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Biodegradable and Bio-Based Polymers: Future Prospects of Eco-Friendly Plastics

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bio-based plastics · biodegradable plastics · polymers

1. Introduction

Considering their widespread usage in various fields, such as food packaging, clothes, shelter, communication, transportation, construction, health care, and the leisure industries, plastics are very important materials. Currently used plastics are mostly produced from petrochemical products. However, there is a growing demand for eco-friendly plastics, namely bio-based plastics, which are produced from renewable resources, and biodegradable plastics, which degrade in the environment, to establish a more sustainable society and to solve global environmental and waste management problems. Such materials have thus be intensively studied, and their current uses as well as future prospects are discussed in this Essay.

2. Eco-Friendly Plastics

Biodegradable plastics were first studied as materials that contribute to environmental conservation. The definition for biodegradable plastics was standardized by ISO/TC61/SC5/WG22 (ISO 472/DAM3, Amendment 3, General Terms and Terms Relating to Degradable Plastics).[1] Ideal biodegradable plastics are defined as materials that are completely degraded to carbon dioxide and water by the action of naturally occurring microorganisms, such as bacteria, fungi, and algae (Figure 1). Accordingly, it does not matter whether

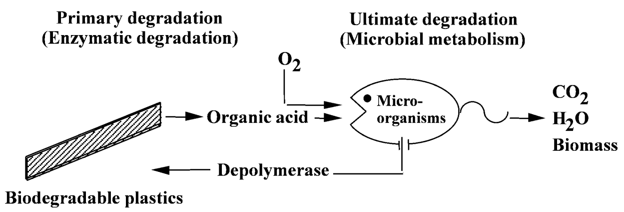

Figure 1. Biodegradation routes of biodegradable plastics.

non-renewable fossil resources or renewable biomass resources are used as the raw materials because biodegradable plastics are eco-friendly from the view point of biodegradability.

On the other hand, bio-based plastics are defined as materials that are produced from renewable carbon resources. Extracted components from plant and wood biomass, such as starch, cellulose, hemicellulose, lignin, or plant oil, which are produced by photosynthesis from atmospheric carbon dioxide, are used as renewable carbon resources (Figure 2).

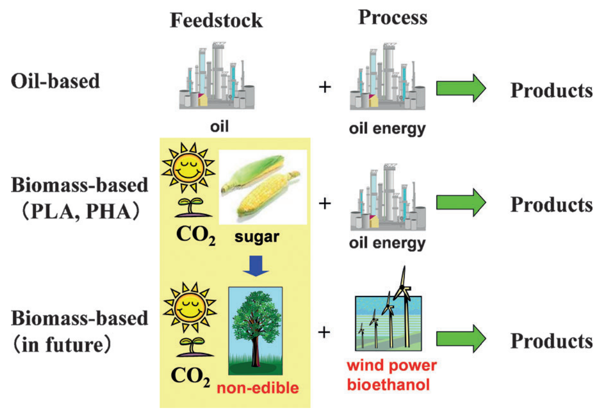

Figure 2. Production of oil-based and bio-based plastics.

Accordingly, when bio-based plastics are burned after use, they are considered as eco-friendly materials, based on the concept of "carbon neutrality"; the generated carbon dioxide is again converted into biomass by photosynthesis. Thus, it does not matter whether bio-based plastics are biodegradable or not. Recently, more sophisticated calculations over the whole life cycle of a product taking into account several environmental categories have been employed in order to demonstrate the benefits of bioplastics.[2]

Biodegradable plastics and bio-based plastics are often confused with each other as eco-friendly plastics, although they are not identical in terms of the original concept. Biodegradable plastics have been developed from the view point of biodegradability, whereas for bio-based plastics, biomass is used as the raw material instead of oil.

In this Essay, we will explain why these two plastic types are discussed at the same time and describe the historical development of both plastics.

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Table 1: Classification of plastics.

	Bio-based plastics (renewable resources)	Oil-based plastics (fossil resources)
Biodegradable plastics	poly(lactic acid) (PLA) polyhydroxyalkanoate (PHA) polysaccharide derivatives (low DS)[a] poly(amino acid)	poly(ε-caprolactone) (PCL) poly(butylene succinate/adipate) (PBS/A) poly(butylene adipate-*co*-terephthalate) (PBA/T)
Non-biodegradable plastics	polysaccharide derivatives (high DS)[a] polyol–polyurethane bio-polyethylene (bio-PE) bio-poly(ethylene terephthalate) (bio-PET)	polyethylene (PE) polypropylene (PP) polystyrene (PS) poly(ethylene terephthalate) (PET)

[a] DS = degree of substitution.

3. Classification of Eco-Friendly Plastics

Plastics can be classified into four categories considering their biodegradability and raw materials (Table 1).

Polyethylene (PE), polypropylene (PP), and poly(ethylene terephthalate) (PET), which have contributed to the development of today's human society, are typical oil-based non-biodegradable plastics. Whereas most of the oil-based plastics are recognized as non-biodegradable, poly(ε-caprolactone) (PCL), poly(butylene succinate/adipate) (PBS/A), and poly(butylene adipate-*co*-terephthalate) (PBA/T) are biodegradable.[3] These polymers feature ester bonds, which can be degraded by certain enzymes that are secreted by microorganisms, and are thus categorized as oil-based biodegradable plastics.

On the other hand, all bio-based plastics are considered to be biodegradable. However, polysaccharide derivatives with a high degree of substitution (DS), for example, cellulose acetate, which is used in films and filters, are not biodegraded in the environment, even though cellulose is a natural polysaccharide and completely degraded by cellulase. Furthermore, bio-PE is not biodegradable, even though bio-PE is synthesized from bio-ethanol, which is produced by the fermentation of glucose. Recently, bio-PET has also been produced from biomass by using bio-based ethylene glycol. The biomass content in bio-PET is approximately 30%. Bio-PET is of course not biodegradable. Thus, bio-based plastics are not necessarily also biodegradable.

There is a historical reason for why bio-based plastics were misunderstood to be always biodegradable. When eco-friendly plastics were first developed, poly(lactic acid) (PLA)[4–6] and microbial polyesters[7–10] were mainly studied. PLA is chemosynthesized from lactic acid, which is obtained by fermentation from glucose extracted from corn starch and sugar cane. Microbial polyesters are microbially synthesized from glucose and plant oil and accumulate in microorganisms (Figure 3). PLA and microbial polyesters are produced from biomass and are biodegradable in compost, which was the main end-of-life option studied during the 1990s. Therefore, it was misunderstood that bio-based plastics are identical to biodegradable plastics, and this misunderstanding has caused various problems. The true practical value of eco-friendly plastics has yet to be realized.

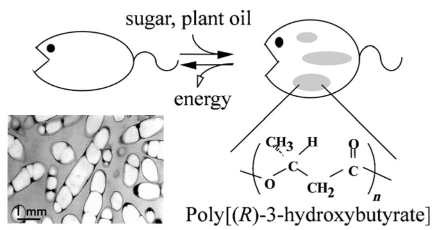

Figure 3. Biosynthesis of microbial polyesters. Inset: TEM image of microorganisms that consist of polyhydroxyalkanoate (PHA) to 86%.

Tadahisa Iwata obtained his PhD degree in Wood Science & Technology from Kyoto University in 1994. Afterwards, he spent 10 years at RIKEN Institute, Japan, as a researcher and then as the Vice Head of the Polymer Chemistry Laboratory. In 2006, he became Associate Professor at the University of Tokyo, where he was promoted to Professor in 2012. Since 2013, he has been the Head of the Department of Biomaterial Sciences, Graduate School of Agricultural and Life Sciences at the same university. His research interests include polymeric materials, bio-based polymers, biodegradable plastics, polymer crystallography, and polymer physics.

4. Problems and Prospects of Biodegradable Plastics

Biodegradable plastics have already been utilized as food packaging materials or in miscellaneous disposable goods with daily usage. In the future, biodegradable plastics are expected to be used in the environment as agricultural engineering materials, such as mulch films or sandbags, (Figure 4), as materials for fisheries, for example, as fishing lines or fishing nets, in a medical context as bioabsorbable materials, such as surgical sutures or scaffolds (Figure 5),[11] and as sanitary goods, such as paper diapers. However, their true practical use is hampered by many problems.

One such problem concerns the blending with other polymers. When a biodegradable plastic on its own does not have the desired properties, another polymer has to be blended to obtain the desired properties. When a non-biodegradable plastic is blended with a biodegradable plastic,

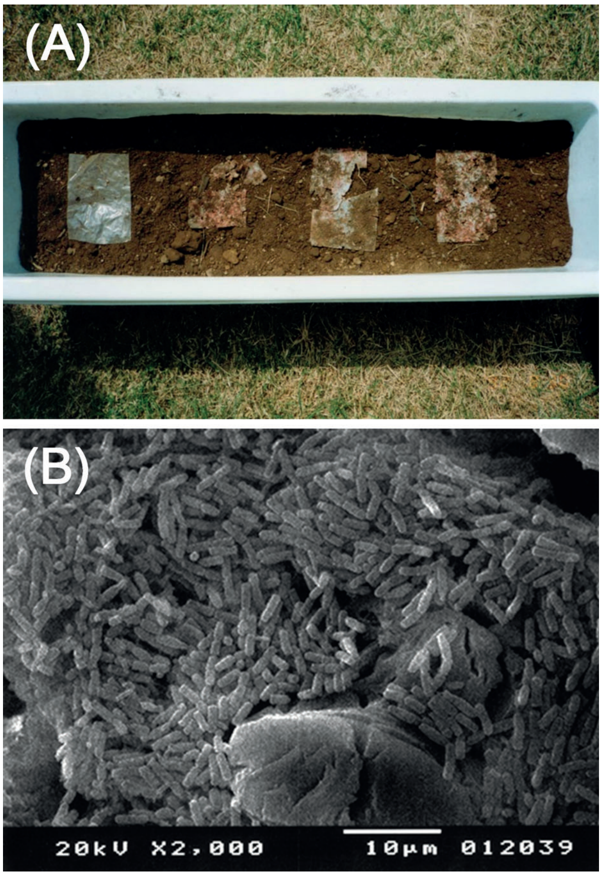

Figure 4. A) Biodegradation of a PHA film placed in soil. The film disappeared completely within less than four months in summer time. B) SEM image of degrading microorganisms on a PHA film surface.

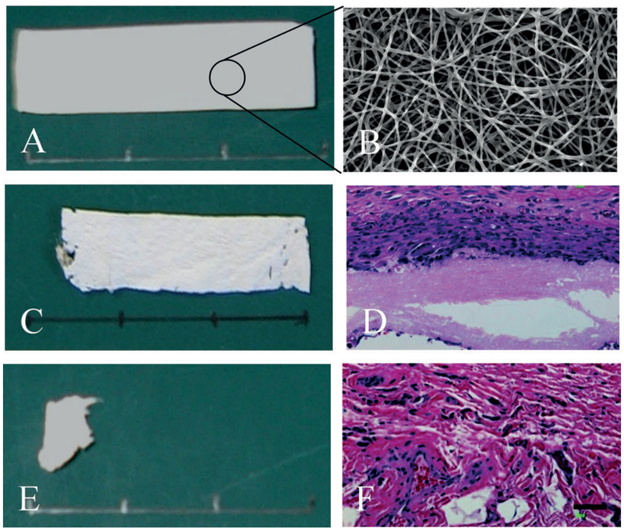

Figure 5. Physical appearance of electrospun PHA nanofiber scaffolds before (A and B) and four (C) and twelve (E) weeks after subcutaneous implantation in a rat. Phase-contrast images of hematoxylin/eosin-stained ultrathin sections of PHA nanofiber scaffolds after in vivo degradation for four (D) and twelve weeks (F). Scale bars: 50 μm.[11]

only the biodegradable components will be degraded in the environment. As a result, non-biodegradable plastics that are broken up into smaller particles diffuse into the environment and will cause environmental pollution. Furthermore, the usage of copolymers that consist of biodegradable and non-biodegradable monomers might cause more serious pollution, and these copolymers should never be used as biodegradable plastics.

Another problem of biodegradable plastics is the control of the biodegradation rate and the addition of a biodegradation trigger. The desired rate of biodegradation and bioabsorption depends on the purpose of use. It is well-known that crystallinity, lamellar thickness, and molecular conformation are important factors controlling the biodegradation rate in addition to the various biotic and abiotic factors in different environments.[9,12,13] The desired biodegradation rate can be obtained by devising better molding processes and by controlling the molecular and highly ordered structure of the materials.

Furthermore, biodegradable plastics are also required to show superior performance during their entire use. In other words, it is necessary to be able to trigger off biodegradation immediately after usage and disposal. To that end, the addition of a start function for biodegradation is indispensable.

A long-term concern with biodegradable plastics is the influence of biodegraded products on the environment, including plants and animals. Molded plastics may cause certain problems, for example, a sea turtle could swallow a plastic cap. However, the influence of chemical substances in such molded plastics has been of little concern. On the other hand, once biodegradable plastics have started to degrade, the corresponding products dissolve into water. Considering the definition of biodegradable plastics, these partially biodegraded products have to be completely degraded into water and carbon dioxide by degrading microorganisms (Figure 4B). However, when the amount of partially biodegraded products increases too strongly, the soil becomes acidic owing to their high concentration. Accordingly, it is necessary to monitor the long-term influence of water-soluble biodegradable products on plant growth and soils.

Nevertheless, biodegradable plastics should be collected as much as possible and used for energy production, for example, in the form of biogas, and in composts by microorganism fermentation. Furthermore, biodegradable plastics should be used where diffusion into the environment is inevitable or when garbage separation is difficult. Needless to say, the availability of biodegradable plastics should not encourage littering with plastic products.

Recently, several three-dimensional structures of enzymes that catalyze the degradation of biodegradable plastics, for example, polyhydroxybutyrate depolymerase (Figure 6)[14,15] and cellulases,[16] were revealed. I believe that in future, it will be necessary to develop novel artificial enzymes that degrade non-biodegradable plastics, such as PET or polystyrene (PS), by modification of the structures of these naturally occurring degrading enzymes.

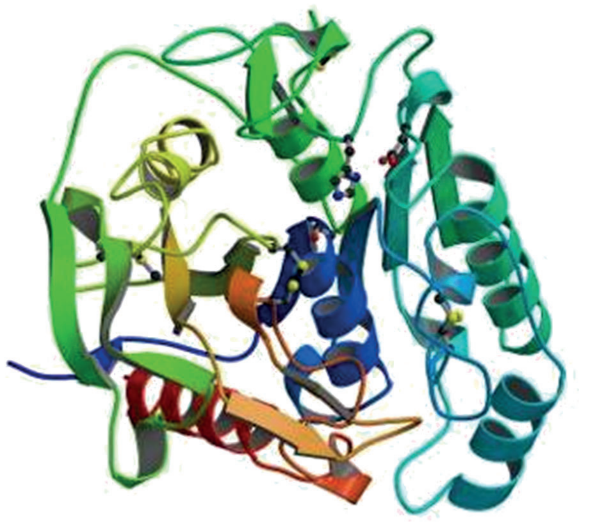

Figure 6. Three-dimensional structure of polyhydroxybutyrate depolymerase.[15]

5. Problems and Prospects of Bio-Based Plastics

The word "biomass" was coined by combining biology (bio) with quantity (mass) and stands for organic resources, such as wood or plant biomass. Apart from a growth period, biomass can be reproduced semi-permanently and artificially by photosynthesis.

The term "bio-based plastics" has only been used for a few years, but such plastics have existed for a long time and have been extensively used as fiber and film materials. For example, cellulose is the most abundant biomass material on earth and has been used as natural fibers, such as cotton and jute, and as regenerated fibers, such as rayon. However, cellulose is not a thermoplastic. Therefore, cellulose derivatives, such as cellulose acetate or carboxymethylcellulose, are also commonly employed. Cellulose acetate is widely used in filter, fiber, and film materials in many areas.

In nature, as well as in cellulose, there are many kinds of natural polysaccharides with various characteristic structures such as hemicellulose containing xylan, chitin, and chitosan, which are obtained from crabs and prawns, or curdlan and pullulan, which are synthesized by microorganisms (Figure 7). The usage of these polysaccharides as plastic raw materials has not attracted any attention until now as these polysaccharides have a small molecular weight and a branched structure, they lack a uniform composition, and production costs are very high. The predominant route to thermoplastic biopolymers today is consequently the depolymerization of either starch or cellulosics into their monomeric sugars and subsequent monomer and polymer synthesis by fermentation and/or chemical catalysis. For the development of new highly functional bio-based polymers by making use of the characteristic structures of natural polysaccharides, additional research in order to compete in future will be necessary. In particular, these natural polysaccharides are categorized as non-edible biomass, and their use as bio-based plastics should thus be positively promoted.

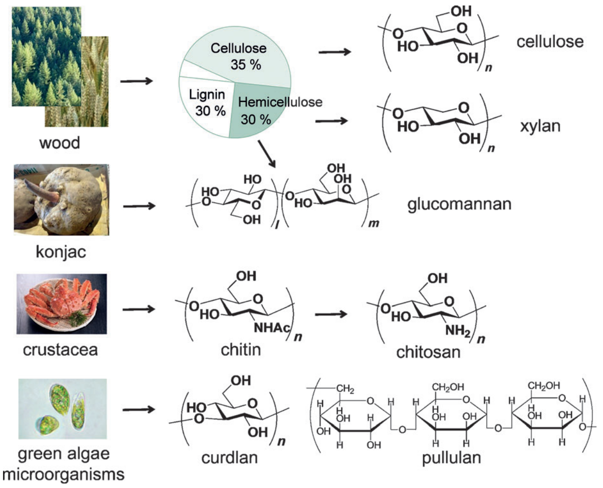

Figure 7. Natural polysaccharides.

Currently, PLA is the most commonly used bio-based polymer and produced from lactic acid (LA). LA is synthesized by microorganisms that use glucose obtained from corn starch and sugar cane as the carbon source. The microbial synthesis of new monomers represents a so-called biorefinery method.

The use of monomers with aromatic moieties is essential to develop polymers with a high thermal stability. The microbial synthesis of aromatic compounds by fermentation is expected to become a very important but challenging research area as aromatic molecules are very difficult to produce via fermentation. Recently, Suzuki et al. succeeded in microbially synthesizing a novel aromatic compound (3-amino-4-hydroxybenzoic acid) from C_3 and C_4 primary metabolites with two enzymes,[17] and Suvannasara et al. developed a new polyimide with a high thermal degradation temperature of over 390 °C.[18]

On the other hand, the study of how to extract these aromatic compounds from wood lignin (Figure 8) has already begun.[19] However, as many kinds of aromatic compounds are isolated simultaneously from lignin, it is difficult to use them as plastic raw materials. Inexpensive and energy-efficient

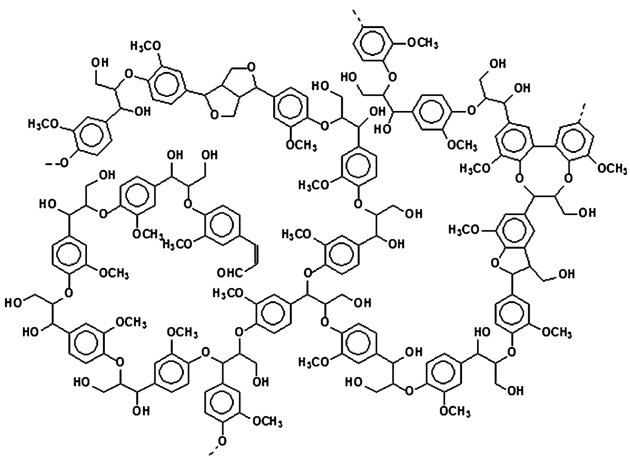

Figure 8. Proposed wood lignin structure.

isolation methods for individual aromatic compounds are not available today and should be researched in the future. Accordingly, I believe that a new approach for the use of lignin is necessary, that is, crude aromatic compounds isolated from lignin should be used directly to produce high-performance materials. Bio-based plastics that are produced from natural polysaccharides and crude aromatic compounds have unique structures and different properties and processing procedures to those of oil-based plastics. New fundamental research on bio-based plastics, including the development of molding and material processing techniques that can be used for all plastics, is thus required.

Another trend for bio-based polymers is the development of techniques to produce common plastics such as PE, PP, or PET from biomass. Bio-PE has already been obtained from bioethanol in Brazil. Furthermore, the poly(ethylene glycol) part of PET has also been obtained from biomass. For these plastics, biomass was used as the raw material instead of oil, but the final products have the same structure as the oil-based plastics. In other words, the same processing equipment and methods can be used, and the properties of the final products are also the same. The problems associated with the high cost of most bioplastics will become less important with a rise in oil prices in the future, but the fast development of non-conventional oil recovery processes from shale gas, for example, is expected to significantly prolong the time frame during which cheap fossil resources will be available. Accordingly, high-performance bio-based plastics that can be produced from biomass alone should be developed.

6. Unification of the Certification System and Social Acceptance

The establishment of a certification system and standard experimental methods are necessary to promote the use of biodegradable and bio-based plastics. For biodegradable plastics, the ISO standard has been established, and each country carries out biodegradation examinations according to this standard; the certification organizations of each country then authenticate "biodegradable plastics" (Figure 9). The Japan Bioplastic Association (JBPA) labels such plastics as "green plastics". Furthermore, an international agreement has been established between Japan, Germany, and the USA. For example, when a plastic that is certificated as a "Green Plastic" in Japan is exported to Germany or the USA, the company can apply for this plastic to receive the certification and logo of "kompostierbar" in Germany or "compostable" in the USA without further testing of the biodegradability in either country. At the present time, most biodegradation tests are only carried out under aerobic conditions. However, in the future, biodegradation tests under anaerobic conditions will also be necessary.

The use of biodegradable plastics is promoted positively in Europe, particularly in Italy, where it was decided in 2010 that all disposable shopping bags should be either reusable or produced from biodegradable plastics. Furthermore, the utilization of biodegradable plastics that are produced from renewable resources is strongly promoted in several European countries, which significantly increases the demand for bio-based biodegradable plastics.

Figure 9. Currently used logos for biodegradable plastics (Copyright permitted by JBPA).

Whereas for biodegradable plastics, unified international standards have been established, some problems related to the certification of bio-based plastics must still be solved. Recently, the synthesis of bio-PE and bio-PET from biomass has been developed. When bio-based variants of common plastics come to be used alone or in composites, it should be disclosed whether these plastics were really made from biomass or what the exact percentage of the bio-based plastic in the composite is (biomass content). As oil-based PE and bio-based PE have the same chemical structure, it is impossible to determine whether a certain PE product was produced from biomass or oil from its appearance. Recently, a method to distinguish between these materials was developed, and the biomass content can be calculated by measuring the amount of radioactive ^{14}C present in the sample by accelerator mass spectrometry.[20] Currently this method is rather expensive (ca. 70000 Yen or 500 € per sample). Nevertheless, the accurate determination of the biomass content in the final product is necessary for regulatory (evaluation and authentication) and inventory purposes. Furthermore, knowing the biomass content in a product will also be an advantage when promoting green products and for securing consumer confidence and satisfaction.

Regarding the certification of bio-based plastics in Japan, there are two different logos, namely the "biomass plastics" logo of the JBPA and the "biomass products" logo of the Japan Organic Resources Association (JORA; Figure 10). The "biomass plastics" logo is given to materials with a bio-based plastic content of greater than 25%. For example, a composite of oil-based PE and wood flour in a ratio of 75:25 is not permitted to use the "biomass plastics" logo. However, the "biomass products" logo is already given to a composite with a wood flour or plant fiber content of more than 5%. Therefore, there is a big difference between these two labels. To make bio-based plastics more popular and to achieve a better understanding of the overall concept, it is necessary to unify these two logos.

Figure 10. Logos used in Japan for products derived from biomass. A) Logo for biomass plastics used by JBPA. B) Logo for biomass products used by JORA (Copyright permitted by JBPA and JORA).

7. Conclusion

Next-generation bio-based and biodegradable plastics, which will contribute to establishing a more sustainable society, should not only be produced from non-edible biomass, but also show a superior performance; they must be strong and last a long time. On the other hand, the biodegradation and recycling of these plastics should be balanced, and recyclable plastics must be recycled as much as possible. Until now, plastics were synthesized from oil by catalytic processes. From now on, we must develop an in-depth understanding of the structure of biomass, which nature created so well, and new functional plastics should be produced by modifying the structure and properties of biomass little by little. To that end, biomass researchers, microbiologists, synthetic chemists, and process engineers should make use of their individual expertise and collaborate to develop materials for human prosperity and a more sustainable society.

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[1] H. Sawada, *Polym. Degrad. Stab.* **1998**, *59*, 365.
[2] a) M. Akiyama, T. Tsuge, Y. Do, *Polym. Degrad. Stab.* **2003**, *80*, 183; b) J. Hong, Y. Zhang, X. Xu, X. Li, *Biomass Bioenergy* **2014**, *67*, 304; c) T. A. Hottle, M. M. Bilec, A. E. Landis, *Polym. Degrad. Stab.* **2013**, *98*, 1898; see also Ref. [4].
[3] Y. Tokiwa, H. Pranamuda in *Microbial degradation of aliphatic polyesters*, *Biopolymers*, *Vol. 3b* (Eds.: A. Steinbüchel, Y. Doi), Wiley-VCH, Weinheim, **2002**, pp. 85–104.
[4] E. T. H. Vink, K. R. Rabago, D. A. Glassner, P. R. Gruber, *Polym. Degrad. Stab.* **2003**, *80*, 403.
[5] R. Auras, B. Harte, S. Selke, *Macromol. Biosci.* **2004**, *4*, 835.
[6] *Poly(Lactic Acid): Synthesis, Structures, Properties, Processing, and Applications* (Eds.: R. Auras, L.-T. Lim, S. E. M. Selke, H. Tsuji), Wiley, Hoboken, NJ, **2010**.
[7] Y. Doi, *Microbial Polyesters*, VCH Publishers, New York, **1990**.
[8] R. W. Lenz, R. H. Marchessault, *Biomacromolecules* **2005**, *6*, 1.
[9] T. Iwata, *Macromol. Biosci.* **2005**, *5*, 689.
[10] B. Laycock, P. Halley, S. Pratt, A. Werker, P. Lant, *Prog. Polym. Sci.* **2014**, *39*, 397.
[11] H. Y. Tang, D. Ishii, A. Mahara, S. Murakami, T. Yamaoka, K. Sudesh, R. Samian, M. Fujita, M. Maeda, T. Iwata, *Biomaterials* **2008**, *29*, 1307.
[12] K. Sudesh, H. Abe, Y. Doi, *Prog. Polym. Sci.* **2000**, *25*, 1503.
[13] T. Iwata, Y. Aoyagi, M. Fujita, A. Takeuchi, Y. Suzuki, K. Uesugi, *Macromolecules* **2006**, *39*, 5789.
[14] D. Jendrossek, R. Handrick, *Annu. Rev. Microbiol.* **2003**, *57*, 403.
[15] T. Hisano, K. Kasuya, Y. Tezuka, N. Ishii, T. Kobayashi, M. Shiraki, E. Orudjev, H. Hansma, T. Iwata, Y. Doi, T. Saito, K. Miki, *J. Mol. Biol.* **2006**, *356*, 993.
[16] B. Henrissat, *Cellulose* **1994**, *1*, 169.
[17] H. Suzuki, Y. Ohnishi, Y. Furusho, S. Sakuda, S. Horinouchi, *J. Biol. Chem.* **2006**, *281*, 36944.
[18] P. Suvannasara, S. Tateyama, A. Miyasato, K. Matsumura, T. Shimoda, T. Ito, Y. Yamagata, T. Fujita, N. Takaya, T. Kaneko, *Macromolecules* **2014**, *47*, 1586.
[19] K. Ehara, D. Takada, S. Saka, *J. Wood Sci.* **2005**, *51*, 256.
[20] M. Kunioka, F. Ninomiya, M. Funabashi, *J. Polym. Environ.* **2007**, *15*, 281.