

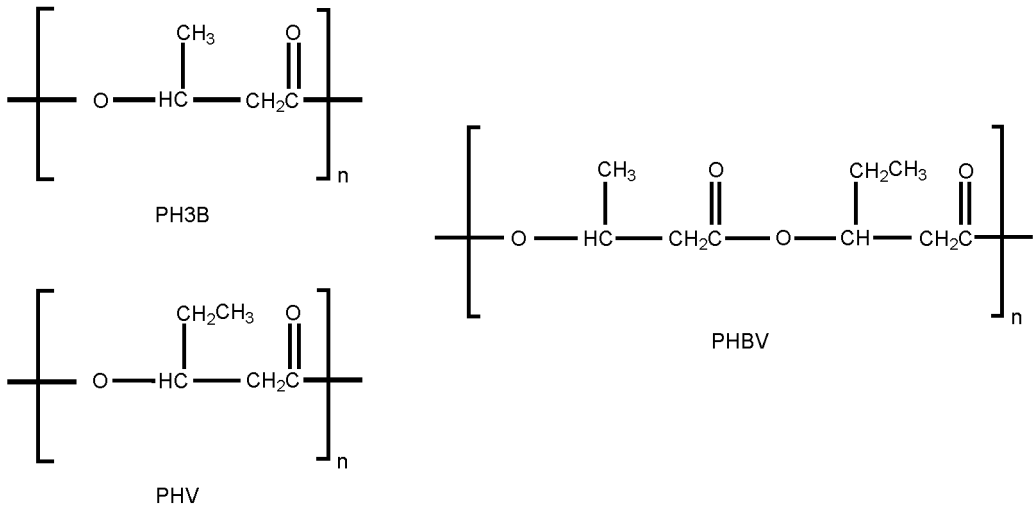
## **4.4 Polyhydroxyalkanoates (Including Polyhydroxybutyrate (PHB) and Copolymers)**

### **4.4.1 Production and Properties of PHA Polymers**

PHA polymers are true ‘biopolymers’, as they are synthesised within the bodies of bacteria grown in special digesters, and subsequently extracted from the biomass. The polymer can make up to 80% of the biomass, stored by the bacteria as an energy reserve. These polymers have been of interest (though sadly not sufficiently to make them profitable volume materials) for a number of years and ownership of the technology has changed hands several times since ICI first marketed Biopol in 1990. One current manufacturer is MetaboliX (as Mirel) which has a 50,000 tonnes per year plant in Iowa, USA, while other companies are reportedly also investing in PHA capacity [2]. Cost remains a severe handicap [46], and has to date inhibited the introduction of these materials into the very cost-sensitive foam packaging market – Mirel prices were quoted in 2008 [47] at more than \$4.4 per kg, far above the price of oil-derived polymers such as polystyrene or polyolefins. As for all potential applications of ‘sustainable’ polymers, legislation or customer diktat can change the economics to some extent, but it appears that unless the production costs of PHA reduce significantly with increased scale (for other applications), they are unlikely to become a major player in the near future.

The composition of a PHA copolymer – polyhydroxybutyrate-*co*-hydroxyvalerate (see **Figure 4.3**), with 5–12% of valerate units randomly incorporated along the chains – is controlled by manipulation of the ‘food’ (mostly glucose) supplied to the bacteria.  $T_g$  of pure PHB is 5 °C and its melting point is 170–180 °C – the presence of the hydroxyvalerate (HV) units acts to lower the melting point, increase impact strength and flexibility and reduce tensile strength. The copolymers are crystalline, although as the HV content rises so the rate of crystallisation reduces, and nucleants are routinely

added to accelerate crystallisation during processing. Plasticisers are also used to improve processability and flexibility.



**Figure 4.3** Structures of polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and the copolymer, PHBV

The properties of PHA vary with the composition, but generally speaking the more common grades resemble polyolefins – at mid-range HV contents they are tough like polypropylenes, at higher levels they are softer and more like polyethylenes. This has led to applications in packaging such as films and bottles where their degradability brings added value sufficient to offset their high cost.

#### **4.4.2 Blowing Agents and Processing of PHA Foamable Beads**

Kaneka Corporation, also known as Kanegafuchi, has been active in the technology of foaming biodegradable polymers, and has

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filed two patents in recent years on expandable PHA. In the first of these [48], solid beads of poly(3-hydroxyalkanoate) (Kaneka's patent writers prefer this version of the chemical name for PHA copolymers) are formed, then suspended in a blowing agent in a sealed vessel, pressurised and heated to start the expansion. The blowing agent is preferably dimethyl ether, diethyl ether or methyl ethyl ether – all have low boiling points and will impregnate the polymer. Once the beads are sufficiently saturated with ether and heated to a temperature not far below their melting point, the vessel is opened and the beads complete their expansion. The patent goes into much detail about the necessity for controlling the valerate comonomer level and having two crystalline melting points, and much less detail about the way the beads are first produced. Moulding of the expanded beads into shaped products is discussed without much detail – they are first prepressurised with air (as in EPP moulding), then fused with steam.

The second Kaneka patent [49] follows much the same lines, but additionally claims benefits from the addition of an isocyanate compounded into the polymer (as a chain extender). A wider range of blowing agents is also claimed, including isobutane and pentane. There are no details of the bead-making process, and again the moulding process is barely discussed. In the given, the temperature in the impregnation vessel is 120–130 °C, close to the polymer melting point, and the pressure is held at 2.5 MPa for an hour.

The importance of controlling crystallisation behaviour is emphasised by a joint 2008 patent application from Kanegafuchi Chemical (Kaneka) and the Tokyo Institute of Technology [50]. The text of this patent is in Japanese, but the English abstract reveals that it is claimed that there is a need to accelerate crystallisation in PHA in order to improve processability. This applies to all melt processing – injection moulding, blow moulding, fibre spinning, extrusion foam moulding and bead foam moulding are all quoted – and is achieved by the use of a sugar alcohol (galactitol) as a nucleating agent. Differential scanning calorimetry traces shown in the abstract have melting curves of PHB and PHBV (the valerate used as co-monomer)

with no nucleant, with 2% hexagonal boron nitride and with 2% galactitol – clear differences are visible, with the galactitol increasing the size of the melting peaks but also their peak temperature.

#### **4.4.3 End-of-life Aspects of PHA Foam Products**

When PHBV articles are exposed to microbially active environments, enzymes begin to attack the surface of the polymer, eventually breaking it down into carbon dioxide and water in aerobic conditions, or carbon dioxide and methane in anaerobic conditions. In composting conditions it may take a reasonably long time for solid parts to decompose fully, but foamed material can be expected to degrade rather more quickly. As with all thermoplastics, PHA are potentially melt reprocessable, although their heat stability is limited, and temperatures above 180 °C should be avoided.