVAc obtained differs in molecular weight and molecular weight distribution but also in the amount of branching by side reactions. These properties are of considerable importance when it comes to biodegradation. As a rule of thumb, the molecular weight of emulsion-polymerised systems is very high while suspension- and solution-polymerised systems usually show relatively low molecular masses.

2.3 Polymer Composition

VAM is used to produce a homopolymer and, together with a wide array of different monomers, a number of copolymers. Copolymers with ethylene are one of the most important classes of copolymers known and, depending on the ratio of ethylene and vinyl acetate, are abbreviated as EVA (high ethylene and low vinyl acetate content) or VAE (high vinyl acetate and low ethylene content) [18] polymers.

Copolymers with acrylates (vinyl acrylics) or other vinyl esters are also commonly produced, mostly as aqueous dispersions. They are, independent of the nature of the comonomer, often referred to as "copolymers" or "terpolymers". The presence of comonomers of course heavily influences a number of physical properties like the glass transition temperature and melting point, water solubility or flexibility, to name just a few.

2.4 Derivatives of PVAc

To obtain PVA, PVAc is saponified in a polymer analogous reaction using methanolic sodium hydroxide. The reaction 5 in Fig. 2, which is better described as a transesterification rather than a simple basic hydrolysis, leads to PVAs with different degrees of saponification (see Fig. 4).

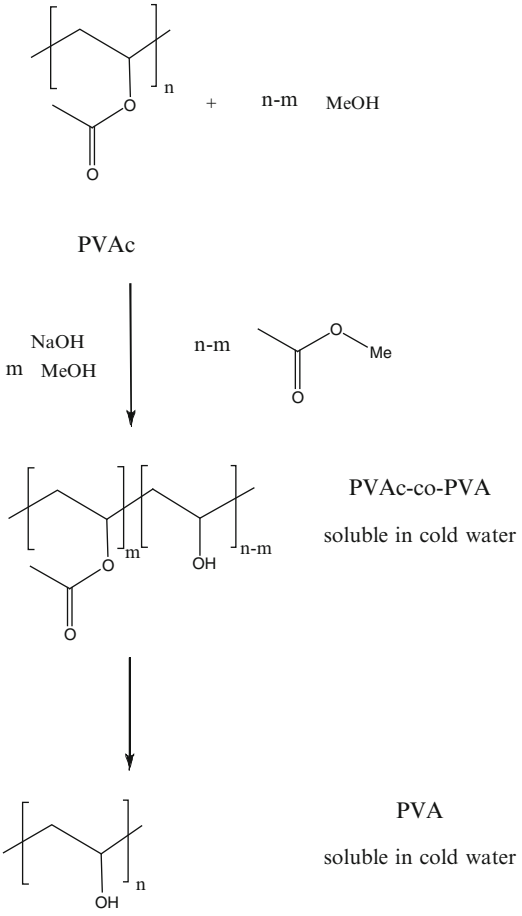

Fig. 4 Transesterification of PVAc with methanol (often regarded as saponification) to completely hydrolysed PVA via partially hydrolysed PVAc-*co*-PVA

It is important to note, that neighbouring group effects affect the alkaline hydrolysis rate of the individual acetate groups. Acetate groups adjacent to alcohol groups are more readily hydrolysed than acetate groups having only other acetate groups in close proximity. As a consequence, partially hydrolysed PVA exhibits a block-like structure rather than a random structure and is best described as a (multi) block PVAc-*co*-PVA.

The degree of hydrolysis (DH) can be adjusted by the reaction time. Many common PVA resins have a DH of about 88 mol%. These resins are soluble in cold water. Higher DH lead to a reduced water solubility. A totally hydrolysed PVA is almost insoluble in cold water and can only be dissolved by boiling in water for an extended period of time. The insolubility is caused by the build-up of intramolecular hydrogen bonds, leading to a high degree of crystallisation not achieved by only partly hydrolysed PVA grades.

PVA subsequently can be acetalised (reaction 6 in Fig. 2) with aldehydes, the most important of them being butyric aldehyde, leading to PVB. However, since PVB only plays a minor role, both according to the total volume produced and the number of applications that make use of PVB, it will not be discussed in much detail in this chapter.

2.5 Manufacturers

The worldwide production of PVAc and its copolymers containing more than 50 wt% of VAM reached about 2,300 ktons by 2007, with an annual growth of about 3.4% [19]. Another major part of the VAM produced is converted to PVA. The major production regions are the USA, Western Europe, China and Japan.

The major producers of VAM and VAM-based polymers include, but are not limited to, BP of the UK and Wacker Chemie of Germany. Celanese Chemicals, Dow Chemical Corp., DuPont and Millenium are important USA-based producers. In Asia, Kuraray, Nippon Gohsei and Showa Denko of Japan; Dairen Chemical and Asian Acetyls of Taiwan; and Shanghai Petrochemical and Sichuan Vinylon Works of China produce VAM and their polymers. These regions are also the major markets for the different products obtained from PVAc and its derivatives.

2.6 Applications

PVAc, PVA and PVB are used in a vast number of different applications [19]. The most common use of PVAc-based dispersions and dispersible polymer powders is in the construction and adhesives industry. The polymeric binders are used as

additives to enhance the properties of e.g. tile adhesives, mortars and self-levelling compounds. PVAc dispersions are also used in many other adhesive formulations. Wood glues (white glue) are often based on PVAc. It is also commonly used as a binder in the paper industry and as a binder in latex paints, although binders based on acrylics are far more common in paint technology. Almost one third of the PVAc produced goes into binder and adhesive applications.

Because PVAc is approved by the FDA it has also several uses in the food industry. PVAc can also be found in just about every chewing gum. It is a major component in the so called gumbase, a mixture of different polymers that in combination with sugar, sweeteners, flavours, and other additives make up a chewing gum.

EVA is a copolymer of ethylene with minor amounts (ca. 10–40%) of vinyl acetate. EVA has many uses as a foam rubber in everyday goods (like shoes etc.), as cable insulation and as encapsulation material in photovoltaic cells.

VAE, a copolymer of vinyl acetate with minor amounts of ethylene is used as an adhesive for paper, plastics and leather and as a binder for different paints. Shoes, tubes, toys and other articles of daily use also contain VAE polymers. The hydrolysis product of VAE polymers, EVOH, is a thermoplast and can therefore be processed by extrusion and injection moulding and is used as barrier polymer for O_2 and CO_2 (e.g. in packaging applications).

PVA is used for example as a water soluble dispersing agent for many different polymer dispersions used in the construction industry. An important property of PVA is the ability to redisperse polymer dispersions that have been dried to powders.

PVB, apart from its importance in laminated safety glasses, is also used as an additive for various printing ink and lacquer formulations because of its ability to form tough and transparent coatings while being compatible with solvents often used in the printing industry.

As pointed out above, PVAc is frequently not used as a hompolymer but rather as the major component of a copolymer (VAE, terpolymers, vinylacrylics, etc.). Additionally, in the applications mentioned above PVAc and the related polymers are usually not used alone but as a part of a more or less complex mixture with other components. These components can be, for example, fillers, plasticisers, impact modifiers, compatibilisers, or other polymers. These components need to be taken into account when discussing biodegradability. They influence the biodegradability of the mixture as a whole but they may in particular influence the biodegradability of the PVAc moiety by altering the physical circumstances under which degradation reactions can take place.

As mentioned, vinyl ester polymers are used in every part of the world for a vast number of different applications. They can be found basically everywhere in everyday life, from housing to personal effects and in goods as well as in food. The environmental fate of poly(vinyl ester)s is therefore of great importance.

3 Aspects of Degradability

3.1 Chemical Motifs

PVAc, PVA and PVB homopolymers as well as the different copolymers mentioned above all have a similar chemical motif in common. They exhibit an all carbon–carbon single bond backbone, which needs to be broken at some point in a potential biodegradation mechanism. With respect to the backbone, poly(vinyl ester)s are closely related to poly(olefin)s, poly(styrene)s and poly(acrylate)s. These three are known not to be biodegradable. Instead, they usually decompose by the impact of UV radiation, oxidation and hydrolysis reactions, which are not considered to be biological degradation.

Apart from the all-carbon backbone, poly(vinyl ester)s also exhibit a unique 1,3-diol structure (see Fig. 1). This structure is a common motif in many natural materials, e.g. carbohydrates. A number of oxidative or reductive electron transfer processes catalysed by natural redox systems are imaginable for this motif. The 1,3-diol structure is unique for a synthetic polymer and cannot be found in any other synthetic polymer class of significance. This explains the unusual biodegradation properties discussed below.

3.2 Physical Properties

Growing public interest in the conservation of an intact environment can be observed. A general consensus on the fundamental limits in the magnitude and accessibility of many crucial natural resources is developing in many areas concerning industrial production. Fewer raw materials and less energy must be used in a future economy.

In the area of chemically synthesised polymers, two approaches can be distinguished for reducing their impact on the environment: (1) use of durable materials that are resistant to attack and can perform for a long period of use, or (2) use of materials that after their projected lifetime easily disintegrate into small molecular components that are compatible with our living environment. Thus, degradability is an aspect of very great concern for all polymeric materials that might finally end up in the environment.

The classification of a polymer as a degradable compound has a very positive impact on public perception of this chemical, which can still be exceeded by a classification as biodegradable. Not surprisingly there exists a huge variety of ways, procedures and test protocols to evaluate this aspect of polymer behaviour. Orientation in this diversity of methods and related classifications is not easy and cannot be fully discussed in this chapter [20, 21]. The aspects that come into consideration when dealing with degradability or biodegradation are quite diverse. At the end of all the different test procedures there is always a classifying attribute given to the

particular polymer. To obtain the right conclusions from this labelling, the specific background and context of the evaluations must carefully be kept in mind.

The landscape of testing methods is quite heterogeneous. In discussing the fate of a polymer like PVA there are different ways of looking at the substance, which can be found in different test protocols.

The alteration of polymer identity can be followed directly, but other methods try to look at derivatives originating from the polymer, at oligomeric cleavage products, or at small molecules derived therefrom down to CO_2, the final product of mineralisation.

Changes in the specific properties of the polymer can also be taken as a hint of some form of degradation. Properties examined include different aspects of physical behaviour of the polymer, different microscopic images, or changes in simple parameters such as the total weight of the polymer in the test or an altered molecular mass of the polymer under evaluation.

Changes in the neighbourhood of the polymer under the specific test conditions are also accessible parameters that indicate potential degradation processes. Common tests are monitoring of the oxygen consumption or evaluation of the impact on microbial growth. The time period of testing is quite crucial. Some methods are run for only two weeks, but other procedures involve monitoring for many months. Many different standardised methods (ASTM, OECD, ISO) dealing with oxygen consumption or biological oxygen demand are compiled in Part I of Eubeler et al. [20].

The biological tests offer a wide field of parameters that cannot be easily reproduced. Many microbial strains, microbial communities and biotopes can be used to run specific tests. Some are well adapted to the polymer under consideration, like specifically engineered microbial strains or indigenous sewage sludge from production sites. Other test systems use microbial communities that are not yet prepared for these compounds, like sludge in municipal sewage treatments. Aerobic or anaerobic conditions can be maintained, but intermediate or changing oxygenation situations may occur without being monitored. Soil as a degradation matrix is very complex and not evenly distributed around the Earth. Even identical soils differ in their degradation performances quite substantial just by changing the water content. Water sediments are extremely important, but reproducible handling is difficult. Much testing is done in compost, which is rich in microbial life, but great differences are seen between a backyard heap and artificial or commercial systems.

This sophisticated picture is reflected by the many test procedures dealing with degradation or biodegradation that are published by different national, international, or industry-driven organisations (e.g. ISO, ASTM). The aim of all these efforts is to obtain comparable data on the behaviour of the polymer under consideration, but a driving force is also the marketing need to present an attractive classification and labelling for the polymer product.

In this chapter, we aim to summarise current knowledge on the biodegradability of PVA. It is necessary to distinguished precisely between biological mechanisms and non-biological routes, even if they are intrinsically intimately entangled.

Abiotic forces will not be in the focus of the discussion, but it is obvious that a polymeric material like PVAc or PVA exposed to outdoor conditions will undergo different alterations at the macroscopic and microscopic scales. Depending on its interaction with mechanical forces, thermal stress, radiation or chemical attack, the polymer properties might be changed in a way that is relevant for its interaction with biological systems.

Mechanical forces like shear or compression in synergy with temperature can have strong influence on the material structure upon approaching the glass transition temperature or melting point of the polymer. Irradiation by light might be of concern if the surface is amenable, but chemical interactions can hardly be avoided as all materials display interfaces to different solids, to different solvents like water, or to atmospheric gases.

Many experimental findings can at first glance be interpreted as some form of polymer degradation. But, scientifically valid data must try to make up the balance of the polymer and its degradation products to avoid false interpretation due to adsorption phenomena, inappropriate analytical tools or detection limits, or changes in its chemical identity.

Biological mechanisms comprising some kind of disintegration of the polymeric starting material, its fragmentation (possibly down to mineralisation), and assimilation of polymer-derived substructures into the living organism can be summarised as a complete biodegradation process [22]. In this general sequence organisms act on polymer substrates not only via classical biological tools like small or large biogenic molecules to attack the polymer. The living cells or organisms create a living interface to the polymer that imparts a new physico-chemical environment for the polymer degradation. The living nature of the degraders or the complex microbial consortia cooperating in degradation results in an intimate link-age of biogenic and abiotic factors often working in a synergistic way.

Biodeterioration at the beginning of the biodegradation process works on the accessible surface of the polymeric material, infiltrating porous structures and altering the macroscopic structure of the polymer. In addition to this physical process, the chemical biodeterioration is a powerful mechanism. Many compounds produced by microbial systems are active substances that weaken the polymeric structure. Mineral acids like nitrous acid and sulphuric acid or organic acids like oxalic, citric or glutaric acid are just a few examples of a huge list of acids produced by different microorganisms operating in this process, often via complexation of metal cations. Biosurfactants are a further category of supporting agents that facilitate the interaction of hydrophilic and hydrophobic areas. Microbial extracellular polymers stabilise a water coating on the polymeric materials, causing effects like polymer swelling or hydrolysis.

Microbial vulnerability of polymers is often ascribed to enzyme activity, enzymes being crucial players in the biological biodeterioration process. As enzymes are macromolecular polymers, their attack on the polymer is usually only possible via superficially exposed polymer structures readily accessible via a microporous structure. Alternatively, the enzymatic attack works indirectly via

small active mediating molecules like radicals or other active mediators [23] that are generated by appropriate enzyme systems.

Enzymes are the main actors in breaking down the polymers into oligomeric structures, monomers or other small metabolites. This biofragmentation is a necessary event in the degradation process because the polymer is usually unable to cross the cell wall or any cytoplasmic membrane of the degrading organisms. Thus, scission of chemical bonds via biological means must be accomplished by the degraders, if no abiotic involvement has already succeeded.

The biological aim of biodegradation is not to eliminate man-made polymers from the biosphere but to mobilise densely packed organic material as nutrient for microbial or higher life forms. This implies that the integration of polymer-derived atoms into the microbial biomass has to be the last step in true biodegradation. This assimilation step can finally end in the observation of cell growth or even a complete mineralisation via metabolism these intermediates to CO_2. This assimilation can only occur if the polymer can be absorbed in some way by the degrader or can be broken down to molecules that can be transported via the cell wall and membrane. In both cases, a metabolically compatible form of the polymer-derived structures must be obtained to channel these molecules into the metabolic pathways of the degrading organisms. The energy for these vital activities is generated by the different ways in which organisms are able to gain energy by their catabolic pathways using different electron transport chains. Reviewing the huge diversity of aerobic or anaerobic life and the many microbes utilising fermentative processes, it is not surprising that degrading organisms are found in quite different biotopes all over the planet.

Biodegradation is a complex natural process covering many parameters that are often interdependent. The sequence or the simultaneous action of the different degrading forces is often highly relevant, which makes it difficult to get reproducible results. But, it is exactly this complexity that makes it fascinating to illuminate the interplay of nature with our man-made polymers.

Discussed here is the fate of PVAc and PVA polymers with respect to the biodegradation events described above. In technical applications and products, additives are used to improve the performance in different processing steps, and blending with other polymers is used to tailor the application profiles to the demands of customers or the needs of the producers. These wanted contaminations make it difficult when biodegradation of PVAc- and PVA-containing products must be used exclusively to evaluate the degradation process. It is obvious that processing aids, blending partners and other components in an intimate composition containing PVAc and PVA play some role in the multistep biodegradation process, either as supporting components or as substances that may slow down biodegradation or make it even impossible.

Wherever possible we will therefore focus on degradation studies with pure polymers. The degree of biodegradation of PVAc and PVA depends on characteristics that are intrinsically related to the physical and chemical properties of the polymer. As many of these factors can differ to some extent depending on the

synthesis and processing of the polymer, a range of polymer products can be obtained that behave slightly different in biodegradation trials.

3.3 Solubility in Water

Solubility behaviour in aqueous solutions is a crucial factor in many aspects of biodegradation because almost all living organisms are dependent on the availability of sufficient water phase. A low molecular weight PVA molecule shows a good solubility in water, be it only in molecular amounts or in bulk quantities.

To date, PVA is only accessibly via removal of the acetyl groups from the precursor polymer PVAc. The highly acetylated polymer is not soluble in water. By generating OH groups via removal of the acetyl residues from the polymer backbone, the interaction with water solvent molecules becomes more favourable and the tendency to dissolve in water increases.

Upon further increasing the DH many hydrophilic hydroxyl groups are exposed, which can additionally form strong intermolecular hydrogen bonding between different polymer molecules. These attractive interactions lower the water solubility of the polymer and give rise to a more crystalline structure of the polymer domains. Because the glass transition temperature and hardness concomitantly increase, degradability becomes more difficult at very high DH.

Due to the neighbourhood of secondary alcohol groups and remaining hydrophobic acetyl groups in a not fully hydrolysed polymer, a balanced situation results that dictates the overall water solubility. Temperature plays an important role in that interplay between the intermolecular attracting forces and the polymer water interaction. An optimum in cold water solubility can be observed with a DH of 87–89 mol% for molecular weights between 25,000 and 100,000 Da (degree of polymerisation, DP, 600–2,400).

In evaluation the biodegradability of PVA, it is necessary to discriminate between two fundamentally different environmental situations. The fate of PVA can be analysed by looking at a fully dissolved aqueous PVA found in activated sludge of an adapted sewage plant or by following PVA molecules in a solid state compost environment, offering many stabilising interactions with other surfaces of different origin. High levels of biodegradation of dissolved PVA via microbial communities can be observed (Tang 2010). Only moderate or marginal biodegradation is reported from soil and compost biotopes [24].

PVAc is not water soluble, which should be a major obstacle for a potential biodegradation mechanism. However, PVAc resins show a certain amount of swelling when exposed to water. This swelling facilitates the degradation by biologically active substances by making the resin more hydrophilic. Further abiotic release of acetic acid residues generates the 1,3 *cis*-diol motifs in the polymer backbone, which are relevant as entry points for biodegradation as outlined further below in Sect. 6.1.

3.4 Molecular Weight

The biodegradation of macromolecules generally comprises a number of steps that can proceed at different sites from the perspective of the active microorganism. The macromolecule can be taken up into the cell, where it is cut down and further metabolised. Alternatively, the splitting of the macromolecule can be done outside the cell, and the small degradation products then transported into the cell.

The cellular uptake of high molecular weight compounds can be accomplished by engulfing those molecules, a mechanism called endocytosis that is widely distributed because large polar molecules cannot pass through the hydrophobic environment of a plasma or cell membrane. Alternatively, a specific cellular uptake machinery called a superchannel [25] is described in a *Sphingomonas* strain for polysaccharide macromolecules (27 kDa) like alginate. This kind of transport is mediated by a pit-dependent ATP-binding cassette (ABC) transporter. The function of the transporter is dependent on a pit, a mouth-like organ formed on the cell surface only when cells are compelled to assimilate this specific macromolecule. The system allows direct import of intact macromolecules into the cellular cytoplasm. Experimental results showing the import of high molecular weight PVA into microbial cells have not yet been published, but a *Sphingomonas* strain (*Sphingomonas* sp. OT3 [26]) is one of the few PVA-degrading microorganisms.

The molecular weight aspects can be discussed for different sites of the degradation topology: the situation outside the cell, at the interface, or inside the cytoplasm of a degrading organism. Two classes can be discriminated in the spatial organisation of the PVA degradation pathway. Some organisms begin with an extracellular enzymatic depolymerisation via oxidation and hydrolysis, others use their periplasmatic compartment. This compartment can also be regarded as an extracellular site, separated by the inner membrane from the cytoplasm, but is better controllable by the organism.

3.5 Extracellular Polymer

Molecular weight and water solubility are related in the case of large PVA molecules. Perfectly comparable results are not easily available because the DH usually differs to some extent. The fully hydrolysed high molecular weight PVA shows a marginal propensity to biodegrade in soil environments. Many possibilities are given to explain that behaviour. The overall rare distribution of degrading organism is cited but other physical and chemical factors make the degrading situation very unfavourable. High crystallinity and the strong complexing interactions of the many hydroxyls with polar mineral components hinder microbial or enzymatic accessibility to the PVA surface [27].

Aqueous systems are favourable for the degradation of PVA. Kinetic monitoring of the molecular weight distribution in liquid cultures of mixed microbial

populations showed a progressive disappearance of the higher molecular weight fraction irrespective of the DH (72–98%). In water, fully dissolved polymer is completely biodegradable.

As a general mechanism, the degradation of PVA starts outside the cells via enzymatic attack on the polymer. The resulting products are a mixture of acetoxy hydroxy and hydroxy fatty acids. Upon intracellular enzymatic deacetylation, hydroxy fatty acids are generated that can be further metabolised via the classical β-oxidation pathway and TCA cycle.

The extracellular enzymatic attack on the 1,3-diol repeating unit in the polymer proceeds via oxidative enzymes, introducing structures in the PVA backbone that can serve as breaking points for subsequently acting enzymes. The enzymatically introduced 1,3-diketone moieties or β-hydroxy ketone structures are split by specific hydrolases or aldolase enzymes. The resulting polymer fragments show that this enzymatic endocleavage of the polymer is a random process. The reaction is not much affected by the molecular weight of the PVA (DH >80%). This basic cleavage mechanism is common to all PVA-utilising microorganisms so far studied [28].

3.6 Intracellular Polymer

Organisms of different systematic classification are described as PVA degraders. All candidates show different types of cell walls or membrane systems covering the cytoplasm. The organisms include prokaryotic Gram negative (Periplasm) and Gram positive bacteria but also some eukaryotic fungal degraders [29]. The mechanism of transfer of modified PVA and PVA-derived fragments across the cytoplasm membrane is not clear.

As a result of external extracellular or periplasmic fragmentation, small PVA oligomers exhibiting residual acetylation (PVA-PVAc) enter the cell. A pronounced effect of molecular weight on the fate of these PVA pieces was found. Specific esterases catalyse the intracellular hydrolysis of residual acetyl groups on not fully hydrolysed PVA [30]. Lower molecular weight species of PVA-PVAc structures are preferentially accepted as substrates for this activity located in the cytoplasm and the cytoplasm membrane. The decreasing chain length during PVA degradation reaches a point where very short segments predominate. Some authors have discussed a mechanism whereby the residual PVA molecules are degraded starting from the terminal hydroxyls, in analogy to the β-oxidation of fatty acids. Those pathways would not necessitate a PVA-specific biochemical repertoire or an induction/adaption period for the microorganisms [31–33]. It can be concluded that biodegradation of water-soluble PVA in the extracellular compartment works in a broad molecular weight range of 530–90,000 Da (DP 12–2,000) [34]. Inside the microbial cell smaller fragments are further deacetylated and funnelled into the standard biochemical degradation pathways.

3.7 Saponification

The DH of technical grade PVA varies in the 70–98% range. What the number does not tell is the distribution of these acetyl groups along the polymer backbone. A uniform statistical distribution or a clustered partitioning on the polymer gives rise not only to changes of the melting behaviour, surface tension or colloidal properties of the polymer but also to its degradability properties. For good biodegradation an intermediate degree of acetylation is necessary, meaning that very high or very low acetylation is unfavourable. Samples with comparable DP differing in their vinyl acetate monomeric units were synthesised by acetylation of fully hydrolysed PVA. Biodegradation tests in different media were performed. In solid media like soil or compost, a high recalcitrance of fully hydrolysed PVA with respect to mineralisation was recorded. The same behaviour was monitored with PVA samples with a very low DH, very similar to PVAc. Good biodegradation (50–60%) in soil can be found with a balanced PVA hydrophobicity at DH of 24–73 mol%. In aqueous aerobic environments, biodegradation runs parallel with water solubility [35]. Surprisingly, microbial strains showing external esterase activity were not identified as superior degraders; esterase was only found as intracellular activity [36, 37].

3.8 Stereoregularity

PVA generated from PVAc shows a certain ratio of tacticities distributed over the polymer backbone. Dominating atactic areas are mixed with isotactic and syndiotactic segments. Interestingly, the stereo configuration of the vicinal hydroxyls influences the degradability. Degradation was preferentially observed with isotactic and syndiotactic moieties, increasing the relative amount of atactic regions [31]. The esterases involved in degradation can neither distinguish the stereoregularity of the polymer nor change it [29].

4 PVA Polymer Products

4.1 Blends and Additives

Growing discussion about the limited availability of cheap fossil basic materials, and customers paying more and more attention to product life cycles, brings aspects of the biodegradability of polymer products again to the focus of attention. The replacement of synthetic polymer products with biopolymers is attractive but limited because the properties of natural polymers do not always fit the demands of processability and final product performance. PVA with its beneficial rheological

and film-forming properties has been widely used to improve this shortcoming by the preparation of blends. Several natural polymers of plant or animal origin have been used as partner polymers, like the polysaccharides cellulose, starch and chitin; the proteins silk and gelatine; or the polyaromatic lignin. A broad compilation covering blends and copolymers is given in [38].

The polar PVA shows a perfect dispersibility of cellulose owing to the many hydrogen bonds that are possible between these two polymers. With high cellulose contents (>70%) no crystallinity of PVA could be detected. Cellulose nanofibers can be used for the production of promising PVA blends but there are no data about biodegradation available yet [39]. Polymer blends in the farming and food production industry are highly attractive when cheap and readily available materials can be used. Lignocellulose materials are ideal candidates, as structural properties like their fibre elements can be incorporated into the polymer matrix. A favourable effect on biodegradation was not found. Lignin seems to influence the kinetics of the overall degradation scenario but shows no overall positive impact [40]. Although lignin is generally regarded as very recalcitrant to biodegradation, the opposite is true for starch. Starch is a polyglucose polysaccharide that has evolved as a widely distributed biological storage compound that can be easily depolymerised to generate glucose that is channelled into energy metabolism. Its poor mechanical properties as a technical material have led to a high number of blends, amongst others with PVA [41]. Polymer compatibility of natural starch and synthetic PVA is not as good as might be expected between these two highly polar polymers. Microscopic analysis of the morphology of the composites shows a phase separation between a continuous PVA phase with immersed starch islands. Polymer behaviour and characteristics of PVA starch are described, but the biodegradation behaviour was not the focus of the published data. The presence of starch cannot be regarded as a positive input to improve PVA biodegradation. In contrast, such starch blends degrade more slowly than controls without starch, PVA even inhibited the degradation of the starch from the blend [42].

Adding a solid inorganic phase (e.g., particles of Montmorillonite) to such blends causes biodegradability to become even worse [43]. The findings support a model of PVA biodegradation that works well in a dissolved state, but is downgraded upon introducing too many interacting and possibly stabilising forces for the PVA polymer into the system.

PVA as an attractive blending partner is used for almost all biopolymers that have to be tailored in their material properties for special applications. The most abundant cell wall polymer in the animal kingdom is chitin, a poly(*N*-acetyl-D-glucosamine) polysaccharide commonly found in exoskeletons of arthropods. Chitin has many useful properties, such as nontoxicity, lack of odour, biocompatibility and biodegradability. For solubility reasons it is not chitin but its derivatives that find use in many technical, biomedical or food applications. Chitosan is the most prominent derivative and is produced via deacetylation of chitin. With many other biopolymers, many blends were made with different technologies, starting with simple solution casting techniques [44] up to elaborate electrospinning technologies

[45]. No clear data are given to indicate that these blending partner polymers have a supporting effect on the PVA biodegradability in the resulting composite material.

Good melting and film-forming properties are attractive parameters that make protein polymers attractive blending partners in many PVA applications. Some proteins are available in sufficient amounts for technical applications. Gelatine, a product made from animal connective tissue, has found entry in different fields ranging from high value pharmaceutical medical applications, via food to high volume technical products.

By mixing of aqueous gelatine and PVA solutions, films can be obtained that are usually stabilised by chemical crosslinking. However, microscopy shows the limited compatibility of these two components. Degradation trials with blends containing different ratios of gelatine and PVA showed no improvement of PVA biodegradability by the presence of the readily biodegradable protein, but some inhibition of the protein degradation by PVA. Latter could be explained by strong physical adsorption of PVA on the protein microdomains.

A similar effect is seen in the behaviour of PVA blends with soy protein. This plant-derived protein is used in many applications that range from food to uses as emulsifiers and texturising agents in resins, paints or fibres. Aerobic biodegradation trials of soy protein/PVA films in soil proved that the PVA part imposes negative effects on biodegradation of these films, prolonging their decomposing time. It is suggested that addition of PVA decreased the ability of soy protein molecules to absorb water [46], thus lowering biodegradability.

The inhibitory effects of PVA can also be found in degradation studies of polycaprolactones (PCLs). These polyesters can be readily split by lipase enzymes binding to hydrophobic domains of that linear substrate. PVA/PCL films in contrast are not biodegradable by PCL-degrading microorganisms. It can be assumed that the surface properties of PCL change upon interaction with PVA in a manner that enzymatic accessibility of the hydrolysable PCL backbone motifs is decreased.

4.2 Vinyl Alcohol Block Copolymers

Water-soluble polymers are highly attractive candidate molecules in many applications. Many of these polymers are not easily biodegradable. Good examples are polycarboxylates that are widely used as dispersing agents to avoid particle aggregation and to improve the flow characteristics of suspensions. As PVA is known to be a polymeric chain that can principally be degraded by biological means, it is quite obvious to introduce PVA sequences into those polymer backbones. Functional vinyl monomers were copolymerised with vinyl acetate followed by saponification to obtain poly(carboxylate-*co*-vinyl alcohol) copolymers. Using selected PVA-degrading microorganisms, an average block length of about 5–6 vinyl alcohol units was found to be necessary to obtain enzymatic cleavage of the copolymer backbone [47]. Experiments with pure

enzymes showed a minimum vinyl alcohol length of 3 diol units, with a preference for isotactic stereochemistry rather than atactic stereochemistry.

A similar strategy was followed to impart biodegradability to polyacrylates, a group of polymers we cannot imagine being without in our daily life. The polymer's application as superabsorber not only helps diaper management but also aids water retention in the root area of plantations to retain and deliver limited water resources, especially in arid agricultural areas. PVA was functionalised, copolymerised and crosslinked with acrylic acid or its partially neutralised form to give crosslinked polyacrylates that could swell in water. The three-dimensional acrylic acid vinyl alcohol graft copolymer network still retained its swelling properties. Enzymatic degradation could be easily monitored by the loss of its water-absorbing properties in vitro [48].

Copolymers of ethylene with vinyl alcohol are high volume technical polymer products. Poly(ethylene-*co*-vinyl alcohol) (EVOH) is synthesised by hydrolysis of poly(ethylene-*co*-vinyl acetate) with an ethylene content of 40–45 mol%. This high value makes the EVOH almost insoluble in water. In data sheets, EVOH products are categorised as biologically inert and not biodegradable (e.g. [49]). Many efforts have been made to show biodegradation of EVOH in different biotopes or by applying enzyme mixtures. Convincing results showing biodegradation of pure EVOH using radiolabelled [^{14}C]EVOH samples have not yet been presented, but hints on some degrading activity in noncrystalline regions are published [50]. Blending with a biodegradable biopolymer to readjust such a nonbiodegradable material to a bioplastic product classified as biodegradable has been applied. The thermoplastic starch blend (e.g. starch/EVOH 60:40; trademark Mater-Bi, Novamont) is a successful example of that strategy. A waterproof bioplastic is obtained by an extrusion process whereby the hydrophilic disperse starch phase is intimately compounded in a continuous hydrophobic EVOH phase. Structural characteristics of the blends are described in great detail and show that all starches were destructurised upon the EVOH compounding to generate new interfaces for enzyme-etching treatments. Data on the fate of these mixed phases in the biodegradation process have not been disclosed [51]. It is not expected that crystalline EVOH phase residues can be rendered biodegradable by this process. The product shows acceptable biodegradation behaviour for marketing [52, 53].

4.3 PVA Biodegradation

There is broad consensus that PVA is among the few vinyl polymers that are principally biodegradable. As already outlined, this rating of PVA is only correct if certain requirements in structural features are met. Besides the intrinsic polymer parameters, biodegradation is strongly dependent on the surrounding conditions that PVA encounters on being released into the environment. Availability of water plays a crucial role, as well as the occurrence of biotic or abiotic structures than can interact with the polymer surface. In the end, the determining factor for

biodegradation is the existence of microbial organisms that have the repertoire to modify, hydrolyse, metabolise and finally assimilate the PVA molecule.

Comprehensive reviews of many aspects of PVA biodegradation are given by Chiellini [37] and Matsumura [54] . A more biochemical focus is compiled in a recent detailed review by Kawai and Hu [28]. Here, we will try to give an updated survey to make orientation in that biological area easier.

5 Microbial Systems

5.1 Organisms and Communities

The search for biodegrading microorganisms does not necessarily have to start in areas with massive exposure to the polymer compounds. The hunt for microbes can often very successfully be done in any municipal sewage sludge or backyard compost heap, as many potent strains that break down polluting substances can be found all over the planet. However, in contrast to many other polymer-degrading organisms, the strains that are able to deal with PVA are not easily isolated from biotopes that have no PVA exposition history. Many examples are available in the literature that describe successful isolation of those species from PVA polluted environments [55]. This general finding for PVA degraders might be explained from an evolutionary point of view. PVA as a synthetic polymer entered natural environments at a late stage of evolution. Microorganisms are not yet prepared to use such resources as a standard carbon source as they do with many other polymers that show more similarity to naturally occurring counterparts.

A broad taxonomic survey of PVA degraders is not very fruitful as the organisms known until now that are able to productively deal with PVA cover just a few families. Among the degrading strains, many species can be found in the genus Pseudomonas and Sphingomonas [56]. Other genera include Alcaligenes and *Bacillus*. Examples of the microbes involved in PVA biodegradation are given in Table 1.

Besides their occurrence in bacteria, there are also some publications describing PVA degradation by organisms belonging to the kingdom of fungi. Among them, yeasts represent a prominent group as well as some lignolytic basidiomycetes like *Phanerochaete* that are known for their capacities in wood rotting and breaking down of potentially harmful chemicals.

Surveying the PVA-degrading microbial candidates, a broad range from specialists to generalists is described, which is not uncommon with many other compounds. The single degraders, microorganisms that can exclusively grow with PVA as carbon source, can be screened quite easily by applying selective enrichment conditions. Those candidates were first indentified. Quite interesting is a second group of degraders, the biodegradation community. A lot of examples are known where two or even more strains work together to make the PVA source

Table 1 Examples of single cultures and microbial communities (mixed cultures) that show PVA degradation

Microorganisms	Reference
Single cultures	
Pseudomonas sp. A41	Fukae et al. [57]
Pseudomonas 113P3 (*Sphingopyxis* sp. 113P3)	Hatanaka et al. [58]
Achromobacter cholinophagum SB98	Lee et al. [59]
Alcaligenes faecalis KK314	Matsumura et al. [31]
Penicillium sp. ASH02-21	Qian et al. [60]
Brevibacillus laterosporus	Lim et al. [61]
Streptomyces venezuelae GY1	Zhang et al. [62]
Geobacillus tepidamans	Kim et al. [51]
Microbial communities	
Pseudomonas sp. VM15C, *Pseudomonas putida* sp. VM15A (PQQ delivery)	Shimao et al. [63]
Bacillus megaterium BX1/unknown bacteria PN19	Mori et al. [64]
Sphingomonas sp./*Rhodococcus erythropolis* (PQQ delivery)	Vaclavkova et al. [25]
Sphingomonas sp. SA3/*Sphingomonas* sp. SA2 (PQQ delivery)	Kim et al. [65]
Brevibacillus brevis, *Brevibacillus limnophilus*	Kim et al. [51]

Cultivation is usually described using PVA as a single carbon source. PQQ could be identified as the molecule sine qua non in some communities with an auxotrophic partner

accessible and usable as a nutrient (see Table 1 and references therein). Symbiotic pairs can be identified where each single partner cannot utilise PVA, but cooperatively they perform well using the PVA polymer for their metabolism.

Different cooperation models are described, but not in all cases are the individual roles and the molecular factors that each partner contributes or demands clear. In some cases, the partners work together by providing different sets of PVA-degrading enzymes that work both extracellularly and cell-associated on large and small PVA molecules [66]. The predominating symbiotic communities were composed of strains owning a PVA-degrading system and others supplying an essential cofactor (being themselves unable to grow on PVA). This factor could in some cases be unequivocally identified as pyrroloquinoline quinone (PQQ), a redox cofactor that plays an essential role in electron transfer capabilities of enzymes and redox chains similar to the widely distributed nicotinamide and flavin systems. In other communities, the mutual dependencies that might possibly also be a cross-feeding system, are not yet fully understood.

Microbial communities dealing with different substrates are stable and successful systems, as they are able to react to different availability of resources. Data on the further integration of PVA-degrading symbiotic communities in such networks involving also PVA blended components and other substrates have not yet been described in detail.

A third group of organisms was studied that are usually regarded as very potent degraders [67]. Wood-rotting fungi have to deal with the most recalcitrant natural material on the planet and are good candidates for investigation. Though degradation could be shown by a *Phanerochaete* fungi using preoxidised PVA [68],

a substantial role of those fungi as natural degraders is questionable. The sites where PVA predominantly enters the environment is not densely colonised by white-rot fungi. Thus, PVA degradation by these lignolytic strains should be discussed as an interesting mechanism in an artificial experimental array and as a coincidental effect of the natural fungal enzymatic repertoire.

5.2 Aqueous Systems and Composting Sites

Most of the species shown in Table 1 were isolated from aqueous sites. Locations rich in water are exactly those points with extensive PVA release into the environment. Production sites of textile and paper manufacturers were identified as hot spots of PVA entry into the environment.

Successful biodegradation of dissolved PVA is usually described for aqueous conditions on sites with a common PVA load. Under aerobic conditions, degradation rates of PVA and PVA blown films comparable to cellulose could be obtained; however, incubation time in adapted sewage sludge was considerably longer [69]. It must be mentioned that microbial degradability is not only a characteristic or a property of the organic compound, but also a matter of the conditions encountered in a specific degradation environment like a sewage plant. In many cases, the system with its requirements determines whether an organic chemical like PVA degrades or not and how fast the processes proceed. PVA is an outstanding example showing that terms and conditions are crucial. Quantitative degradation can be seen in a system of biological wastewater treatment plant and activated sludge with an adapted microbial population, with a low food to microorganism ratio (F/M), constant influx and temperatures above 18 °C. In contrast, PVA passes through the same system largely unchanged given only temporary influx, low input concentration (making adaption impossible), a high F/M ratio and temperatures below 10 °C [70]

Anaerobic trials generally showed poor biodegradation. A preferential degradation of low molecular weight PVA specimens was found [71]. Anaerobic and aerobic degradation are thought to proceed in very similar biochemical way. Anyway, an anaerobic PVA-degrading microorganism has yet to be isolated.

According to composting and soil trials, biodegradation rates of PVA are worse for solid PVA products like blown films. PVA-based blown films were evaluated in compost from urban waste by measuring the percentage of polymer that is converted to CO_2. Even for long incubation periods, only a very moderate biodegradation was monitored and did not exceed 7%. PVA with a DH of 88% performed only marginally better than almost complete deacetylated PVA (DH 98%).

PVA films buried in soil were tested after 120 days and showed only very limited signs of biodegradation, and even field tests with PVA sheets buried for 2 years in different natural soil sites showed only limited (10%) weight loss. No traces of colonising microorganisms were detected on the incubated material. Degradable polymers like poly(hydroxy butyrate), PCL or starch are usually extensively

covered by degrading microorganisms in such experiments. The low propensity towards biodegradation can be explained by the general scarcity of microbial degraders in average soil and the stabilising interaction of different hydrolysed PVA with soil components like minerals [27] or humic acids [72].

6 Biochemical Systems

To break up the polymeric structure of PVA, i.e. to disintegrate the large polymer to more comfortable small sized oligomers that can be transported through the cellular membranes, and finally to channel those components into the primary metabolism is the task to be done to complete the biodegradation process. The main tools available for the degrading organisms are enzymatically active proteins that work outside and inside of the membrane-enclosed cell. Depending on the structural organisation of the species under consideration, additional cell walls and membranes can complicate this basic situation.

In the literature of PVA biodegradation, the orientation with respect to the enzymatic activities that are described is not clear-cut and sometimes even perplexing. This originates in the historical development of the field that gave rise to the nomenclature used today. Table 2 aims to give a clear denomination of the enzymes that are directly involved in the biodegradation of PVA, and that are cited in the literature so far. As an unambiguous denomination for enzyme activity, the Enzyme Commission number (EC number) is used. Every EC number is

Table 2 List of enzymes involved in the biodegradation of poly(vinyl alcohol)

EC number [a]	Name (recommended)	Synonyms (found in literature)	Gene[b]
1.1.3.30	Poly(vinyl alcohol) oxidase	PVA oxidase, poly(vinyl alcohol) oxidoreductase, poly(vinyl alcohol) dehydrogenase	–
1.1.3.18	Secondary-alcohol oxidoreductase	Polyvinyl alcohol oxidase, PVA oxidase, SAO	–
1.1.1.x (no entry)	Secondary-alcohol dehydrogenase	SADH (NAD) [73]	–
1.1.2.6	Polyvinyl alcohol dehydrogenase (cytochrome)	Poly(vinyl alcohol) dehydrogenase, PVA dehydrogenase, PVADH, PVADH-S, PQQ dependent PVA-DH, EC 1.1.99.23 (from 2010), apoenzyme acts on oxiPVA as specific aldolase [74]	*pvaA*, *cytC*
3.7.1.7.	Beta-diketone hydrolase	Oxidised poly(vinyl alcohol) hydrolase, oxiPVA hydrolase, OPH, OPH hydrolase, BDH	*pvaB*, *bdh*, *oph*
3.1.1.1	Acetylesterase (PVA)	Poly (vinylalcohol-*co*-vinylacetat) esterase, P(VA-*co*-VAc) esterase	–

[a]SADH as well as the specific acetylesterases are not yet finally classified in the databases
[b]The corresponding list of genes is not complete yet

associated with a recommended name for the respective enzyme. The enzymes can be easily found in databases. To get a good overview covering the relevant literature linked with the enzymes, updated databases are a valuable tool. Two examples are BRENDA, The Comprehensive Enzyme Information System, which compiles a collection of almost all relevant publications for every enzyme given in Table 2, and the Universal Protein Database, UniProt http://www.uniprot.org.

6.1 Enzymes

Surveying our present knowledge about the enzyme activities in PVA biodegradation, a trend toward increasing integration can be seen. There are free enzymes working in the extracellular space of the cells, including also the periplasmatic volume, and there are membrane-associated enzymes that are presumably linked to the cellular cytochrome-based electron transport chains.

Highly specific enzymes are described as acting on the PVA polymer. The primary degradation products, after breakage of the polymeric backbone, are substrates for enzymes with differing stringencies with respect to the specific PVA-derived substrate. Finally, cellular enzymes take over, that do not discriminate between the PVA metabolites and similar molecules in the metabolic pathways. In contrast to the PVA-specific enzymes are those activities that can be summarised as unspecific degradation enzymes or enzyme mixtures. Those systems have evolved to break up highly reluctant biological composite materials developed for stability and longevity and might do a good job in PVA degradation, but are not yet evolutionarily fine-tuned for that target molecule.

The degradation of PVA in bacteria proceeds in basically two steps. The 1,3-diol moieties in the C–C linked PVA main chain are first transformed at many sites by dehydrogenases or oxidase enzymes into a backbone structure containing β-hydroxy ketone structures or vicinal 1,3-diketone elements. Subsequent chain opening proceeds via specific hydrolases or aldolase-like enzymes that generate shorter segments. Acetyl groups still present on the PVA oligomers are removed by intracellular acetyl esterases delivering acetic acid into the cellular metabolism. The residual molecule can be funnelled into the standard β-oxidation pathway and serve as building material or is used as an energy source and finally oxidised to CO_2.

The specific oxidative enzymes working on PVA introduce a β-hydroxy ketone structure into the PVA backbone. Oxygen serves as an electron-accepting molecule that is reduced on the active site of the oxidase to hydrogen peroxide. These oxidases are not described in much detail. PVA oxidase (EC 1.1.3.30) and the secondary-alcohol oxidoreductase (SAO; EC 1.1.3.18) acting on PVA are described in the databases. In contrast, a secondary-alcohol dehydrogenase (SADH) activity acting on PVA is described that differs in its electron-accepting partner molecule. The dehydrogenase uses NAD as electron acceptor, which is concomitantly transformed to its reduced state $NADH_2$. Besides O_2 and NAD, a third electron

acceptor is known among the enzymes described for oxidising the PVA backbone. This molecule was identified as pyrroloquinoline quinone (PQQ), a small (molecular weight 330 Da) molecule with two adjacent ketogroups in its structure that can undergo an appropriate redox cycle. PQQ (also known as methoxatin) is a recently discovered organic molecule and considered by most to be a vitamin because the human body cannot produce it on its own. Enzymes using this compound as redox cofactor are called quinoproteins. A PVA dehydrogenase (PVADH) was found in some bacterial strains (*Pseudomonas*), which could grow on PVA but were deficient in PVA oxidase. The enzyme with its recommended name polyvinyl alcohol dehydrogenase (cytochrome) owns a binding site for PQQ. The PVADH is classified as EC 1.1.2.6., the former classification as EC 1.1.99.23 was recently cancelled. The PVADH is also designated with the systematic name polyvinyl alcohol: ferricytochrome-*c* oxidoreductase, which reflects the observation that the enzymatic oxidation of PVA is coupled to the respiratory chain of the microbe via the heme-containing redoxprotein cytochrome *c*. Such a coupling could not be observed with PVA oxidases. Although PVADH could be successfully cloned and heterologously expressed [75], a non-quino-hemoprotein PVA oxidase has not yet been cloned [76].

The initial oxidative enzymatic transformation of PVA by the enzymes described above (PVA oxidase, SAO, SADH and PVADH) gives rise to a PVA backbone with a series of β-hydroxy ketone groups; direct introduction of a vicinal diketone structure is also described with a different enzyme, PVADH-S [54]. The generation of diketone elements in the PVA chain is catalysed by the same enzymes that started the oxidative attack. Depending on the organism, the SAO, SADH or PVADH, or combinations thereof, oxidise the β-hydroxy ketone to 1,3-diketone moieties, which are the breaking points for further degradation (Fig. 5). Besides this specific enzymatic transformation via the PVA-specific oxidase or dehydrogenase enzymes, a nonspecific oxidative attack on PVA polymers is also possible.

Oxidative degradation mechanisms with low substrate specificity are described for many recalcitrant naturally occurring polymeric substrates. The most difficult substrates are found among the lignocellulose composite materials, representing the dominant biomass component on the planet. The two main components, cellulose and lignin, are intimately linked by different kinds of noncovalent and covalent bonds. Both partners are by themselves strong materials requiring specialised enzyme systems for degradation. Cellulose exists in the form of highly crystalline phase. In this respect, it shows some similarity with extensively deacetylated PVA. The activation of cellulose proceeds via specialised enzymes that specifically bind via their binding domains to the surface of the cellulose polymer, which is not soluble in water. Local enzymatic endohydrolysis of single polymer chains by cellulases opens the macroscopic polymer, thereby facilitating further degradation by other specialised enzymes. In addition, fundamentally different mechanisms to attack the crystalline cellulosic structure exist using oxidative enzymes. Oxidative enzymes are the active species in the degradation of lignin. This polymer has evolved as a matrix polymer, which imparts durability and strength to the cells. Thus, it is not surprising that its enzymatic degradation needs a sophisticated

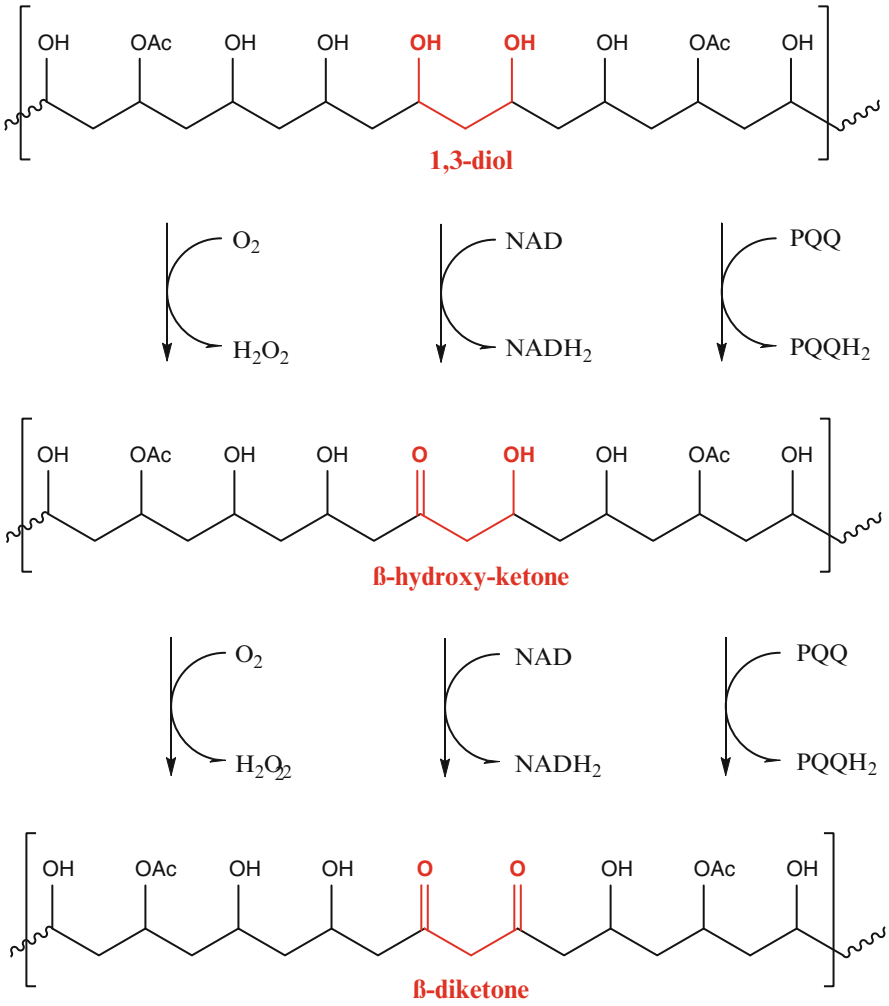

Fig. 5 Enzymatic oxidation of highly hydrolysed PVA proceeds in two steps: 1,3-diol elements in PVA are oxidised via the β-OH-ketone to form a diketone moiety. Three enzyme systems using different electron acceptors as cofactors/cosubstrates are shown

toolbox. Again, Nature uses oxidases with low substrate specificity like lignin peroxidase, manganese peroxidase or laccase to weaken the lignin structures before attacking the macromolecule with more specific enzyme activities.

Such unspecific oxidative attack is also discussed as a possible route in the biodegradation fate of PVA. Oxidation of PVA should be possible, as very aggressive oxidative species can be generated by the extracellular enzyme mixtures of wood-rotting fungi. Unspecific oxidative incidents are to be expected when strongly oxidising low molecular mediators react with PVA, a mechanism that is described as the indirect action of laccase enzymes [77]. Reports about the beneficial

influence of oxidation on biodegradability of PVA are published [78]. Scarce data are available that show specific changes in the PVA structure upon contact with white-rot fungi like *Phanerochaete chrysosporium* [79]. A substantial biodegradation of PVA by wood-rotting fungi has not yet been described.

Chain degradation proceeds at the oxidised sites, where two different routes can be discerned. One way uses the β-hydroxy ketone functionalities introduced by the initial enzymatic attack as direct substrates in an aldolase-like scission reaction. The other way proceeds via further oxidation of this structure to a 1,3-diketone, which serves as a target structure for a hydrolase-type splitting enzyme.

The first route was found in an *Alcaligenes faecalis* KK314 strain. The enzyme that split the PVA on the β-hydroxy ketone element, like an aldolase, was surprisingly found to be identical with the PVADH apoenzyme of the same strain (Apo PVADH). The identical protein is capable of oxidising (with bound PQQ) and splitting (without bound PQQ) the PVA chain, depending on its binding state [68]. A homologous PVADH enzyme from *Pseudomonas* did not show this bifunctional activity of its PQQ-free apoform. As a product of the enzymatic polymer splitting, a methyl ketone-terminated PVA moiety is formed together with an aldehyde-terminated PVA piece that can be easily oxidised to a terminal carbonic acid.

The preferred route for reducing the molecular weight of PVA involves chain scission at the 1,3-diketone site (see Fig. 6). As the diketone element is chemically not very stable, a spontaneous degradation of oxidised PVA was also discussed [80]. Nevertheless, the preferred degradation pathway is most likely the biochemical process because enzymes were identified that showed high activity with diketone substrates [81], especially with oxidised PVA. The β-diketone hydrolase (BDH; EC 3.7.1.7) hydrolyses aliphatic β-diketones to form methyl ketones and carboxylic acids in equimolar amounts [82]. The enzymatic cleavage of C–C bonds in β-diketones is not well studied [83]. BDH enzymes could be isolated from different PVA-degrading strains, purified, characterised and cloned [84].

As enzymatic oxidative transformation of the PVA polymer can act as a multiple simultaneous event on the polymer with concurrent chain fission by the appropriate enzymes, the polymer can be broken down into small oligomers that can be channelled into the primary metabolism. This picture is not complete because PVA is usually more or less acetylated. The DH is a pivotal factor in almost every aspect of PVA application. Surprisingly there are very few data dealing with the enzymes involved in the deacetylation of not fully hydrolysed PVA polymer. In technical processes, esterase enzymes are widely applied to deal with PVAc structures. A good example is from the pulp and paper industry [85], where PVAc, a component of “stickies”, is hydrolysed to the less sticky PVA. Esterases from natural sources are known to accept the acetyl residues on the polymer as substrate but little detailed knowledge exists about the identity of acetyl esterases in the PVA degradative environment [86].

Attempts to identify extracellular esterase activity in PVA-contaminated sites with proven microbial degradation activity showed no substantial results. The breakdown of the polymer proceeds without concomitantly high extracellular esterase activities [36]. These findings suggest that intracellular esterases are the

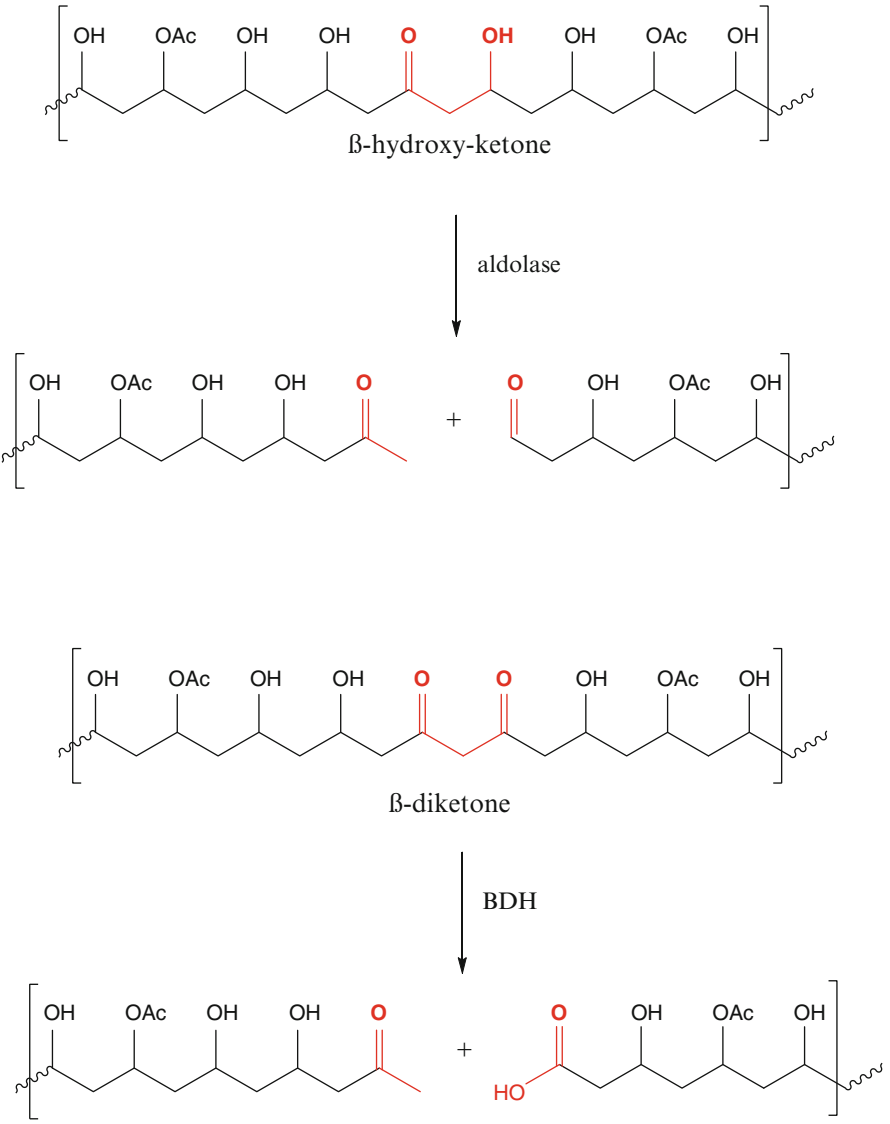

Fig. 6 Enzymatic splitting of the oxidised polymer backbone proceeds by two different enzymes depending on the target moiety in the oxidised polymer backbone. *Above*: the β-OH-ketone can be opened by an aldolase activity (apoenzyme of PVADH). *Below*: the diketone element is cleaved by a specific β-diketone hydrolase (BDH). A non-enzymatic mechanism is also possible

dominant players in finally removing the acetate groups, which can easily be funnelled into the microbial metabolism. Esterases were detected in the cytoplasm of different PVA-degrading organisms, but their activities and specificities remain to be studied in more detail [61]. A clear picture has not yet been presented covering

the interplay of the different activities, but progress especially in the molecular biology of the PVA degradation pathway will hopefully make one available in the near future.

6.2 Genes and Genomic Organisation

The availability of advanced methods in molecular biology suggests an easy approach to any genetic or biochemical question. This statement might be true in the mainstream of biological research but in the narrow side streets scientific progress is demanding and not so fast. Cloning of the enzymatic activities identified in PVA degradation is highly desirable because DNA sequence information explicitly alleviates the interpretation of much biochemical data. By comparing the genetic information of different enzymes one can easily group them in a non-ambiguous system (e.g. by EC classification), a task that still has to be completed for the PVA degradation activities. Sequence analysis can identify homologies of the enzymes involved, show the relationships with other known enzymes and give hints on still unrecognised properties with respect to the single protein or its possibly coordinated regulation in the interplay with neighbouring activities.

Although PVA degraders do not densely populate all niches of the biosphere, a few organisms have been isolated from contaminated sites. Enzymes from two organisms are described in detail down to the molecular genetic level. Some workers have analysed PVA degradation genes in *Pseudomonas* sp. strain VM15C and another group focused on a different strain, *Pseudomonas* sp. 113P3, which was later newly identified as a *Sphingopyxis* sp. strain 113P3, again later reclassified as a *Sphingomonas* sp. strain 113P3. Two genes from the degradation pathway in *Pseudomonas* sp. strain VM15C could be identified (see Fig. 7). The *pvaA* gene codes for the PVA dehydrogenase, and the *pvaB* gene encodes for the oxidised polyvinyl alcohol hydrolase of this strain.

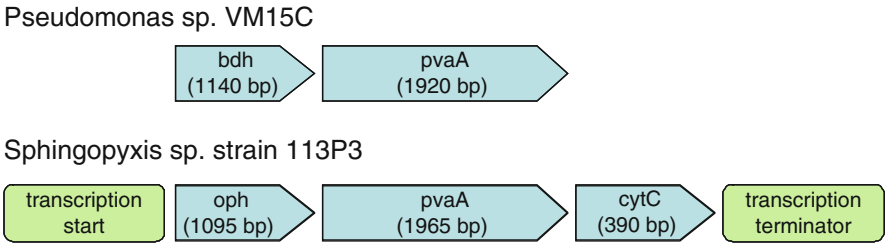

Fig. 7 Genes coding for PVA degradations are organised in an operon structure. The scheme (simplified from Kawai [70]) shows the situation in two well-studied PVA-degrading strains (*Pseudomonas* and *Sphingopyxis*). The genetic organisation in other strains has not yet been examined in such detail

The *pvaA* gene (coding for a 68 kDa protein, PVADH) shows, besides a signal sequence, two sites for the binding of redox-active partner molecules, as expected from the biochemical behaviour [87]. A PQQ binding area was identified as well as a sequence with high homology to known cytochrome *c* binding domains. This latter finding could unequivocally be demonstrated experimentally by in vitro studies with recombinant protein (cloning in *Escherichia coli*) showing cytochrome *c* reduction in the presence of PQQ and PVA [88]. Upstream of the *pvaA* gene, the *pvaB* gene could be localised encoding oxidised PVA hydrolase [89]. This finding indicated that *pvaA* and *pvaB* constitute an operon in the order *pvaBA*. The *pvaB* gene (encoding for a 41 kDa protein, BDH) shows a lipoprotein signal sequence and a lipase consensus sequence characteristic of the active-site region in serine hydrolases.

Similar results are published from PVA degradation with *Sphingomonas* sp. strain 113P3. In the periplasm of this microorganism, a constitutively expressed oxidised polyvinyl alcohol hydrolase (OPH) and polyvinyl alcohol dehydrogenase were found [76]. Sequence analysis of the *oph* gene (cloning in *E. coli*; 330 amino acid residues, homodimer with 35 kDa subunits) showed a signal sequence (34 amino acid residues) and a serine hydrolase motif similar to those in the *pvaB* described above. The two enzymes (from strains 113P3 and VM15C) show a high degree of homology (63%) but also some minor similarity with polyhydroxy butyrate depolymerases from different organisms.

Further downstream of the *oph* gene, a periplasmic PVADH (*pvaA*) was cloned [69]. The deduced amino acid sequence of the PVADH again showed some homology with PVADH from *Pseudomonas* sp. strain VM15C especially with regard to their conserved superbarrel domain (presumably bearing the PQQ binding domain) and their heme binding site. Interestingly, the quinohaemoprotein alcohol dehydrogenase strongly resembles the PVADH, giving rise to speculations about natural ancestor proteins that have gained changed substrate specificity by inverting their domains. This finding additionally supports the observation of a redox chain that transfers electrons from PVA via PQQ and cytochrome *c* in a highly organised molecular arrangement on the PVADH protein into the respiratory chain. Not surprisingly, the gene for cytochrome *c* (a monomeric protein of 16.5 kDa) in *Sphingopyxis* sp. strain 113P3 was cloned (*cytC*) in proximity to the *oph* and *pvaA* genes [90].

The three genes (oph, pvaA, cytC) encoding oxidised PVA hydrolase, PVADH and cytochrome *c* are expressed constitutively and form an operon. Operon organisation of specific pathways is a standard feature of many organisms and enables them to fulfil the specific metabolic challenge in an economic way. The operon structure allows coordinated regulation, balanced expression and spatial organisation with respect to the specific task, as shown for PVA degradation. Such gene bundling makes it also possible to transfer the enzymatic set for the complete pathway to other organisms, given that a genetic transfer system is available. Mobile genetic elements are one element of the standard repertoire of cells that contribute to a horizontal gene transfer.

Sphingomonads have a high capacity to adapt to a new environment and to degrade wide range of xenobiotics, including synthetic polymers. This high capacity is considered to be conferred by a plasmid-borne mechanism, and many sphingomonads contain large plasmids responsible for xenobiotics like polyethylene glycol (PEG). *Sphingopyxis* sp. strain 113P3 was shown to carry megaplasmids including the *pva* operon [91]. Thus, PVA degradation capability can be transferred to other organisms and can be dispersed in the environment given that appropriate conditions are on hand.

The cloning and study of the genes involved in PVA degradation in these two strains have very much promoted our understanding of the fate of PVA in the environment. However, it must be stated that relevant aspects of the PVA biodegradation metabolism still wait to be resolved with respect to a more detailed investigation of these two strains and also in the analysis of the many different organisms capable of catabolically dealing with PVA. The corresponding genes of many enzymes known to be involved have not yet been cloned, like the non-PQQ enzymes or the esterases. The genetic analysis could be very helpful in discriminating between the membrane-bound activities and the enzymes working in the extracellular space or the intracellular cell lumen. It is not clear which apparatus is involved in the transport of PVA across the different cell wall or membrane barriers in the different organisms. The genetic regulation is an open question, both regarding natural or artificial triggering molecules [92] and regarding the transducing and sensing structures. Constitutive expression and inducible activities have not yet been studied on a satisfying level.

7 Conclusion

PVA can generally be regarded as a biologically degradable synthetic polymer. However, real life makes this definite statement a bit more complicated, as pure PVA is in many cases not encountered in its final form of application. First, PVA is generated from the precursor polymer PVAc, a process in which different amounts and distribution patterns of acetyl groups still remain on the polymer backbone, triggering polymer crystallinity and affecting interaction with water, which is indispensible for biodegradation. Second, PVA is mostly used in blends with different polymeric or low molecular weight partners. Depending on each case, supporting or retarding effects on biodegradation are described or must be expected. These aspects make it very difficult to compare biodegradation rates of different PVA products with other polymers classified as biodegradable [93].

PVA is an outstanding example showing that conditions are crucial for biodegradation. Quantitative degradation is described in wastewater treatment plants run with an activated sludge containing an adapted microbial population; however, the biodegradation rate decreases significantly in systems lacking such a prepared microbial population. This must be kept in mind because degrading organisms or communities are not evenly distributed in all biotopes.

Beyond the biological fate of the PVA polymer, the PVA motif is highly attractive as a polymer degradation insert. PVA blocks in copolymers represent potentially cleavable moieties that can impart breaking points in otherwise highly reluctant polymeric species.

In contrast to many other polymers classified as biodegradable, PVA exhibits a backbone solely made up of carbon. The presence of a heteroatom like O or N in the main chain is definitely not a prerequisite for Nature to handle a polymeric structure that does not exist in nature. PVA degradation starts with random oxidations of the polymer backbone in the extracellular or periplasmic space of some microbes. Specific enzymes able to detect such sites of first attack continue in a hydrolytic way, yielding ever smaller polymer fragments that finally can be metabolised by the microbe or the microbial community.

Central key steps are described in the depolymerisation of PVA on the biochemical and genetic level, but further efforts are necessary to completely understand the interrelated steps in PVA degradation.

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