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Materials derived from biomass/biodegradable materials

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ABSTRACT Interest in biodegradable plastics made from renewable resources has increased significantly in recent years. PHBV (polyhydroxybutyrate-polyhydroxyvalerate) copolymers are good examples of this type of materials. This paper provides an overview of the manufacturing process, properties, biodegradability, and application/commercial issues associated with PHBV copolymers. They are naturally produced by bacteria from agricultural raw materials, and they can be processed to make a variety of useful products, where their biodegradability and naturalness are quite beneficial. PHBV copolymers are still in the first stage of commercialization. But they are presented in this paper as an example of how new technology can help meet society's needs for plastics and a clean environment.

Polymeric materials occurring naturally or produced from renewable resources were recognized as extremely useful many years ago. These materials have become increasingly more interesting and attractive in recent years as alternatives to petrochemical-based polymers and plastics (1).

Meanwhile, consumers and the plastics industry have shown a growing concern about the disposal of plastics and their environmental impact. Industry is actively looking for ways to minimize the unnecessary use of plastics to complement recycling and reuse programs. Others are working on new materials or modifications to old ones to reduce the environmental impact of plastics.

ICI has concentrated on developing a family of plastic materials which are produced from renewable resources while being completely biodegradable. ICI combined its strengths in biotechnology and materials science to develop PHBV (polyhydroxybutyrate-polyhydroxyvalerate) biodegradable plastics. These thermoplastic materials are a family of PHBV copolymers which fit neatly into our ecosystem.

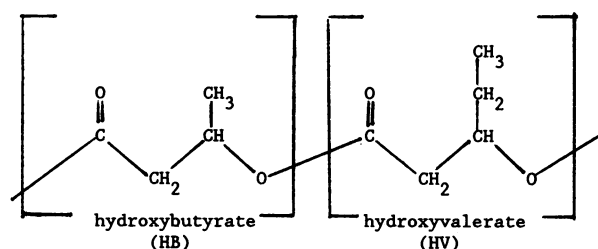
MANUFACTURING PROCESS

Chemical Makeup. Polyhydroxybutyrate (PHB) homopolymer is produced in nature by a wide variety of bacteria which store it as a ready source of carbon and energy in a similar manner to the storage of fat in humans. PHB is useful for some applications. But its brittleness, deficiencies in thermal stability, and difficult processability limit its usefulness. However, the addition of polyhydroxyvalerate to the polymer chain overcomes these limitations (2).

PHBV copolymers are thermoplastic polyesters. They are composed of hydroxybutyrate (HB) units with between 0 and 24% of hydroxyvalerate (HV) units appearing randomly throughout the polymer chain (Scheme I).

Fermentation. ICI produces PHBV by fermentation. Though a wide range of microorganisms will make PHBV, we have chosen to work with one from the genus *Alcaligenes*.

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Scheme I

These bacteria are quite common in the environment, and they can grow on a wide range of carbon sources in both aerobic and anaerobic conditions. Current production uses *Alcaligenes eutrophus*. This strain grows very efficiently on glucose, and it is safely handled in large quantities.

For balanced growth, bacteria need a carbon source, an energy source, nitrogen, phosphorus, sulfur, trace elements, water, and oxygen. If one nutrient is limited (e.g., N, P, or S), bacteria cannot produce amino acids and proteins. As a result, they cannot grow. PHBV production exploits these facts.

To begin the fermentation process, *A. eutrophus* is inoculated into a fed-batch reactor containing a balanced glucose medium. All nutrients are in excess except phosphorus. The medium's phosphate content is limited to support only a certain amount of cell growth. The phosphate content decreases as the culture grows such that the culture eventually reaches phosphate starvation. Up to this point in the fermentation, very little PHB has accumulated in the cells. But in stage two of the process in which glucose is added, the cells cannot convert the glucose to amino acids/proteins because of the low phosphate availability. Consequently, the dry weight of the biomass rises significantly as the cells convert the glucose feed to PHB, causing massive amounts of PHB to accumulate in the cells. The PHB concentration can account for up to 80% of the biomass's total dry weight at the end of the fermentation process.

Table 1. Typical properties of PHBV

Property	HV content, mol %		
	0	10	20
Melting point, 0°C	177	140	130
Crystallinity, %	80	60	35
Tensile strength, MPa	40	25	20
Flexural modulus, GPa	3.5	1.2	0.8
Extension at break, %	8	20	50
Notched izod impact strength, J/m	60	110	350

Abbreviations: PHBV, polyhydroxybutyrate-polyhydroxyvalerate; PHB, polyhydroxybutyrate; HV, hydroxyvalerate; HB, hydroxybutyrate.

Carbon sources other than glucose can be used. Much work is under way to assess the use of various agricultural by-products (e.g., molasses and sugar beets).

A. eutrophus produces PHB homopolymer when fed exclusively glucose under the appropriate conditions. However, PHBV is formed if in addition to glucose the bacteria are fed a controlled amount of an organic acid (e.g., propionic acid) during the second stage of fermentation. *A. eutrophus* incorporates a predictable amount of HV units randomly with the HB segments to form the PHBV copolymer. Therefore, a family of polymers

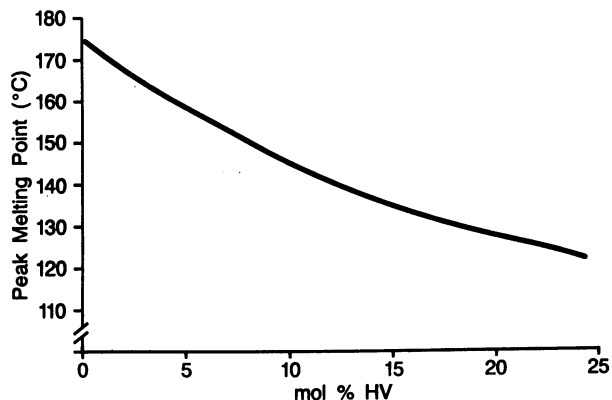


FIG. 1. Influence of HV content on peak melting point.

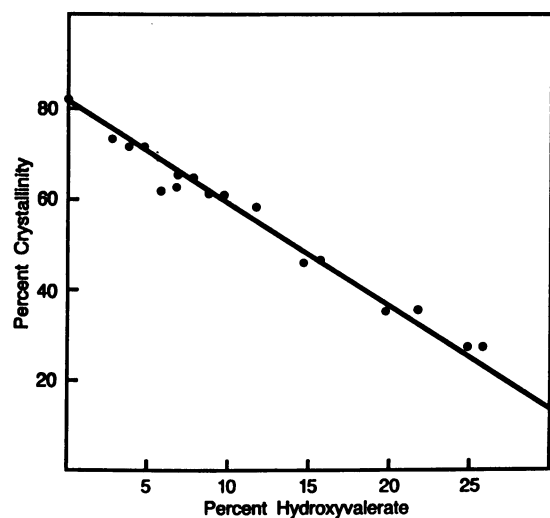


FIG. 2. Effect of composition on crystallinity of PHBV copolymers.

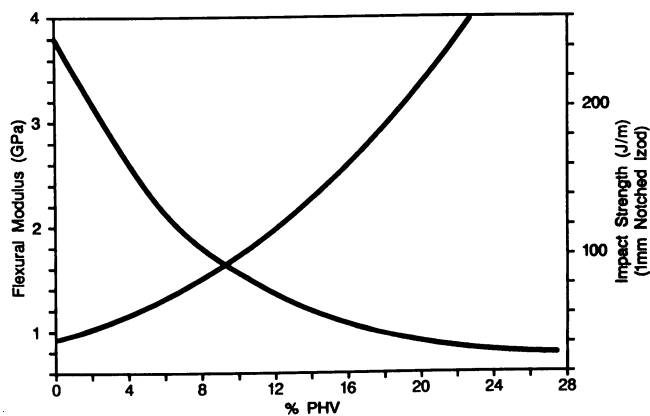


FIG. 3. Effect of composition on mechanical properties of PHBV copolymers.

Table 2. PHBV biodegradable polyester biodegradation

Environment	1-mm molding	
	100% weight loss, weeks	Surface erosion, $\mu\text{m}/\text{week}$
Anaerobic sewage	6	100
Estuarine sediment	40	10
Aerobic sewage	60	7
Soil	75	3
Sea water	350	1

with specific HV contents having a range of different properties can be biologically manufactured.

Polymer Extraction. The last stage of PHBV production involves separating the polymer from the cells. To do this a solvent or aqueous extraction can be used. ICI favors the aqueous process, where the cell walls are broken and the polymer is then extracted and purified. The aqueous process is less expensive, but the process reduces molecular weight. For example, solvent extraction can produce copolymer weights of 1 million, whereas typical molecular weights of aqueously extracted copolymers are in the 600,000 range. But the solvent process presents some safety concerns. The objective, of course, is to produce a consistent, usable, clean product while keeping production costs down.

PHBV PROPERTIES

Some typical properties of PHB homopolymer and PHBV copolymer are shown in Table 1. PHB is a rather brittle material which is somewhat difficult to process since it decomposes at a temperature roughly 10°C above its 177°C melting point. But adding HV to the polymer leads to several improvements (Figs. 1-3),* including drop in melting point, reduction in average crystallinity, and increased flexibility and toughness.

Some of the properties of the PHBV range span those of polypropylene to polyethylene. But PHBV properties can also be enhanced by adding normal polymer additives such as natural plasticizers, fillers, colorants, etc.

*Lloyd, D. R., SPI Symposium on Degradable Plastics, May 10, 1987, Washington.

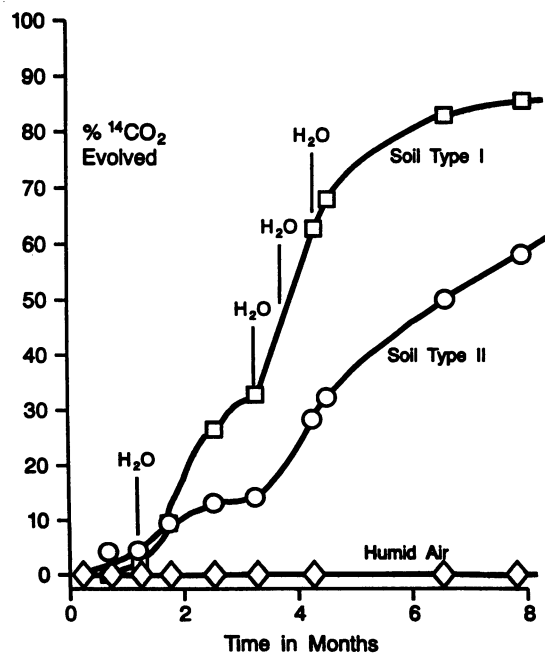


FIG. 4. Biodegradation of PHB.

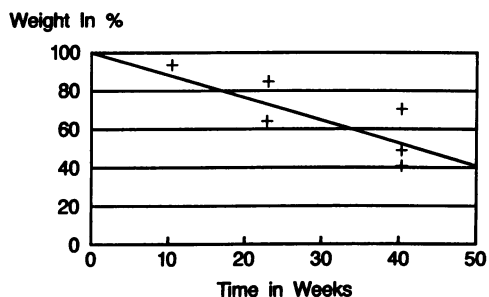


FIG. 5. Degradation of PHBV landfill simulation.

PROCESSING

PHBV is currently supplied as either powder or pellets. These materials have been processed on conventional equipment to produce injection-molded articles, blow-molded bottles, extruded sheet, film, paper coatings, and fibers. Most early applications work focused on injection and blow molding, and processing conditions for these techniques are now quite well defined.

The other processing techniques mentioned require further application development work. This is under way and led by customers with specific, end-product performance targets.

BIODEGRADABILITY

Microorganisms view PHBV as an energy source. Therefore, PHBV biodegrades in microbially active environments. Microorganisms colonize on the surface of the polymer and secrete enzymes which degrade PHBV into HB and HV segments. These fragments are used by the cells as a carbon source for growth.

Biodegradation rates depend on a variety of factors, including surface area, microbial activity of the disposal envi-

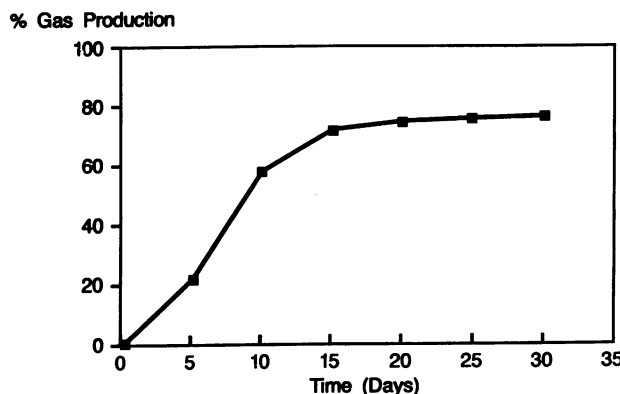


FIG. 6. Anaerobic degradation of PHBV 27% copolymer.

ronment, pH, temperature, moisture level, and the presence of other nutrient materials. PHBV is not affected by moisture alone. The environment must be microbially active. No degradation occurs under normal storage conditions, and the material is stable indefinitely in air.

PHBV degrades in a wide range of environments. Degradation occurs most rapidly in anaerobic sewage and slowest in seawater (Table 2) (3). In aerobic environments, the end products are carbon dioxide, water, and humus. Under anaerobic conditions methane is also produced. No harmful intermediates or by-products are produced during the degradation process.

Fig. 4 shows results of a soil biodegradation experiment. Radiolabeled PHB film was buried in two types of soil. Biodegradation was observed by measuring the radiolabeled carbon dioxide gas that was evolved as a direct measure of polymer degradation (i.e., disappearance). Moisture was added to the soil periodically. The data suggest significant

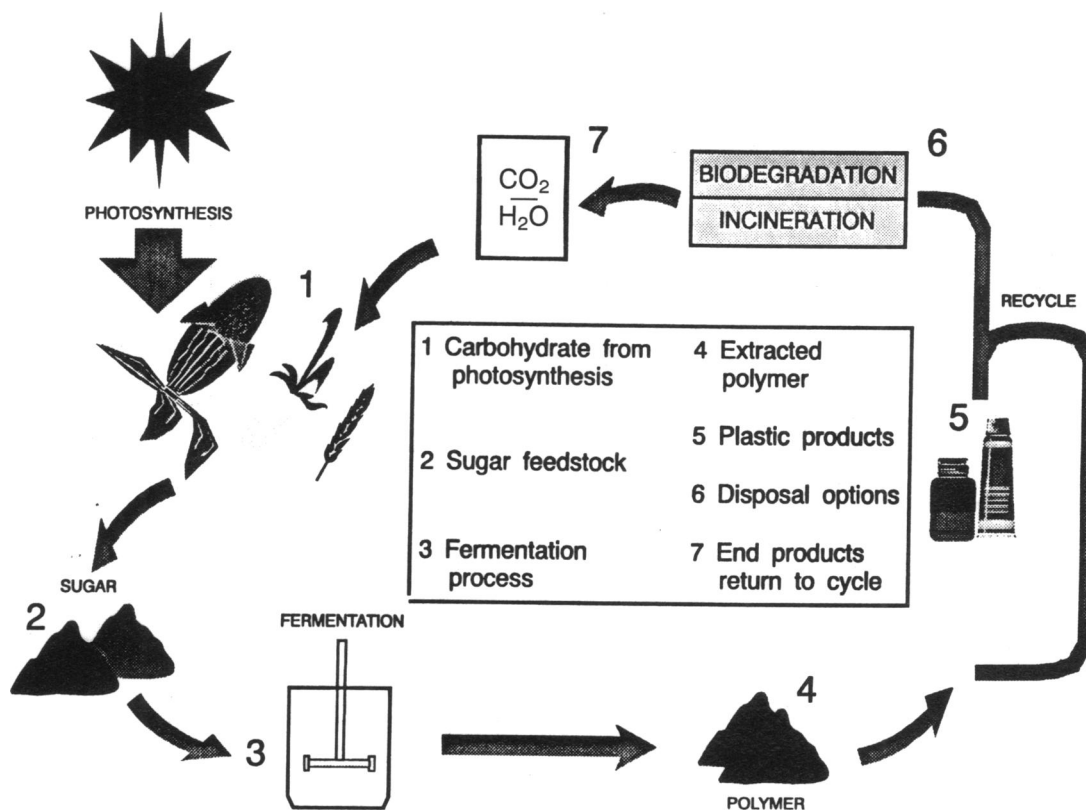


FIG. 7. PHBV cycle: Striking a balance with our environment.



degradation, over 70% in one soil type, during an 18-week study period. Note PHB's stability in humid air.

In a simulated landfill environment, PHBV showed about a 60% weight loss after 50 weeks (Fig. 5). Shredded municipal waste was used at 35°C with percolating water to neutralize and accelerate the system.

Under anaerobic sewage conditions, again biodegradability of PHBV was determined by measuring gas evolution relative to a control. After just 30 days, gas evolution was 78% of theoretical, reflecting significant, rapid degradation (Fig. 6).

APPLICATION AREAS/COMMERCIAL ISSUES

PHBV's key properties are its biodegradability, apparent biocompatibility, and its manufacture from renewable resources. Primary application areas in which these features meet some market needs are (i) disposable personal hygiene: PHBV could be used as the sole structural material or as part of a degradable composite; (ii) packaging: PHBV could be used for films, blow-molded bottles, and as a coating on paper; and (iii) medical: PHBV's biocompatibility coupled with its slow hydrolytic degradation (4) lead to potential in reconstructive surgery and controlled release fields.

The global interest in PHBV is high, with many companies developing products from the material. But we are still at an early stage in technical and market development, and capacity is currently limited. This year capacity will be in the range of 200–300 tonnes. But we intend to increase this incrementally in line with demand, building to a capacity of several thousand tonnes per year by the mid-1990s.

As capacity increases production costs will decrease, continuing the trend of the last decade. Costs have fallen from \$800 per pound in 1980 to \$16 per pound in 1989, and the price of PHBV should be below \$5 per pound by the mid-1990s. Further cost improvements will depend largely on scale, raw material costs, and future technology improvements.

CONCLUSION

PHBV fits quite neatly into the ecosystem (Fig. 7)[†] It is a polymer which is naturally produced by bacteria from agricultural raw materials. PHBV can then be processed to make a variety of useful products where its biodegradability, biocompatibility, and naturalness are beneficial. But when these end products meet disposal, PHBV completely biodegrades into carbon dioxide and water. These compounds are of course used for photosynthesis, so the cycle repeats.

PHBV is still in the first stage of commercial development. But it is an excellent example of how new technology can help meet society's needs for plastic materials and a clean environment.

[†]Brunger, P. M., RAPRA Technology Limited and Pira International Conference, January 30–31, 1991, Birmingham, U.K.

1. Sperling, L. H. & Carraher, C. E. (1985) *Encyclopedia of Polymer Science and Engineering* (Wiley, New York), Vol. 12.
2. Holmes, P. A. (1985) *Physics Technol.* **16**, 33.
3. Galvin, T. J. (1990) *Business 2000+* (Winter), pp. 12–13.
4. Holland, S. J., Jolly, A. M., Yasin, M., Tighe, B. J. (1987) *Biomaterials* **8**, 289–295.