Materials sell by properties

Urs J. Hänggi, Biomer (Haenggi@Biomer.de); presentation at EMPA St. Gallen, May 2004

PHB (polyhydroxybutyrate) is a thermoplastic polyester produced by bacteria. Evolution has optimized it for biological uses like ion channels, monorail in protein synthesis, or energy storage but not for being a plastic. In order to function as a plastic the polymer has to be compounded as with other polymers by adding nucleating agents, plasticizers, and other processing aids. PHB currently can not compete on price with mass produced thermoplasts because of production scale. On the other hand the biological role (complex forming properties) and the structure of the PHB chain (absolutely linear, absolutely isotactic) suggest uses that are beyond those of standard mass products. It will be shown how such hints can applied to produce material with properties other plastics can not offer such as specific surface properties used in medical analytics, induced degradation in aerobic as well as in anaerobic environments an in firework rockets, fast cycle times on molding machines in microinjection where machine time is the key cost factor. Such applications tend to be less price sensitive. Developing the hints allows to increase production scale to orders that are used in conventional plastics at prices that finally are competitive with conventional plastics.

About 20-25 years ago, while teaching applied biochemistry to students interested in microbiology, I had to occupy myself for the first time with the phenomenon PHB (polyhydroxybutyrate). The new biotech material popped up like a supernova in the dark sky. No way, to not to present it to biotech students. It were the pictures of people strolling on empty autoroutes during the first oil crisis in the early eighties that thoroughly shattered the then prevailing view that increases in economy and wealth would continue as it had since the end of world war II. The impact of the first oil crisis on the Europeans was massive. Suddenly sustainability, not growth was seen as the route to the future. On this background it is easy to understand why the idea of producing a plastic from renewable resources was identified as a new start. A number of companies initiated research on PHB including ICI in England, Grace in Italy, Chemie Linz in Austria, Solvay in Belgium, and Fluntera in Switzerland. Supernovas, as anybody knows, actually are dying stars. This also happened with PHB. With the end of the oil crisis interest in PHB faded as fast as it had emerged. Nobody had a use for.

Is there actually no need for sustainable plastics? If somebody builds a house he chooses between concrete, bricks, or wood for the walls, or between glass, polystyrene, or polycarbonate for the windows. His selection solely will depend on the properties of the materials with respect to the given purpose like a private home, a public hall, a factory, or something else. He does not care at this moment where the material actually is coming from. In other words: materials are selected by their properties, not by their origin. Only at he very end personal preferences come into play and only if two materials have interchangeable properties. So it is perfectly right to ask "who needs a renewable plastic"? Or worse, why should intelligent people convene here to discuss materials possibly nobody needs? Me, for my part, I didn't come to talk on renewable plastics, but on material properties exclusively.

PHB, just to explain its origin to those not familiar with, is produced by any living cell be it a bacterium, a fungus, a plant, an animal, or a human being. Certain bacteria also store it in the presence of excess nutrients very much like others store starch or oils (Fig. 1). This storage property is used to produce PHB industrially. The bacteria are grown in a fermenter and feed with excess sugar or starch (Fig. 2). At the end, cell mass is collected and the polymer extracted (Fig. 3).

Before talking on PHB as a plastic I would like to stress that the polymer has evolved in nature (Fig. 4) to form ion channels in the cell walls and to act as monorail in the ribosomes for aligning mRNA in protein synthesis. Later in evolution it also was optimized by some bacteria to become a storage material. At no time in evolution it was meant to become a plastic. Its thermoplastic property is a purely fortuitous function.

To act as an ion channel it is vital for the cells that the ester groups are arranged stereoregular (Fig. 5). For this PHB is absolutely isotactic. This is unique among thermoplasts. Wouldn't it be worth looking carefully at such a property? Or, to function as a monorail to guide the mRNA during protein synthesis, it is essential that the molecule is linear. Branches would spell derailment, disaster. For this PHB is absolutely linear. No other thermoplast can claim the same. Again, wouldn't it be worth looking at such a property?

It is this kind of questions that directs us at Biomer in working with PHB. It is our aim to "transform" the inherent properties of PHB into useful bioplastics. In a minute I will present 4 examples. Clearly we do not neglect "renewable" nor "biodegradable". As a matter of fact PHB is the only waterproof thermoplast available that is fully biodegraded both in aerobic as well as in anaerobic environments. Thus for an application like this firework rocket (Fig. 6) the choice of PHB is a very sensible one: after explosion the shattered plastic parts fall on grassland, into lakes, brooks, or rivers. There they are degraded on topsoil, in the aerobic parts of river banks, and in the anaerobic parts at the bottom of lakes. If cows or sheep happen to forage the parts before they are fully degraded the cattle is not harmed at all. So next time you buy firework, look at the inscription "bioabbaubar" on the support and buy it. You will do something good for nature, demonstrate that you are a good guy, and finally you also will boost our profits.

Let me come back to the 4 examples I promised before. I would like to start with two developments were we experienced failures (Fig. 7). One of those are natural fiber composites. Since PHB is one of the most crystalline thermoplasts available we reasoned that the crystals (the spherulites) would take up the pressure and the fibers the tension similar as stones take up pressure and steel ropes take up the tension in steel reinforced concrete. We further reasoned that the linear arrangement of the carbonyl groups would strongly interact with the hydroxyl groups of cellulose. To my knowledge no other thermoplast shows these two properties together. Therefore we expected to create a thermoplastic composite that has no match anywhere else. Unfortunately we had to realize that the annealing forces between the polymer chains to form crystals is much larger than the bonding forces towards cellulose. Because of this, the composites obtained so far behave as simple fiber filled, but not as fiber reinforced composites.

Another failure is films. It is well known that crystallinity is good for gas barrier properties. As PHB is highly crystalline we expected to get a good barrier film. PHB can crystallize in at least 2 conformations. One of these have strong extended chains. Tomorrow Dr. Schmack will present fibers with extended chain configuration. We were able to realize this in two dimensions in the lab. The resulting films have a high strength. We think that in addition they have oxygen barrier properties that could compete with the best on the market. Unfortunately we have not yet succeeded so far in scaling up the laboratory results on commercial film blowing machines. We will continue hard to achieve this goal.

Fortunately there also are positive results. One of them is an ELISA dip stick that is based on the stereoregular conformation of the ester bonds (Fig. 8) This results in exceptional surface properties. Small peptides bind with high affinity. Thus the sticks open a low cost approach to test antigens. The sticks simply are dipped into the analyte, rinsed with water, and finally dipped it into a solution with labeled antibodies. A positive result is seen if the white stick turns colored. As there is no need for ELISA readers nor of other expensive lab equipment the tests can be done right in the field like for veterinarian use at farms and for bedside testing at home or in remote areas.

The second example is based on the absolutely linear properties of PHB. Keeping this in mind we were able do formulate PHB in such a way that it can compete with polyolefines (Fig. 9). Biomer®P226 matches the tensile strength of PP, that is the resistance to be torn apart under load. It matches its elongation at break, that is the deformation before yielding. And it matches, no it exceeds, its modulus, that is a measure for stiffness. Another example is Biomer®P240. It behaves like high density polyethylene, but is much easier to mold. The take home lesson of this comparison is not, that the formulations match classic polymers, but that the articles made of them, while matching the properties of the classic polymer, in addition are of renewable material. Thus, if an application would ask for properties similar to that of polypropylene, then (Fig. 10) one has a choice. If the producer chooses is PHB then he has the added benefits that the articles are of renewable resources, are fully biodegradable, free of catalysts, neither are thrombogenic nor immunogenic, allow fast cycle times, thinner walls or more complex structures, and are creep resistant.

Please let me come back to what I said at the beginning: Materials sell by properties, not by their origin. This also holds for sustainable materials. So it is futile to stress "renewable". If renewable materials have to make their ways it is essential to work on properties. I hope that I have been able to shown how this might be done, at least with PHB. I also hope that I could enthusiast at least some of you to further explore the inherent properties of the molecule so that new applications can be developed. No doubt, if done right, renewable plastics have a bright future (Fig. 11).