polymer report

# Physical properties of poly(β-hydroxybutyrate)–poly(ε-caprolactone) blends*

**F. Gassner and A. J. Owen†**
*Institut Physik III, Universität Regensburg, Universitätsstrasse 31, 93053 Regensburg, Germany*
*(Received 10 November 1993; revised 24 January 1994)*

Compression-moulded sheets of bacterially produced poly(β-hydroxybutyrate) (PHB) blended with synthetic poly(ε-caprolactone) (PCL) were investigated over the complete composition range from pure PHB to pure PCL. These blends are of potential interest because both components are biodegradable. Although PHB and PCL are immiscible, they formed mechanicaly compatible films containing phase-separated partially crystalline domains. The mechanical properties varied considerably with composition. The low melting point of PCL (~60°C) prevented temperature-resistant blends from being obtained for compositions containing less than 60% PHB.

**(Keywords: poly(β-hydroxybutyrate); poly(ε-caprolactone); physical properties)**

## INTRODUCTION

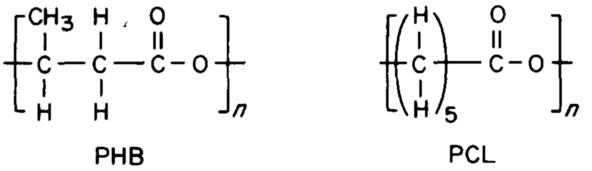
Bacterially produced poly(β-hydroxybutyrate) (PHB) is an interesting polymer from the point of view of basic research[1–6]. However, it suffers from several technical disadvantages compared to conventional thermoplastic polymers. Firstly, PHB is relatively expensive to produce at present, although much less costly than other biocompatible high polymers, such as poly(L-lactide)[7]. Secondly, pure PHB crystallizes slowly when cooled from the melt, and the resulting material shows embrittlement and ageing effects[8]. With the aid of plasticizers and nucleating agents, however, some improvements in processability have been made. By adjusting the feedstock for the bacteria, a series of biodegradable copolymers based on PHB (tradename BIOPOL), with a wide range of physical properties[1], are produced commercially by Zeneca (ICI Biological Products).

It may be possible to obtain a less expensive thermoplastic with improved mechanical properties by blending PHB with a suitable synthetic polymer. Martuscelli and co-workers showed that PHB is miscible in the melt with poly(ethylene oxide)[9] and poly(vinyl acetate) (PVAc), but not with ethylene–propylene rubber[10]. Gassner and Owen[11] investigated the structure and mechanical properties of blends of BIOPOL with ethylene–vinyl acetate copolymers. However, since the synthetic component of these blends is not utilized by bacteria and fungi, such materials are expected to be only partly biodegradable.

The only synthetic high polymers found to be biodegradable are those with aliphatic ester linkages in the main chain, for example, poly(ε-caprolactone) (PCL) (see *Figure 1*), which, when buried in soil, is completely degraded after about 1 year[12]. PCL is generally partially crystalline with a degree of crystallinity in the region of 50% and a melting point near 60°C. The glass transition of PCL lies at approximately −70°C.

PCL has been blended with a variety of polymers[13]. For example, PCL–poly(vinyl chloride) (PVC) blends are molecularly miscible, as evidenced by a single glass transition. The PCL crystallinity is inhibited by the presence of PVC. However, above approximately 30% PCL concentration, the PCL crystallizes after ageing for several weeks. Blends of PCL with PVAc are molecularly immiscible (showing two glass transitions), but they form satisfactory films and can be considered to be mechanically compatible. PCL blended with polyethylene (PE) and polypropylene shows evidence of crystalline interaction, i.e. the α-relaxation of PE is shifted to higher temperatures, indicating possible cocrystallization of the two components[13]. In general, PCL acts as a polymeric plasticizer (i.e. it lowers the elastic modulus); it also improves processability on blending and acts as a mould-release agent, as well as showing biodegradable characteristics. Its poor temperature stability (low melting point) is perhaps its biggest disadvantage, excluding it from many applications.

Kumagai and Doi[14] have recently investigated the miscibility, morphology and biodegradability of blends of PHB with PCL. They found that these polymers are immiscible in the amorphous state; scanning electron microscopy and mechanical measurements indicated a macrophase-separated structure. A complicated dependence on PCL weight fraction of enzymatic degradation behaviour was observed.



$$\left[-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\right]_n \qquad \left[-\left(\overset{H}{\underset{H}{C}}\right)_5-\overset{O}{\overset{\|}{C}}-O-\right]_n$$

PHB PCL

**Figure 1** Structural formulae of PHB and PCL

---

[*] This work was presented at the 13th General Conference of EPS and DPG, Regensburg, Germany, 29 March–2 April 1993, and is dedicated to Professor Dr R. Bonart on the occasion of his retirement

[†] To whom correspondence should be addressed

0032-3861/94/10/2233-04

In the present work we have investigated the compatibility and mechanical properties of PHB–PCL blends. The aims were to understand the basic physical phenomena involved on blending these two polymers, and to attempt to obtain a material with mechanica properties better than those of the individual components. The virtual certainty that these blends would be fully biodegradable served as further motivation for this work.

## EXPERIMENTAL

### *Materials and sample preparation*

The PHB powder used in this investigation was provided by ICI Biological Products (Billingham, Cleveland, UK). The molecular mass was given as $M_n = 222\,000$. The PCL powder was supplied by Union Carbide (tradename TONE P-767; $M_n = 43\,000$).

The powders were mixed thoroughly in various weight proportions and then compression-moulded at 190°C into films 0.4 mm thick. Films were quenched from the melt and subsequently allowed to crystallize at room temperature for several weeks before testing.

### *Experimental methods*

Melting endotherms were obtained by means of differential thermal analysis (d.t.a.) using Mettler equipment at a heating rate of $5°\mathrm{C\,min^{-1}}$.

Dynamic mechanical measurements were obtained at a frequency of 5 Hz over a wide temperature range covering glass and melting regions.

Stress–strain diagrams were obtained at room temperature with a strain rate of $10\%\,\mathrm{min^{-1}}$ using a Minimat materials tester (Polymer Laboratories).

Film surfaces and fracture surfaces were observed with a scanning electron microscope (Philips PSEM500) after coating samples with Au–Pd conducting film using a Polaron Cool Sputter Coater.

## RESULTS AND DISCUSSION

### *Differential thermal analysis*

D.t.a. measurements were made during a heating run from −80 to 200°C. Distinct evidence of glass transitions was not obtained by this method, presumably owing to the fairly high crystallinity which renders detection difficult. It was therefore not possible to adopt the usual criteria: a single glass transition indicating miscibility and two transitions indicating phase separation.

The results obtained above 30°C are presented in *Figure 2*, where two endothermic peaks are seen. In a first approximation the temperature position of these peaks is unaffected by blend composition. The transitions clearly relate to melting of PCL crystallites at approximately 63°C and melting of PHB crystallites near 180°C. The heats of melting calculated from the areas under the two peaks are directly proportional, within experimental error, to the amounts of PCL and PHB present in the sample, irrespective of the blend composition, i.e. the values obtained for heat of fusion are $78\,\mathrm{J\,g^{-1}}$ for PCL (lower peak) and $109\,\mathrm{J\,g^{-1}}$ for PHB (upper peak). Taking the literature[5] values for the heat of fusion as $136\,\mathrm{J\,g^{-1}}$ for PCL crystals and $146\,\mathrm{J\,g^{-1}}$ for PHB, this gives a degree of crystallinity of 57% for the PCL component and 75% for PHB.

The above results suggest that macrophase separation into PCL and PHB domains occurred in the melt[14,15], with independent crystallization of the two phases occurring on subsequent cooling. However, a very slight shift of each melting peak to lower temperatures with increasing amount of the other component (see *Figure 2*) was noticeable. This indicates that a small amount of solubilization of one component into the other could be taking place, thus lowering the melting temperature. (Further work on the crystallization and melting of PHB–PCL will be presented elsewhere[15].)

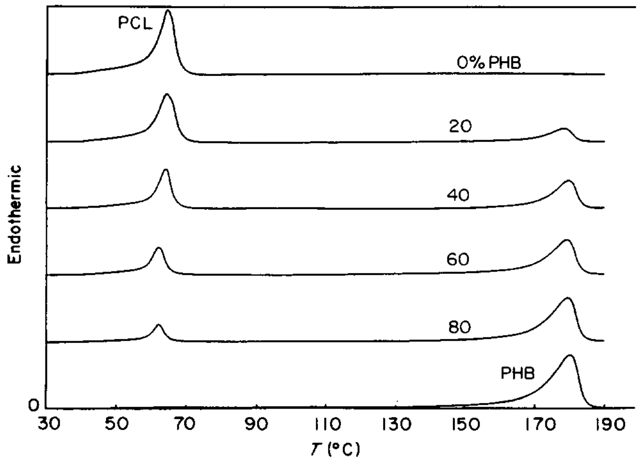


**Figure 2** D.t.a. measurements for PHB–PCL. Heating rate $5°\mathrm{C\,min^{-1}}$

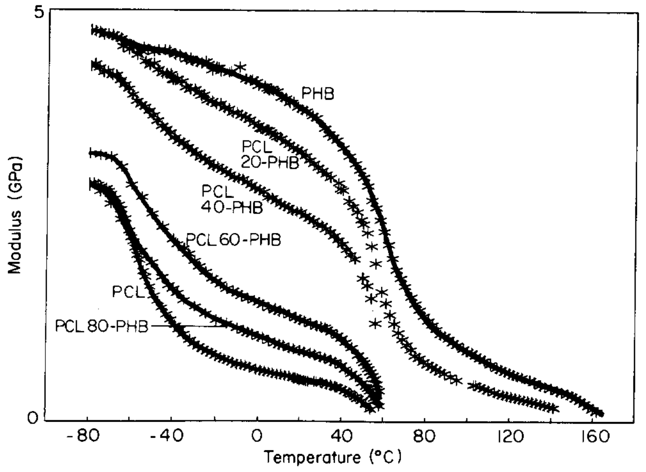


**Figure 3** Dynamic modulus for PHB–PCL at 5 Hz

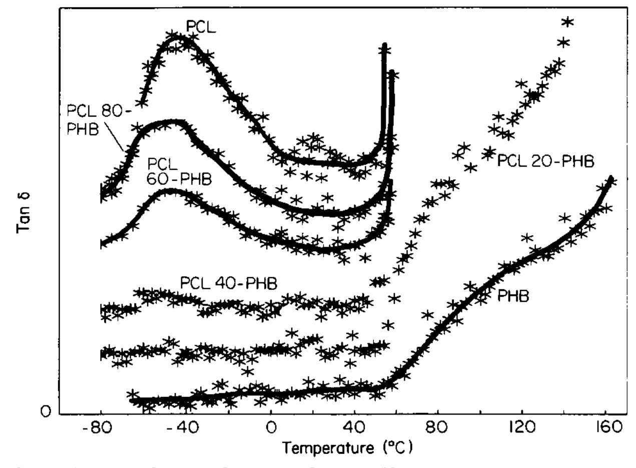


**Figure 4** Loss factor of PHB–PCL at 5 Hz

### *Dynamic mechanical measurements*

The modulus and loss factor for various blend compositions are shown in *Figures 3* and *4* during a heating run from −80°C up to the melting region of each sample. The glass transition of PCL is clearly seen as a steep fall in modulus and a peak in tan $\delta$ at about −50°C for the samples with 100, 80 and 60% PCL, whereas the relaxation process is unpronounced in samples with less than 60% PCL. For samples with 60% PCL and above, the blends flowed at 60°C, whereas with less than about 60% PCL the samples retained their solid character up to the melting region of PHB.

The dynamic mechanical measurements give information on the coupling behaviour of the two phases. For a PCL content of 60% and above, we infer that the PCL phase forms a continuous (semicrystalline) matrix, with PHB spherulites embedded in it as islands. The composite mechanical behaviour is then dominated by the PCL matrix, which shows a glass transition at around −50°C and melts at 60°C. For compositions with less than about 60% PCL, however, the PHB phase becomes continuous. Inclusions of PCL, even though they may show a glass transition and melt at 60°C, do not catastrophically lower the rigidity of the sample, whose properties remain dominated by the PHB matrix up to much higher temperatures. The 40%PCL–60%PHB sample was on the borderline between these two types of behaviour.

### *Load–elongation curves*

Stress–strain diagrams for the samples crystallized and stored for several weeks at room temperature showed clearly that ductile flow occurred when the PCL matrix was continuous (above about 60% PCL), whereas the samples with continuous PHB phase were brittle in that they fractured near the point at which the stress reached a maximum.

Elastic modulus values obtained from the maximum slope of the initial portion of the stress–strain diagrams are shown in *Table 1*. The modulus increased systematically with increasing PHB content owing to the reinforcing effect of PHB.

*Table 1* also gives the values of stress and strain taken from the position of the maximum in the stress–strain diagram. It is clear that the larger the PCL content, the greater the strain before the sample yields or begins to fail. The maximum stress increase with increasing PHB content, and the mode of failure changes from ductile to brittle.

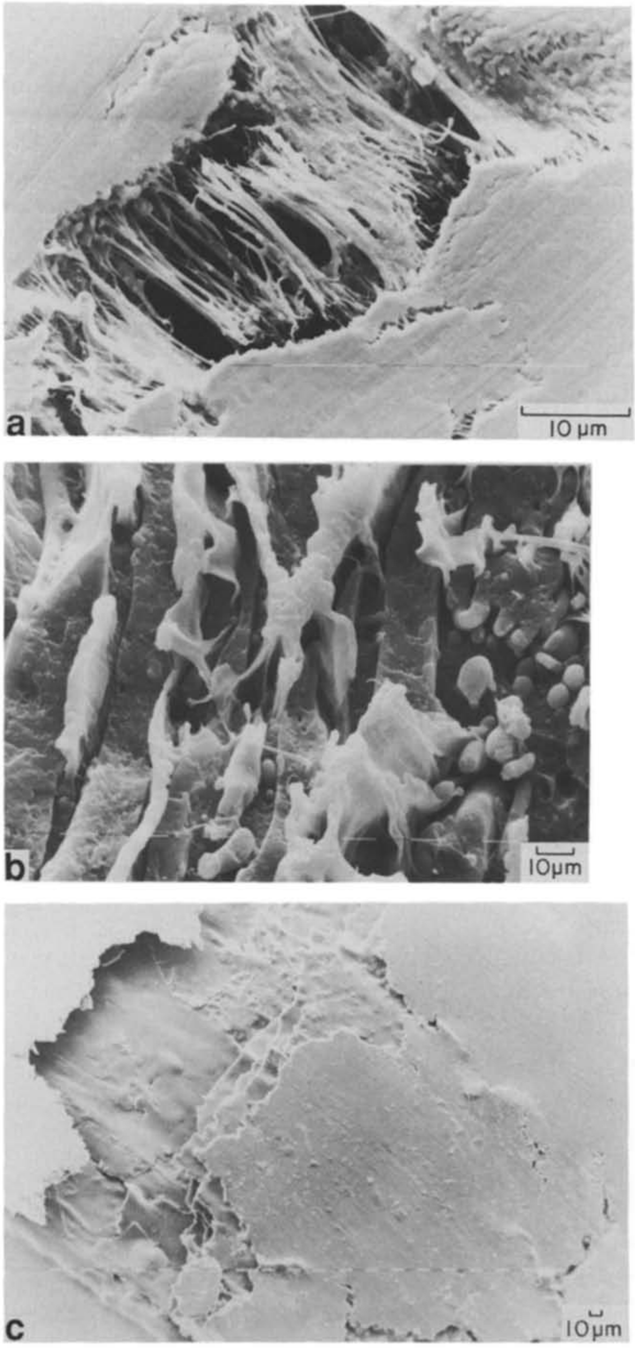


**Figure 5** Scanning electron micrographs of fracture surfaces: (a) 80%PCL–20%PHB; (b) 40%PCL–60%PHB; (c) 20%PCL–80%PHB

### *Scanning electron microscopy*

Some scanning electron micrographs are shown in *Figure 5*. Pure PCL necked and drew to several hundred per cent strain. However, with 20% PHB added to the PCL, the drawing took place with longitudinal cavities forming between fibrils of PCL material. These cavities form as a result of the presence of the relatively undeformable PHB inclusions which are embedded in the relatively soft PCL matrix (*Figure 5a*).

*Figure 5b* shows a freeze-fractured, cross-sectional view of a sample containing 60% PHB; there is evidence of an irregular layered structure of the two components parallel to the film surface.

Samples with less than about 60% PCL fractured just after reaching a stress maximum. *Figure 5c* shows such a blend containing 20% PCL. The crack seen is relatively sharp; the material near the crack is hardly deformed. However, there is again an indication of a layered structure, which is particularly clear in freeze-fractured samples.

**Table 1** Properties of PHB-PCL blends (strain rate 10% min$^{-1}$ at 21°C)

| PHB (wt%) | Tensile modulus (GPa) | Maximum stress (MPa) | Strain at maximum (%) |
|---|---|---|---|
| 0 | 0.36 | 18.4 | 7.4 |
| 20 | 0.53 | 18.0 | 5.5 |
| 40 | 0.86 | 21.4 | 4.4 |
| 60 | 1.47 | 23.7 | 1.8 |
| 80 | 1.92 | 25.0 | 1.3 |
| 100 | 2.10 | 29.4 | 1.0 |

## CONCLUSION

PHB and PCL are immiscible on a molecular scale, and their glass temperatures and melting temperatures are far apart. However, mechanically compatible, opaque films were easily obtained by compression moulding. The properties depended markedly on blend composition. However, no synergetic effects were found that could be exploited to obtain a material with properties better than those of the individual components. Further work is now being carried out on PHB–PCL blends using different crystallization and annealing conditions.

## REFERENCES

1 Holmes, P. A. in 'Developments in Crystalline Polymers-2' (Ed. D. C. Bassett), Elsevier, Amsterdam, 1988, Ch. 1
2 Barker, P. A., Mason, F. and Barham, P. J. *J. Mater. Sci.* 1990, **25**, 1952
3 Bauer, H. and Owen, A. J. *Colloid Polym. Sci.* 1988, **266**, 241
4 Owen, A. J., Heinzel, J., Divjakovic, V. and Skrbic, Z. *Polym. Commun.* 1992, **33**, 1563
5 Barham, P. J., Keller, A., Otun, E. L. and Holmes, P. A. *J. Mater. Sci.* 1984, **19**, 2781
6 Owen, A. J. *Colloid Polym. Sci.* 1985, **263**, 799
7 'Information Booklet', Boehringer Ingelheim Resomer — Resorbierbare Polyester Boehringer-Ingelheim, Ingelheim, Germany
8 de Koning, G. J. M. and Lemstra, P. J. *Polymer* 1992, **33**, 3295
9 Avella, M. and Martuscelli, E. *Polymer* 1988, **29**, 1731
10 Greco, P. and Martuscelli, E. *Polymer* 1989, **30**, 1475
11 Gassner, F. and Owen, A. J. *Polymer* 1992, **33**, 2508
12 Potts, J. E., Clendinning, R. A., Ackart, W. B. and Niegisch, W. D. in 'Polymer Science and Technology, Vol. 3, Polymers and Ecological Problems' (Ed. J. Guillet), Plenum Press, New York, 1973
13 Koleske, J. V. in 'Polymer Blends, Vol. 2' (Eds D. R. Paul and S. Newman), Academic Press, New York, 1978
14 Kumagai, Y. and Doi, Y. *Polym. Degrad. Stab.* 1992, **36**, 241
15 Blümm, E. and Owen, A. J. in preparation