

Virgin PHB has thermoplastic properties, but is not a thermoplast

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Ladies and Gentlemen,

You may ask why, at the end of a two day PHB conference, somebody comes to the floor and tells that PHB is not a thermoplast. The reason is that I like PHB.

At least once a week I receive a mail asking for PHB. In most cases I have to call back and ask if they need plain PHB powder for mixing or compounded PHB for thermoprocessing. Depending on the answer I have to explain that it's not true what is said in the introduction of nearly all papers on PHB, namely that native PHB is a thermoplast with properties like PP. This is wrong. PHB is polymer having thermoplastic properties pretty much like DNA that also has thermoplastics properties. However, in contrast to PHB, nobody labels DNA a thermoplast.

Please look at this slide (slide 1):

	PP bottle	plain PHB bottle
Squeezing	does not break	breaks
Bending	flexes	cracks (a mess all over the place!)
Stability over time	stable for >3 years	changes properties from ductile to brittle
Melting point	~ 170°C	~ 170°C

A PHB bottle breaks when you squeeze it, it cracks when one tries to bend it, and it changes properties over time, that is, it cannot be stored. You can look at any other property.

All essential properties, except the melting points, are different in PHB and far from being useful as a replacement of PP. Knowing such data I certainly wouldn't recommend PHB as thermoplast, either for bottles or for any other application. I am asking you if you would recommend PHB after having seen this slide would you?

It is not my intention to discourage you. On the contrary, I want to show the beauty of PHB and how PHB can become a thermoplast that plastic processors would like to use and have it in their products. (slide 2):

PHB becomes a fantastic thermoplast

- by focusing on the unique (hidden) properties
- by knowing how to compound and process

I first will focus on the unique properties of the PHB polymer chain and then I will discuss how these properties can be used for compounding and processing.

1.1.1. The unique properties

The unique properties are the base of the plastics behavior (slide 3).

Unique properties of PHB polymer chain	Physical consequences
Absolutely C4-C4-C4...	the polymer chain crystallizes
Absolutely stereoisomeric (isotactic), only methyl groups	the polymer chain easily crystallizes
Absolutely linear	the polymer chain does not entangle
Glass temperature at or below 0°C	the polymer chain crystallizes at room temperature

The PHB chain is absolutely regular with only C4-subunits. It is well known by chemists that highly regular substances tend to crystallize.

The PHB chain is absolutely isotactic. It has no variants in the side chains, just methyl groups 100% of them pointing to the same side. These regularities add to ease crystallization.

The chains are absolutely linear without any branches. This means that the polymer chains can not entangle.

And finally, the glass temperature of PHB is at 0°C or below. This means that polymer chains keep on moving and crystallizing even at room temperature.

Such combined properties are not known for any man made thermoplast.

1. Effects of the unique properties on plastics

When plastics processors see these unique properties, they will recognize the potential of PHB (slide 4):

property of PHB	translates in plastics into
Absolutely C4-C4-C4..., Absolutely stereoisomer, no irregularities	allows to get hard, creep resistant parts
absolutely linear, no branching	allows to set the melt viscosity at will
glass temp at around 0°C	no change in properties once the thermodynamic state is attained

The absolute regularity yields hard, creep resistant parts, the linearity of the polymer chains allows to adjust the melt viscosity right on the machine, and finally, the glass temperature results in stable parts.

1.1. Hard, creep resistant parts

The hard, creep resistant parts are due to the fact that PHB does not stop crystallizing until the thermodynamic optimum is reached, that is, until all polymer molecules are fixed in crystals. There they stay forever.

1.2. Setting melt viscosity at will

Setting a viscosity at will is due to the linearity of the polymer chains. They can not entangle. When hot, they behave like hot spaghetti in boiling water: very slippery, very mobile. However, when cooled, the polymer chains get viscous like cooled spaghetti on a plate that you now can handle with your fork. This allows you to set the melt viscosity right on the machine to your specific needs (slide 5).

Setting melt viscosity at will

- faster molding
- => lower tip temp = higher viscosity
- finer structures or complex parts
- => higher tip temp = lower viscosity
- 10°C = forty-fold change in viscosity!

If you aim at high speed molding, you simply lower the temperature at the tip of the screw so that crystallization already starts in the barrel. If you aim at filling the finest cavities in a mold, you increase the temperature at the tip of the screw. I am not aware of any other thermoplast with which you could adjust the viscosity as easily as PHB right in the machine.

1.3. Stability of the final parts

Please let me return to the intrinsic properties of the PHB molecule that affects plastics properties: no change of properties (slide 6):

properties of PHB translates in plastics into

hard, creep resistant parts

melt viscosity at will

no change in properties once the thermodynamic state is attained

Once the crystallization reaches the thermodynamic end point the parts remain stable for years. (slide 7).

Stability of the final parts

- no free amorphous mass left to change
- > no change in mechanical properties

(5 years from minus 40 to plus 60°C)

The reason for the stability is that, after having reached the thermodynamic end point, there is no free amorphous mass left to move. This is also the reason why we can guarantee no changes in properties if the parts are exposed for 5 years from minus 40 to plus 60°C. UV does not harm as there are no double bonds in the chains and no aromatic subunits that might absorb UV light. PP cracks in these conditions, PHB does not. With respect to mechanical and UV stability over time PHB beats PP.

2. Roadblocks in realizing the potentials

Creep resistant parts, melt viscosity at will, and long term stability.

Such properties could induce plastics processors to switch to PHB. But those of you who ever have tried to produce plastics parts with PHB will object and say „This is all fine and might work in theory, but in reality the parts are of poor quality“. And I have to admit “you might be right”.

So yes, there are problems in working with PHB. (slide 8).

Roadblocks in using PHB as thermoplast

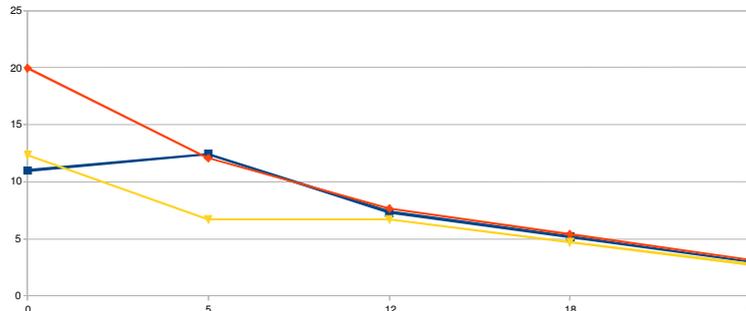
- thermosensitivity
- slow crystallization rates
- getting brittle over time

These are thermosensitivity, slow crystallization speed, and getting brittle.

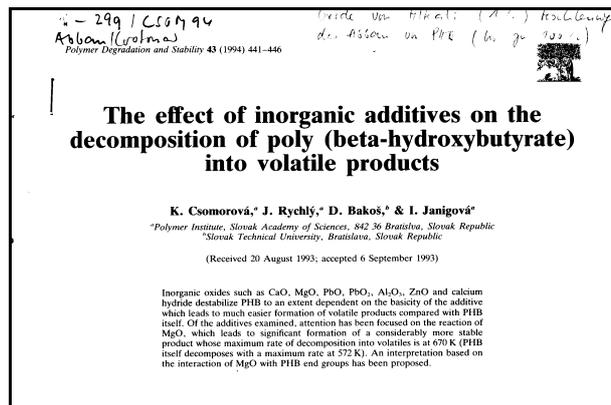
2.1. Thermosensitivity

Let's first focus on thermosensitivity. Chemists know that β -esters like in PHB can form hexa-rings that either can revert to the original linear molecule or split into two subunits.

Splitting of the PHB chains is pretty fast at the melting temperature. This has been a problem since very early times in the development of PHB. We discovered that degradation is not limited to high temperatures but also takes place at room temperature. (slide 9).



For 30 years thermodegradation was accepted as God-given. It was only in 1994 a group at the Slovak Academy of Science in Bratislava published a paper showing that the splitting actually is catalyzed by earth alkali ions. I may well show the original paper as apparently nobody realized that this is the cause of the thermosensitivity neither at that time, nor 12 years later when a Japanese group discovered the phenomenon again (slide 10) and even today if I was getting right the remarks of some of previous speakers.



If PHB is extracted in water then there is no way to avoid Ca⁺⁺. However it is possible to reduce the amount of Ca⁺⁺ and thus to lower thermal degradation by using deionized water in the extraction process, or to add chelating agents to the water during extraction, or to treat the extracted PHB with diluted acid to loosen the interaction of the Ca⁺⁺ in the Ca⁺⁺/PHB complex as suggested by Larson two years ago.

We discovered that if one uses solvent extraction, then there is no Ca⁺⁺ present and PHB is stable even if heated to 220°C for up to 30 minutes!

2.2. Slow crystallization rates

Please let me come back to the other roadblocks. For plastics processors slow crystallization speed is a major problem (slide 11).

Roadblocks in using PHB as thermoplast

- thermosensitivity
- **slow crystallization rates**
- getting brittle over time

To get creep resistant parts all polymer chains have to move into the crystals. That process takes time, a very long time, at room temperature up to 200 days (for PHB/HV about 400 days). During this time the properties of injection molten parts change from ductile to hard.

There are several means to deal with this type of roadblock (slide 12).

How to eliminate the slow crystallization rate?

- reduce crystal (spherulite) size
- allow optimal crystallization temperature
- reduce friction between polymer chains

I will consider just 3 of them: reducing the crystal size, setting the optimal temperature for chain movement, and reducing the friction between the polymer chains.

2.2.1. Reduce crystal size

Let's first focus on the spherulite size. because this is the most effective method to reduce crystallization time. Bacteria will do everything to not have any substance near the PHB particles that might induce crystallization. This is important for them to easily activate the chemical energy stored in PHB. In plastics this means that you have to rely on spontaneous nucleation. This is a rare event so that one eventually ends up in having spherulites sizes of up to 2 mm. By adding substances that induce crystallization one can decrease the size. Decreasing the size means that one reduces the distance the polymer chains have to travel from the amorphous part into the crystal part.

Boron nitrid is usually used as nucleant. However, not every boron nitrid is equally helpful. Only the crystalline part of boron nitrid induces crystallization, not the amorphous part. So one has to select the proper grade of the proper supplier to get an optimum between speed and spherulite size. This means long and tedious tests. By using boron nitrid as nucleant one gets spherulite sizes of around 20 μ m. This still is large, especially if you aim at thin walled parts. However, the size is reduced by a factor of 100 compare to that of the spontaneous crystallization. This dramatically reduces crystallization time from 200 to less than 3 days.

Recently we started to offer grades with a different nucleant that produces spherulites sizes of below 1 μ m. A few weeks ago we started tests with still another nucleant that promises to yield even smaller spherulites.

2.2.2. Setting optimal crystallization speed

The speed of crystallization not only depends on the distance that the molecules have to move, but also on their mobility. Numerous experiments have shown that the optimal temperature for crystallization is around 90°C. So the tools on the molding machines have to be set to allow the melt to rapidly cool to 90°C, in no case less. If the 90 degree window is not attained, the melt just freezes. One gets parts that, please remember, will change their properties during storage at room temperature over the next 200 days till the thermodynamic optimum is reached.

2.2.3. Reduce friction between the polymer chains

Upon lowering the temperature, say to 90°C for fast crystallization, the friction between the polymer chains starts to become an issue. It can be compensated by adding a kind of molecular grease. In plastics such greases are called plasticizers. The only thing with PHB is that one has to take care that the plasticizer is compatible with the crystals, not only with the amorphous mass. If it is compatible with the amorphous mass only, then the plasticizer is expelled from the crystals. It will migrate to the edges of the spherulites and sweat to the surface as oily film.

The most severe roadblock of using PHB as thermoplast is that PHB parts get brittle over time

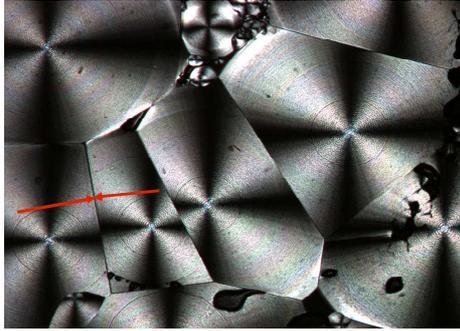
2.3. "Loose" spherulites

(slide 13).

Roadblocks in using PHB as thermoplast

- thermosensitivity
- slow crystallization rates
- **getting brittle over time**

Even if thermosensitivity is taken care of and compounding and processing are handled properly, the resulting parts still are brittle. This is because the transformation from the amorphous to the crystalline state is accompanied by a change in density. The crystals are more dense than the amorphous parts. As the molecules empty the amorphous part in favor of the denser crystalline part, voids emerge between the spherulites. These voids act as cracking gates through the parts (slide 14).



2.3.1. Tying the spherulites together

There are different approaches to tie the spherulites together (slide 15).

- fill them with plasticizers
- fill them with compatible polymers
- „glue“ the spherulites together

One can fill the void with plasticizers, fill them with polymers, or “glue” them together.

A common approach is to fill the spaces with plasticizers, but that does not really help. The spherulites still can slip and the parts still will be brittle. It is better to fill them with other polymers that are compatible with PHB. Only small amounts are needed to get decent results. The best solution is to link the spherulites by molecules that span the voids and interact with the crystals. This type of interaction is very strong and firm. And so you finally end up with hard, creep resistant parts.

Taken all together and processed the right way PHB becomes an exceptional thermoplast:

gets hard, creep resistant parts
allows fast processing cycles or extremely fine structures (melt viscosity at will)
does not change in properties once the thermodynamic state is attained

Plastics processor are keen to use such a thermoplast!

3. Conclusions

Ladies and Gentlemen: I hope that I was able to encourage you to concentrate on compounded and processed PHB and to abandon the silly and wrong notion that plain PHB has properties like PP. Due to its biochemical origin, PHB has unique properties that are hard to get with any man made thermoplast. There are drawbacks in processing, in thermosensitivity, and in filling the voids between the crystal clusters. However these drawbacks are corrected and will be further corrected to get even better products in the future.

Please let me add a personal comment. Plastics sell by properties. PHB is no exception. Biodegradation is a property, but as a matter of fact we have no customers who focus on biodegradation. This might change in the future, but only, and I insist on this, **only if the parts are of equal or better quality** than the original parts. Some of our clients look for “renewables”, but to most of them the term “bio” is of minor importance and considered a fringe benefit. Almost all of our clients focus on the specific properties and, by doing so, have allowed us to make a good living for over 20 years.