

Poly(hydroxyalkanoate) (PHA) Biopolyesters: Production, Performance and Processing Aspects

Sustainable industrial development in a not too distant future, based on approaches of the nowadays vividly discussed “White Biotechnology”, will require fundamental changes regarding processing and engineering techniques¹. This development will indispensably have to be based, on the one hand, on renewable energy sources and, on the other hand, on renewable raw materials for manufacturing of goods. Saving of limited fossil energy and material resources has to go in parallel to minimized release of hazardous side streams and spent end-products into the ecosphere. This means that the products obtained by such new processes shall be characterized by a low ecological impact of their entire life cycle.

This special issue of *Chemical and Biochemical Engineering Quarterly* shines a light on contemporary R&D endeavors managed in various research institutions; these endeavors have one aim in common: The replacing of plastics usually stemming from the conversion of fossil feed stocks by “bio-inspired” alternatives provided by nature. The utmost significance of this task shall be visualized by the annual pile of plastics of almost 300 Mt that is produced worldwide; the predominant part of these plastics is highly resistant against (bio-)degradation, and only an evanescent share of about 20 % of spent plastics is subjected to recycling procedures. Sustainable alternatives, so called “environmentally degradable plastics”, exist, but do not even cover 5 % of the global plastic market. In addition, although very fashionable today, the term “environmentally degradable plastic” is used highly ambiguously and often explicitly incorrectly; in many cases, so called “bio-plastics” do not conform to the attributes “bio-based”, “bio-degradable”, or “bio-compatible”^{2,3}.

Microbial poly(hydroxyalkanoates) (PHAs), a versatile group of poly(oxoesters) produced by nature as prokaryotic storage materials, are contemporarily attracting a great deal of attention as polymeric basic materials to be implemented in various fields of the plastic market. This consideration is manifested by the nowadays exponentially growing number of scientific publications and patent applications related to this topic. Not only has the bio-based nature of PHAs underlined their significance for sustainable future developments, but also the high flexibility and adjustability of their properties, their bio-degradability and, to a steadily increasing extent, their bio-compatibility.

These facts, together with the awareness of the urgent need for strategies to terminate the fatal “Plastic

Age” we live in today, were my motivation for more than twelve years of research on these fascinating bio-materials. Here, I want to emphasize the guidance and still ongoing inspiration by my doctoral adviser Prof. Gerhart Braunegg who, as one of the most distinguished pioneers in the field of PHA research, always developed strategies to transfer promising data from laboratory scale to an industrial application, and steadily emphasized the holistic nature of PHA production. This means that, in order to come to a viable production process, all single steps, starting from the intracellular procedures on the genetic and enzymatic level, the selection of the adequate raw materials, the biotechnological process engineering, until the downstream processing for product recovery and refining have to be understood and optimized.

In order to successfully compete with well-established plastics from petro-chemistry, bio-alternatives like PHAs must be attractive both in terms of material performance and regarding economic aspects⁴. This special issue is dedicated to the enormous efforts accomplished globally to meet these two crucial aspects of PHA production. The selected articles, written by highly recognized scientists among whom several are active in this field since many years or even since decades, address all factors that have to be considered to make PHA production affordable regarding the production costs, and to produce structurally diverse PHAs and PHA-based follow-up materials with tailor-made properties. Particular aspects of de facto and envisaged applications of PHA are considered by special review articles; here, the penetration of PHA into the medical and surgical field, grace to their high bio-compatibility and tunable bio-degradation rate, is comprehensively discussed by K. P. Luef and colleagues⁵. The most popular application for PHA, namely (food) packaging purposes, is addressed by the review contribution provided by K. Khosravi-Darani and D. Z. Bucci⁶ on the one hand, and, on the other hand, by the experiments carried out and described by V. Jost and R. Kopitzky⁷, L. Amaro and colleagues⁸, and J. Rydz et al.⁹.

Addressing microbiological aspects and taking profit from the implementation of genetic tools to enhance the metabolic performance of PHA producing microbes, S. Povolo and colleagues report the knock-out of genes responsible for intracellular PHA-degradation in *Cupriavidus necator*; this way, new high-productive bacterial strains were engineered¹⁰. As a further beneficial aspect, the authors apply these novel strain constructs for

high-throughput PHA production from lipophilic surplus streams of the animal processing industry. Related investigations are reported by C. Klask and colleagues, who scrutinized the heterologous expression of genes responsible for intracellular PHA anabolism in phototrophic non-sulfur purple bacteria. Also these experiments targeted to successfully increase PHA productivity in this new group of microbial candidates for "bio-plastic" production¹¹. Formation kinetics and stability of PHA and accompanying marketable by-products of extremophile organisms from the archaea domain are reported by M. Koller et al. Firstly, the authors investigated the formation of archaeal PHA and polysaccharides, and, secondly, their degradation behavior under different storage conditions. The elaborated data provide hints for an economically more efficient production process based on halophile organisms as whole cell biocatalysts¹².

Up to 50% of the total expenses accruing for PHA production processes, or even more in the case of structurally exotic PHAs, are typically dedicated to the allocation of the needed carbon-rich feed stocks¹³. Therefore, a lot of attention is devoted to the raw material aspects. This is not only of importance to decrease cost for biopolymer production, but also to safe raw materials of high nutritional value, such as sugars, starch, or edible oils. Hence, the application of carbon-rich (agro-) industrial waste streams which do not interfere with food or feed production is nowadays forcefully aspired^{10,14-17}. Considering these economic and ethical issues, the application of diverse surplus streams of various origins was investigated by different contributors to this issue. Application of agronomic waste streams was investigated by Haas and colleagues, who, for the first time, successfully applied hydrolysates of non-edible roots as carbon source for biosynthesis of thermoplastic short-chain-length PHAs¹⁸, whereas the research group around S. Follonier focused on the pilot-scale conversion of grape pomace, available at ample quantity in numerous producing countries. This new and non-conventional feed stock was applied for production of elastomeric medium-chain-length PHAs with chemically functional (unsaturated) building blocks¹⁹. Diverse plant oils were investigated by M. Walsh and colleagues; also here, the focus was directed to the selection of non-edible lipid resources²⁰. (Ligno)cellulosics constitute the most excessively available organic matter both in nature and agro-industrial litter; this was addressed by S. Obruca and associates, who track the possibilities to upgrade diverse lignocellulosic materials to valued feed stocks, also spotting a light on the technological challenges arising during upstream processing of these materials²¹. Grace to the fact that PHA production is also performed by a growing number of identified autotrophic prokaryotic organisms, B. Drosig and colleagues suggest the conversion of CO₂ from gaseous industrial effluents such as flue gases towards PHA by phototrophic cyanobacteria. If successfully implemented, this might result in a multiple ecological benefit: firstly, by diminishing the CO₂ load released to the atmosphere, and, secondly, by achieving nearby carbon-neutral biopolymer production. As pre-requisites for industrially relevant cyanobacterial PHA-productivity, the authors emphasize the need for en-

hanced engineering, including the development of optimized photo-bioreactors, and the application of genetic tools to increase both cell densities in the fermentation broth and specific PHA productivity²².

Engineering aspects of PHA production in diverse bioreactor facilities, encompassing different discontinuous and single- to multistage continuous production modes, constitute the next hot-spot for cost efficient PHA production²³. Challenges for stable and reproducible large scale PHA production, especially regarding the scalability of advanced production techniques such as continuous production mode, are highlighted by the contribution provided by G. Kaur and I. Roy. These authors discuss contemporary weaknesses that hamper a routine production of diverse PHAs on industrially relevant scale²⁴. Solid state fermentation, a technique that is still in its infancy for the field of polyester production, is presented by R. Sindhu and colleagues; their article clearly reveals the high potential of this technique, but also elucidates the challenges that still need to be solved to make solid state processes competitive to current submerge technologies, especially if considering the aspired application on industrial scale²⁵.

Mathematical modelling of bioprocesses becomes an increasingly essential tool to put data from laboratory scale into a solid kinetic frame, to get deeper understanding of the intracellular procedures, to identify metabolic bottle necks, to facilitate up-scaling, and, finally, to keep as low as possible the number of laboratory experiments needed for process development. Therefore, advantages and drawbacks of diverse model types of different complexity, applied to PHA research and production, were compared by M. Novak and colleagues in their exhaustive review article. These authors clearly state that different types of models are most suitable for different tasks; nevertheless, the scientists assume that hybrid modelling approaches might be the future tool of choice to provide holistic pictures of entire PHA production processes²⁶.

Processing of PHAs towards vendible plastic items can be facilitated and improved by the designing of composites and blends by combining PHA with other compatible organic or inorganic materials. This is the last, but nevertheless also crucial and complex step on the long and cumbersome road towards the production of polymeric bio-materials with properties tailored according to the customer's demands. High-performance blends of microbial PHA and poly(lactic acid) (PLA) with suitable barrier properties, explicitly designed for packaging purposes, were created and characterized by V. Jost and R. Kopitzky. The authors emphasize the high dependence of the barrier properties of the obtained blends on the compatibility of the components and the morphology of the blends, and provide formulations to improve the miscibility and compatibility of PHA and PLA⁷. Similar advanced materials were developed by J. Ryzd and colleagues, who investigated the miscibility and compatibility of PLA and in vitro synthesized poly[(R,S)-3-hydroxybutyrate], and the degradation behavior of the resulting blends in paraffin. These authors highlight the benefit of the PHA share in the blends for the properties of the investigated materials, and propose

the application of these blends as compostable polymeric packing materials especially for such products exhibiting long shelf life⁹. PHA-based composite materials were developed by L. Amaro and colleagues, who combined PHA, plasticizers, and lignocellulosic hazelnut shells as a novel, unusual filler material. These experiments aimed at designing new cost-efficient polymeric materials suitable for injection molding and bubble extrusion to be used as easily compostable packaging with lower density if compared to the native PHA⁸. K. Khosravi-Darani and D. Z. Bucci describe established and new state-of-the-art strategies to improve PHA properties in order to get feasible, advanced materials to be conveniently used for food packaging. Especially the improvement of the biodegradation rate, crystallization behavior, morphology, stability, mechanical, thermal and barrier (O₂, CO₂) properties of PHA by incorporation of organic or inorganic nano-sized particles of different geometry was underlined by these authors, who suggest the application of nanotechnology to design smart high-performance biopolymers for food technology⁶.

Finally, a holistic consideration of every new technological process is needed both in terms of economic performance and of its ecological foot print. Environmental hot-spots in a production chain have to be traced already at early stages of the process development; this enables the precocious appropriate adaptation of the process. Modern tools like Life Cycle Analysis, applying e.g., the Sustainable Process Index, facilitate the assessment of new processes, and enable a frank and straight forward comparison to established competing techniques. Endeavors for process assessment in the field of PHA production based on various different feed stocks were analyzed and compared by M. Narodslawsky and co-workers. These authors try to answer the controversial question if ecological performance of biopolymers is inherently superior in comparison to fossil-based competitors. They emphasize that an honest ecological evaluation of PHA production requires the consideration of the impact of all single process steps. Nevertheless, the researchers conclude that, both from an ecological and an economic point of view, PHA production might definitely have the potential to eliminate petrol-based plastics at least from certain niches of the plastic market. As restriction, this can only become possible if improvements at each crucial stage during the production cycle, and especially the switch to "green" energy sources and to inexpensive industrial waste streams as feed stocks, are realized²⁷.

I supremely hope that the investigative and scientific efforts presented in this issue will inspire researchers all over the world to intensify their activities in this area; most of all, these accomplishments shall contribute to accelerate the impatiently aspired market break-through of real "bio-plastics" which honestly deserve this designation. This issue underlines that "bio-inspired" solutions for prevailing ecological problems are already developed by experts from the fields of engineering and life sciences, or at least in an advanced status of development; these solutions are waiting for their broad implementation in "White Biotechnology"!

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