Opinion

Natural PHA materials

The most versatile materials platform in the world?

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We think that natural PHA materials show a much larger application versatility than any other existing material platforms can mimic. The reason for this thought is that natural PHA materials are already used in nature for many purposes and for much longer than the existence of mankind.

PHA stands for Polyhydroxyalkanoate of which there can be an infinite number of different moieties. So it's non-sense to claim properties for *PHA*, because different PHA-molecules have different properties. Even the well-known polylactic acid (PLA) and polycaprolactone (PCL) belong to the PHA group of materials.

However, a number of PHA-materials are naturally occurring materials, like PHB and a number of its copolymers like PHBV, PHBHx, P3HB4HB, PHBO, and PHBD. These materials are not *plastics*, but are natural materials made and found in nature, like cellulose or starch [1].

These natural macromolecular materials are not made by polymerization, but by enzymatically controlled biochemical conversion of naturally occurring nutrients (sugars, vegetable oils, starches, etc.) and they all have a role to play in nature.

These natural PHAs are part of the metabolism in all living organisms (plants, animals, and humans) since the beginning of life on earth. They function as nutritious and energy storage materials, so they are supposed to be used for that purpose. One can call that *biodegradation*, but one could also call that *feed for living organisms in every environment*. In addition, they can fully meet a comprehensive combination of end-of-life options, unlike most other material platforms [2].

Today, these bio-benign materials are made at industrial scale, just by mimicking nature. Many manufacturing capacity expansions are planned and built, especially in Asia/Pacific and North America. The materials appear to be excellent candidates for a very large variety of applications in thermoplastics, thermosets, elastomers, lubricants, glues, adhesives, but also in several non-traditional polymer applications like animal feed, cell regeneration in humans and animals, denitrification, and cosmetics for instance.

Without further ado, we present a limited number of applications that have been successfully developed and already use these PHA materials:

1. Traditional thermoplastic applications

During the past ten years manufacturing companies have invested billions of dollars to develop and build significant capacity to make natural PHA-materials at industrial scale. Simultaneously, applications were developed using these materials, focussing primarily on applications where biodegradability in many environments was seen to be an advantage and added value.

Indeed, the natural PHA-materials are *feed for living organisms in every environment*, so they biodegrade (= carbon conversion to CO_2) in every environment, albeit the rate of biodegradation depends on part geometry and external conditions like temperature, humidity, and others [3].

The result of the BioSinn project [4], on request of the German Federal Ministry of Food and Agriculture, describes 25 product-market combinations where biodegradation is a viable end-of-life option. Biodegradability is an advantage when it is difficult or even impossible to separate plastics from organic materials that are destined for home or industrial composting and when it is challenging or


(Photo: MAIP)


(Photo: Nuez Lounge Bio®)

prohibitively expensive to avoid fragments ending up in the open environment or to remove them after use.

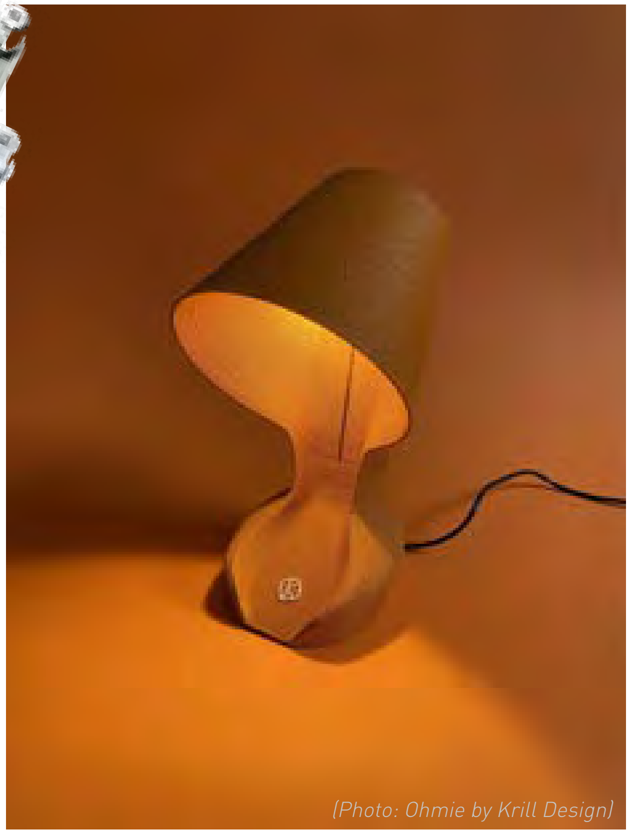
(Photo: Prodir)

Natural PHA-based end products that are currently in the market are for instance coffee capsules, waste bags, mulch films, clips, non-wovens, film for food packaging, micro-plastics in cosmetics, and natural PHA coated paper for coffee cups. The last application has also been accepted as recyclable by the paper industry. There are many more application opportunities according to the BioSinn report. Currently, the main challenge is the total global manufacturing capacity of these natural PHA-materials, but many new plant constructions are underway.

That biodegradability is not the only Unique Selling Point (USP) to talk about has been made clear by a compounding company that significantly elevated the science level and knowledge base for natural PHA-materials [5]. They develop new PHA-compounds that are 100 % bio-based, have high temperature resistance, are easy to process, and are tailor-made for a large variety of durable applications.

This compounding company has developed more than 500 different natural PHA-based formulations from stiff to extremely flexible, thermal resistance up to 130 °C, weather and UV resistance, fast nucleation from the melt, and improved barrier properties, demonstrating that natural PHA-materials can be turned into a new series of bio-technopolymers that can be processed at as fast as or even faster than the currently used polymers in the industry for all conversion technologies currently in use.

Today we see compounders using a combination of different natural PHA-materials to make them the only polymers in compounds for film or 3D printing for instance, while they were often used as additives in combination with PBAT or PLA a few years ago. The availability of high molecular weight amorphous and/or very low crystallinity PHA grades (like P3HB4HB with 50 % 4HB or PHBHx with 30 % Hx) offer the opportunity to blend low and high E-modulus grades to control properties.



(Photo: Ohmie by Krill Design)

Several examples of these so-called bio-technopolymers have been demonstrated and are used in applications for spectacle cases (replacing ABS or PP Talc), pens (replacing ABS), design chairs (replacing GFR-PP), lamps, electrical light switches (replacing PC/ABS), etc. The design chair has an injection moulded core of a 12 kg shot weight made in a 2,500 tonnes injection moulding machine. The chair comes in several colours.

Also, some natural PHA-materials with low E-modulus have been developed for use in hot melt adhesives, pressure sensitive adhesives, and laminating adhesives & sealants. So far, the use is still limited due to the low manufacturing

generic picture

(Photo: Reef Interest)

capacities, but this is a matter of time. Several materials are used for matting agents in coatings to replace silica and resulting in much better transparency and haptic properties (soft feel). These haptic properties are one of the USPs of these materials.

Finally, due to the enormous amount of plastic microfibres ending up in our oceans every year many parties are actively involved in developing fibres from natural PHA-materials for both woven (textiles) and non-woven applications. Although the first applications are on the market, it is still small and application developments are in an early stage, especially for textile applications. There are fibres for textile applications on the market, but those are based on compounds that also contain other polymers in addition to natural PHA-material, so far.

2. Non-traditional plastic applications

Several non-traditional plastic applications have been developed and result in business, given the long-known role and appearance of natural PHA-materials in natural habitats. One could consider applications in animal feed, medical care (both humans and animals), denitrification, artificial turf, and cosmetics for instance.

Denitrification is required when there is too much ammonia in a certain environment (wastewater treatment, aquaria, shrimp, fish and turtle farms, etc.). Ammonia turns into nitrates and nitrites by oxidation. Natural PHA-materials are an excellent carbon source to reduce the nitrates and nitrites to nitrogen or N_2 because through biodegradation it provides the carbon for this denitrification process. Today, material is being sold for these applications.

A completely different segment is to use natural PHA-materials for medical applications. Within the human body one can use microspheres for the cultivation of stem cells. These have a degradation time of about one year, while the degradation product helps cell growth. They can be used for bone/cartilage regeneration, skin damage repair (wound closures), nerve guidance conduits, among others. Scaffoldings made from such materials have been demonstrated to take care of bone repair, but also repair of a damaged oesophagus. The company Tepha (Lexington, Massachusetts, USA) makes several products for the abovementioned purposes for about 10 years and Medpha (Beijing, China) is also active in this field and further extends it. One of the newer applications is to use these materials for controlled drug delivery.

Artificial sports fields like those for soccer always use a filler. Although often ground old car tires have been used for this application for a while, it has become unacceptable for health and environmental safety reasons. Today also natural PHA materials are used for artificial turf infill (FIFA approved).

PHB and other natural PHA-materials are or can be used as feed or feed additives for animals:

Feeding PHB to aquatic organisms has been well studied [6, 7], confirming that PHB had a positive impact on growth, survival, intestinal microbial structure, and disease resistance of aquatic animals, serving as an energy source for European sea bass *Dicentrarchus labrax* juveniles [7], helping to increase the lipid content of the whole body [6].

PHB was also used as an alternative to antibiotics for protecting shrimps from pathogenic *Vibrio campbelli* [8], it was observed to induce heat shock protein (Hsp) expression and contribute partially to the protection of shrimp against V. *campbelli* [9], improving the growth performance, digestive enzyme activity, and function of the immune system of rainbow trout [9], enhancing the body weights of Chinese mitten crab *Eriocheir sinensis* juveniles [10].

PHB also improved the survival of prawn *Macrobrachium rosenbergii* larvae [11], blue mussel *Mytilus edulis* larvae [12] and Nile tilapia *Oreochromis niloticus* juveniles [13].

PHB can not only affect marine organisms but also large livestock. The feed composition shapes the gut bacterial communities and affects the health of large livestock [14, 15].

It is concluded that PHB has no negative effect on the growth of marine animals like large yellow croakers and popular land animals like weaned piglets with sensitivity to foods. In the future, plastics made of PHB, perhaps including its copolymers PHBV and P3HB4HB, can be used again as feed additives for animals. More positively, plastics made of natural PHA-materials could replace petrochemical plastics to avoid the death of marine or land animals that mistakenly consume plastic packaging garbage [16].

Based on the origin of this natural PHA-materials platform and on the application examples discussed here, we are convinced that this new material platform is a sleeping giant [5] with a very promising future.

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References:

[1] Michael Carus, Which polymers are "natural polymers" in the sense of single-use plastic ban?, Open letter to DG Environment signed by 18 scientific experts, 8 October 2019.

[2] Jan Ravenstijn and Phil Van Trump, What about recycling of PHA-polymers?, bioplastics MAGAZINE, Volume 15, 03/20, 30-31.

[3] Bruno De Wilde, Biodegradation: one concept, many nuances, Presentation at the 2nd PHA-platform World Congress, 22 September 2021.

[4] Verena Bauchmüller et.al., BioSinn: Products for which biodegradation makes sense, Report from nova Institute and IKT-Stuttgart, 25 May 2021.

[5] Eligio Martini, The compounding will be the success of the Sleeping Giant, Presentation at the 2nd PHA-platform World Congress, 22 September 2021.

[6] Najdegerami, E. H. et.al., Aquacult. Res. 2015, 46, 801-812.

[7] De Schryver, P. et.al., Appl. Microbiol. Biotechnol. 2010, 86, 1535-1541.

[8] Defoirdt, T., Halet, D., Vervaeren, H., Boon, N., Van de Wiele, T., Sorgeloos, P., Bossier, P., Verstraete, W., Environ. Microbiol. 2007, 9, 445-452.

[9] Baruah, K. et.al., Sci. Rep. 2015, 5, 9427.

[10] Sui, L. et.al., Ma, G., Aquacult. Res. 2016, 47, 3644-3652.

[11] Thai, T. Q. et.al., Appl. Microbiol. Biotechnol. 2014, 98, 5205-5215.

[12] Hung, N. V. et.al., Aquaculture 2015, 446, 318-324.

[13] Situmorang, M. L. et.al., Vet. Microbiol. 2016, 182, 44-49.

[14] Lalles, J. P. et.al., Proc. Nutr. Soc. 2007, 66, 260-268.

[51] Ma, N. et.al., Front Immunol. 2018, 9.

[16] Wang, X. et.al., Biotechnol J. 2019, e1900132.