Macromol. Symp. **127**, *227–240 (1998)*

SOLID-STATE PROCESSING OF PHB-POWDERS

Thomas Lüpke*, Hans-Joachim Radusch, Klaus Metzner‡

Martin-Luther-University Halle-Wittenberg, D-06099 Halle
‡BSL-Olefinverbund, D-06258 Schkopau

ABSTRACT: Poly(3-hydroxybutyrate) (PHB) is a completely biodegradable polyester, produced by bacterial fermentation. Because of poor thermal stability, melt processing of the material is accompanied by thermal degradation and poor mechanical properties.
To prevent thermal degradation, a solid-state processing technology has been applied. The extrusion of PHB-powder at temperatures far below the melting point leads to products of improved mechanical properties. In particular, the ductility of the material increases considerably compared to traditional melt processed PHB. The improved mechanical properties have been attributed to structural differences on the molecular and supermolecular level.

1. INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is a naturally occurring biodegradable polyester, which received increasing attention during the last decade. The industrial production of the material is possible by bacterial fermentation from renewable resources (Ref.1). Biological degradability in combination with advanced mechanical properties is the basis for a variety of interesting applications, including packaging industry and medicine (Ref.2).

According to structure and properties, PHB is often compared with standard polypropylene. It is a crystallizable material with transition temperatures of about 0°C (glass transition) and about 180°C (crystalline melting point). According to its high degree of crystallinity, it is a stiff material of high tensile strength. The major disadvantages of PHB are poor thermal stability

CCC 1022-1360/98/$ 10.00

and brittleness. Traditional melt processing technologies lead to a rapid decrease of molecular wight at temperatures slightly above the melting point.

To overcome these shortcomings and to commercialize the material, PHB has been copolymerized with 3-hydroxyvaleriate. This reduces melting point and degree of crystallinity so that lower processing temperatures can be applied and the elongation at break increases. However, copolymerization reduces modulus and strength of the polymer and increases production costs (Ref.3).

An alternative way to prevent thermal destruction is the processing of PHB-powders below the melting temperature in the solid state. The influence of this technology on structure and properties of the material and the advantages compared to melt processing technology will be discussed below.

2. EXPERIMENTAL PART

2.1. MATERIALS

Sconacell B®, a powder of pure PHB-homopolymer was supplied by BSL-Olefinverbund GmbH, Schkopau (Germany). The material was produced by bacterial fermentation of methanol by methylobactrium MB 126. Four types of PHB were available. Molecular weight and melting temperature of the materials are given in table 1. The mean particle diameter of the powder was about 200µm.

TABLE 1: Characteristics of the PHB-homopolymers studied

Sample	Molecular weight [g/mole]	Nitrogen content [%]	Melting temperature [°C]
PHB 1	171 000	0,29	173.7
PHB 3	350 000	3,29	174.6
PHB 7	500 000	0,048	177.8
PHB 9	1 000 000	0.05	181.0

2.2. SOLID-STATE PROCESSING TECHNOLOGY

The processing of PHB-powders took place as a two step process. In a first step a green body (70mm*15mm*4mm) was produced by cold compaction of the powder at room temperature. After that, this green body was extruded under plain strain compression in a channel die, schematically shown in figure 1. The extrusion process was performed in the temperature chamber of a tensile testing machine (Zwick 1386) at elevated temperatures. Load was applied at a cross head speed of 1 mm/min to a maximum pressure of 95 MPa. Depending on processing temperature, different draw ratios and extrudate densities have been realized, as shown in figure 2.

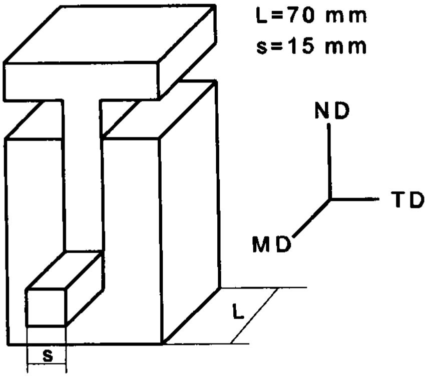


Figure 1: Schematic representation of the channel die (ND: normal direction; MD: machine direction; TD: transverse direction)

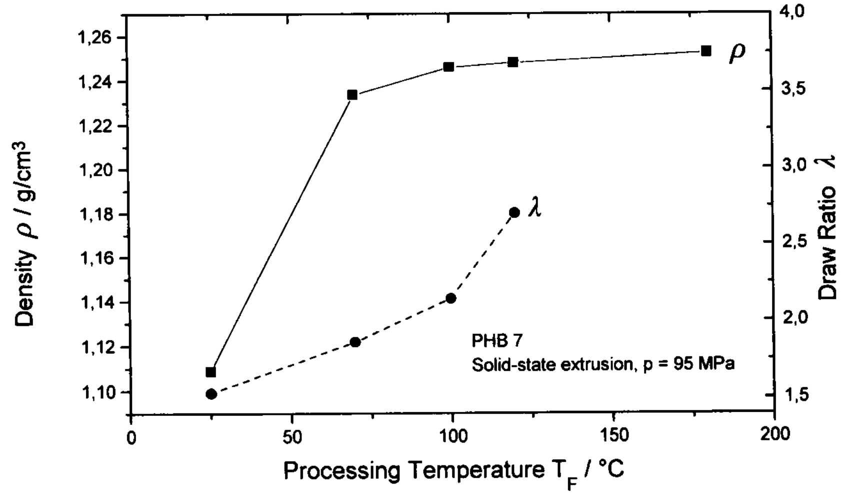


Figure 2: Density and draw ratio of solid-state extruded PHB, produced at different processing temperatures T_F

With increasing compaction, visual changes of the material took place. While the green body is completely non transparent, exhibiting the white colour of the raw material, the extrudate shows the typical opaque appearance of partially crystalline polymers.

For comparison, PHB has been compression moulted at 185°C in the melt.

2.3. CHARACTERIZATION

Stress-Strain Measurements

The stress-strain behaviour of the material has been characterized according to ISO 527/2, using a Zwick 1425 tensile testing machine. Dumbbell shaped samples (l=50mm; s=4.5mm; d=2mm) were investigated at room temperature with a crosshead speed of 5 mm/min. Strain gauges were used to measure sample elongation.

Stress-strain measurements have been carried out eight weeks after processing of the material.

Dynamic Mechanical Analysis

A Mark III DMTA-system produced by Rheometric Scientific was used for dynamic mechanical analysis. The measurement was carried out in single cantilever bending mode at a frequency of 1 Hz and a heating rate of 2K/min. Sample dimensions were 25mm*10mm*2mm.

Creep

Creep experiments in single cantilever bending mode were performed on the Mark III DMA-system. The deformation of bar shaped samples (25mm*5mm*2mm) at a bending stress of 20 MPa was followed at 37°C over a period of 100 minutes.

Wide Angle X-ray Analysis (WAXS)

Wide angle X-ray investigations were used to characterize the crystalline structure of PHB. Scattering pattern were obtained with Ni-filtered Cu K_α-radiation on a goniometer URD 6 (Freiberger Präzisionsmechanik). For texture analysis a texture goniometer TZ 6 was used.

Differential Scanning Calorimetry (DSC)

Melting behaviour of PHB has been investigated with a heat flux calorimeter DSC 820 (Mettler Toledo). The scanning rate was 20 K/min. From the melting peak area, the mass fraction of the crystalline phase has been determined, assuming a heat of fusion of completely crystalline PHB to be 146 J/g.

Optical microscopy

Optical microscopy has been performed on a Leitz DM XR microscope. Thin slices of about 10µm thickness were examined in transmission with polarized light to characterize the spherolitic structure of the material.

3. RESULTS AND DISCUSSION

3.1 MECHANICAL PROPERTIES

The mechanical properties of PHB are known to be strongly dependent on the state of crystallisation. After melt processing for example, the initially ductile material embrittles rapidly because of secondary crystallisation processes, taking place at room temperature over several days. Heat treatment at elevated temperatures, on the other hand, can reverse embrittlement and increase the ductility of brittle melt processed material (Ref. 4). PHB-powder, as received by precipitation after cleaning and washing procedures, seems to be a relatively ductile material. Even after room temperature storage of several months, a plastic deformation of far more than hundred per cent is possible under plain strain compression in the channel die. In the solid-state extruded material the ductility of the powder is preserved. This can be seen from stress strain diagrams, obtained from uniaxial tensile tests in figure 3.

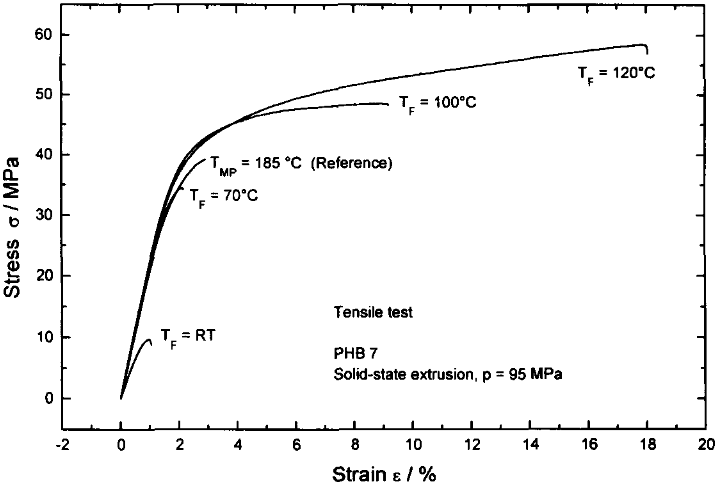


Figure 3: Stress-strain diagrams of solid-state extruded PHB, prepared at different processing temperatures T_F

Solid-state extruded PHB shows a well-defined yield point at about 40 MPa and an elongation at break up to about 20 %. However, the quality of the solid-state extruded material depends on the extrusion temperature T_F. Increasing the extrusion temperature results in larger plastic deformation during processing and increasing compaction of the polymer powder. The density of the material increases. At extrusion temperatures of 70 °C and below, microvoids cause brittle failure. Interesting to note, that the yield point of the polymer seems not to depend on processing temperature.

For comparison figure 3 contains the stress-strain curve of melt processed PHB (T_{MP} = 185 °C). The material behaves in a brittle manner and breaks at less than about 5 % elongation. This clearly shows the potential of solid state processing technology to improve the stress-strain characteristics of the material.

Processing technology also influences the relaxation behaviour of PHB. Long term properties have been characterized in creep test at 36 °C in bending mode. Figure 4 shows the creep curves for different samples, obtained at bending stresses of 20 MPa. According to different initial moduli, the initial deflexion of the solid-state extruded sample (F 120) is a little bit lower than in the case of melt processed material (MP 185). The creep rate, however, is considerably higher in solid-state extruded PHB. Figure 4 also indicates the good creep resistance of PHB in comparison to Polypropylene.

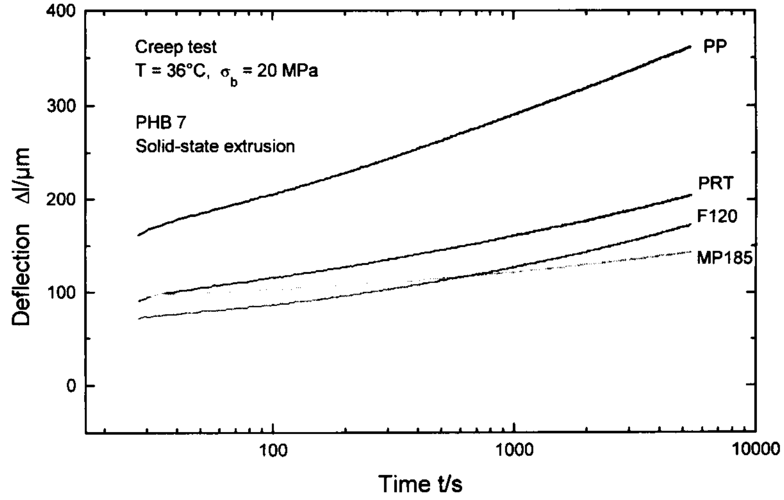


Figure 4: Creep curves of solid-state extruded PHB (F120) compared with the results obtained on melt processed material (MP185) room temperature compacted powder (PRT) and Polypropylene (PP)

Significant differences between melt processed and solid-state extruded PHB have been observed also in dynamic mechanical behaviour. The temperature dependence of modules E^* and loss factor tan δ of both materials is shown in figure 5. The behaviour of the melt processed, PHB is determined by a well-separated glass transition at about 10 °C resulting in a small modules step. Contrary to that, solid-state extruded PHB shows a smeared glass transition, slightly shifted to higher temperatures and a broad relaxation process at temperatures of about 120 °C.

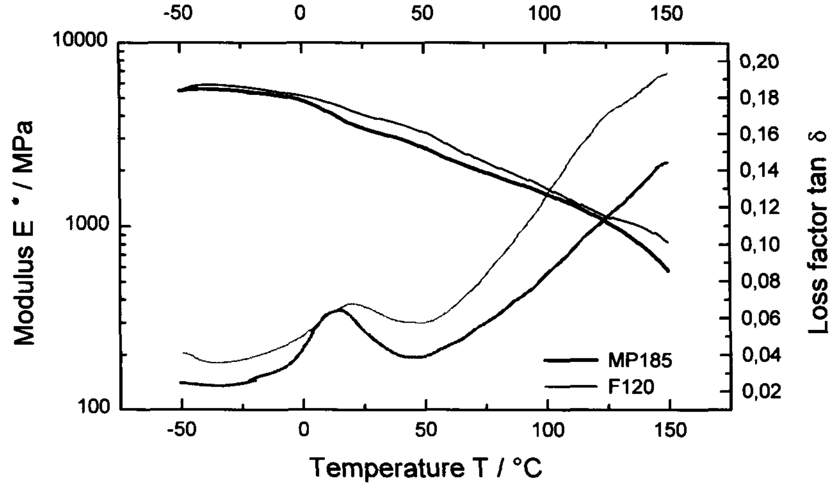


Figure 5: Temperature dependence of modulus and loss factor of melt processed (MP185) and solid-state extruded PHB (F120)

3.2. STRUCTURE - PROPERTY RELATIONSHIPS

Molecular structure

The production of PHB by bacterial fermentation leads to products of a narrow molecular weight distribution. The molecular weight of the thermally unstable material is influenced by the separation processes and by the processing conditions. It has considerable influence on the mechanical properties of the material.

Figure 6 represents the influence of the molecular weight of the initial polymer powder on the stress-strain behaviour of solid state extruded PHB. It is clearly to be seen, that with increasing molecular weight an increase in modulus, yield stress and elongation at break takes place. The transition from brittle to ductile behaviour is observed at molecular weights between 200 000 and 300 000 g/mole.

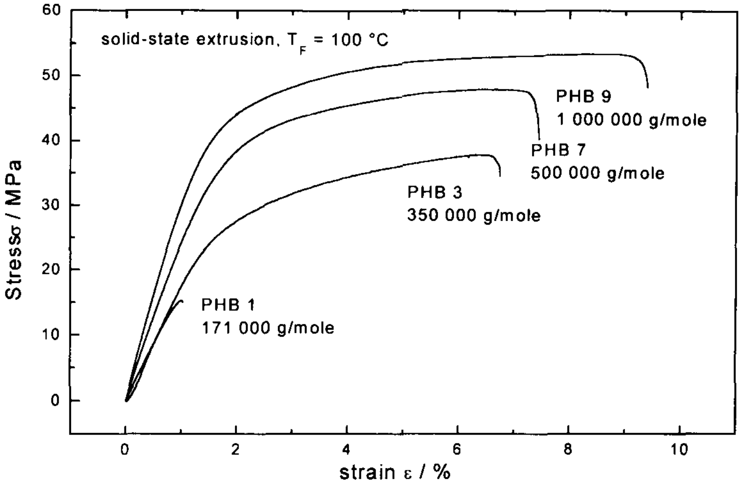


Figure 6: Influence of molecular weight on the stress-strain curves of solid-state extruded PHB

Changes in molecular weight, resulting from solid-state extrusion have not been detected. Contrary to that, melt processing leads to a considerable reduction in molecular weight. Melt processing of sample PHB 7 for example reduces the molecular weight from 500 000 to 420 000 g/mole. However, the reduction in molecular weight can not explain the embrittlement of melt processed PHB.

Crystalline structure

The mechanical properties of partially crystalline polymers like PHB are strongly influenced by the crystalline structure and by the crystalline-amorphous coupling. The crystalline phase of the material has been characterized by wide angle x-ray scattering and DSC. Selected x-ray scattering diagrams of PHB 7 are shown in figure 7. As a result of quantitative evaluation, degree of crystallinity Cr, half with breadth HWB of the (020)-reflection, situated at about $2\theta = 13{,}5°$ and melting temperature T_m are given in table 2 together with the glass transition temperature T_g, determined by dynamic mechanical analysis. increases it considerably.

Characteristic changes in the degree of crystallinity of the initial PHB-powder have been observed depending on processing conditions. While in solid state processing the crystallinity slightly decreases, melt processing increases it considerably.

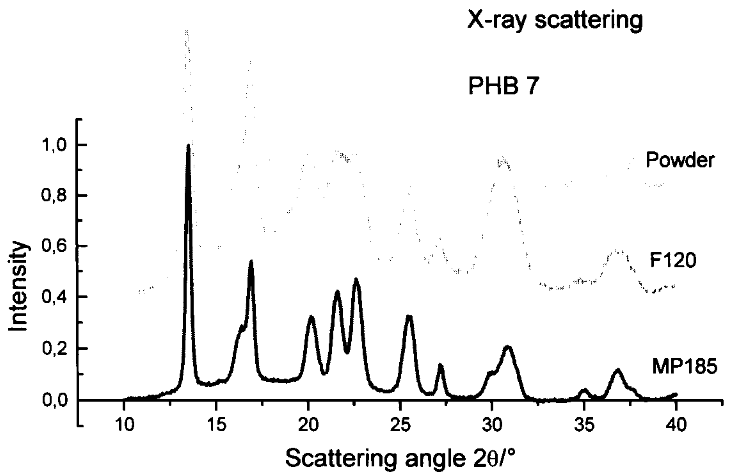


Figure 7: Influence of processing technology on the WAXS-diagram of PHB 7 (F 120: solid-state extruded; MP 185: compression moulded)

TABLE 2: Characteristics of the crystalline and amorphous phase of PHB in dependence of processing technology

Sample	Cr DSC [%]	Cr x-ray [%]	HWB (020) [°]	Tm [°C]	Tg [°C]
melt processed (MP 185)	78	76	0.32	176.7	13.9
solid-state extruded (F 120)	63	64	0.60	181.0	18.4
green body (P RT)	69	67	0.37	178.3	17.5
powder	65	69	0.38	177.5	16.7
amorphous	0	0	-	-	-3.2

The observed changes are corresponding with changes in the crystalline structure. This can be concluded from the shape of the x-ray reflections in figure 7. Melt processing leads to a sharpening of the diffraction peaks, represented by the reduced half width breadth of the (020) reflection or by the improved resolution of the initially smeared peak triplet at scattering angles 2θ between 18° and 24°. This sharpening of x-ray reflections is usually understood as a result of increasing crystalline perfection and the reduction of lattice distortions.

So, melt processing results not only in an increased degree of crystallinity but also in the formation of highly ordered crystalline structures with high resistance to plastic deformation. Solid state extrusion on the other hand reduces the degree of crystallinity and crystalline order. This favours ductile deformation behaviour.

The coupling of crystalline and amorphous phase has been investigated by dynamic mechanical analysis in the glass transition region. As shown by the temperature dependence of the loss factor tanδ in figure 8 completely amorphous PHB as received from melt quenching has a sharp glass transition with a transition temperature of -3° C. Resulting from the interaction with the crystalline phase in the partially crystalline polymer, the intensity of the transition is reduced, the peak maximum is shifted to higher temperatures and the width of the peak is increased. While the peak intensity depends on the amount of material, taking part in the transition process, the temperature position characterizes the influence of the crystalline phase on the mobility of the amorphous chains.

In melt processed PHB (MP 185) the glass transition starts at the same temperature as in the case of completely amorphous material but the maximum of the loss factor is shifted to temperatures of about 14° C. Still higher glass transition temperatures of about 17° C and 18° C have been observed in the case of room temperature compacted PHB powder (P RT) and solid-state extruded material (F 120). This indicates that the interaction between crystalline and amorphous phase in solid-state extruded PHB is more intensive than in the case of melt processed material. Interesting to note, that the integral intensity of the loss factor peak is larger for the highly crystalline melt crystallized material than for the more amorphous solid-state processed samples. Obviously, in the case of solid-state extruded PHB only a limited portion of the noncrystalline material, as detected by x-ray analysis, takes part in the glass transition. It is assumed, that a larger amount of the amorphous phase, closely attached to the crystalline phase, contributes to the broad damping peak at about 120°C, shown in figure 5.

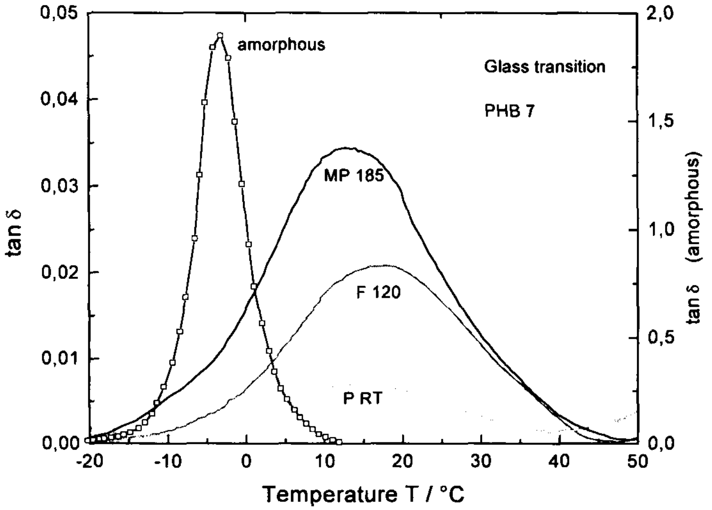
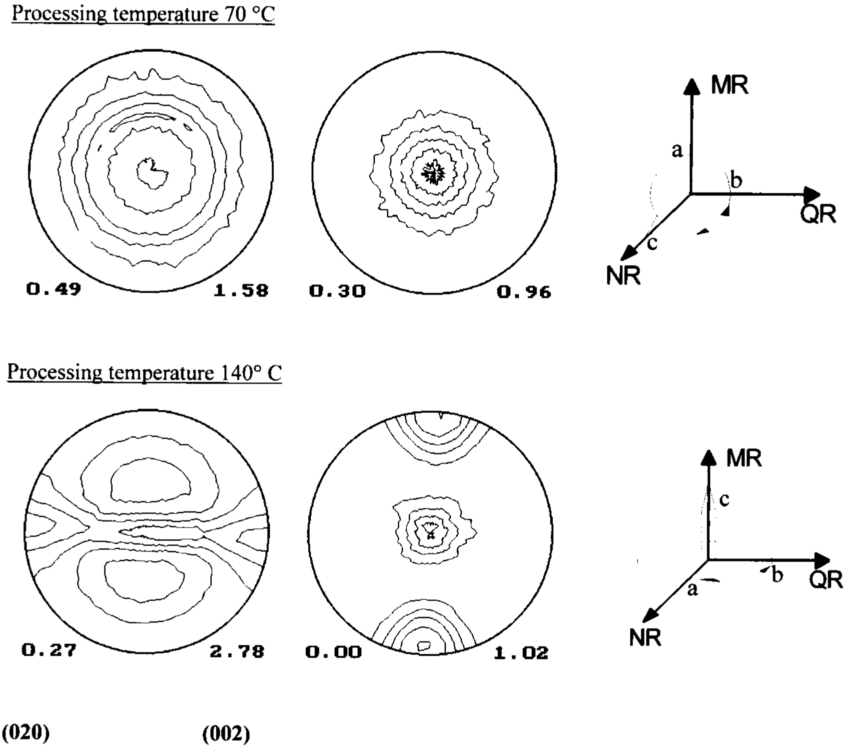


Figure 8: Influence of processing conditions on the loss factor tanδ in the glass transition region of PHB 7 (MP 185: compression moulded; F 120: solid-state extruded; P RT: room temperature compacted powder)

Molecular orientation

Molecular orientation is an important factor, influencing the mechanical properties of polymeric materials. While melt compression moulding results in samples, nearly free from orientation, plastic deformation during solid-state deformation produces a preferential alignment of molecular chains and crystals. Depending on processing temperature two different types of crystalline texture have been observed. At lower temperatures, the crystalline c-axis orients preferentially parallel to the normal direction (ND) of the sample, e.g. the direction of the compressive force in the channel die. Increasing solid-state processing temperature increases the amount of c-axis orientation parallel to machine direction (MD), e.g. the flow direction. Typical pole figures, characterising the texture of solid-state extruded PHB for processing temperatures of 70° C and 140° C are shown in figure 9. A preferential orientation of crystalline a- and b-axis of the orthorhombic unit cells has not been observed.

Different types of texture are resulting from different deformation modes during solid state processing. It is assumed, that at lower processing temperatures interlamelar deformation (lamellar slip) orients the lamellar normals parallel normal direction of the sample. At higher temperatures, intralamellar deformation modes (chain slip) become more and more dominant, orienting the c-axis parallel to the machine direction. Structural changes in the material, based on the increasing amount of c-axis orientation may be an explanation for the increasing elongation at break with solid-state processing temperature.


Processing temperature 70 °C

Processing temperature 140° C

Figure 9: Pole figures of the (020) and (002) lattice plain of solid-state extruded PHB at different extrusion temperatures

Supermolecular structure

Like many other partially crystalline polymers, PHB is able to crystallize in spherolitic supermolecular structures. The size of the spherolites significantly influences the mechanical properties. With increasing spherolit diameter, the danger of brittle fracture by crack propagation along unstable spherolitic boundaries increases.

In melt processed PHB, large spherolites with diameters of more than 100 µm have been observed by polarized light microscopy as shown in figure 10. Because of the extreme purity of the biopolymer the number of nuclei in the melt is small, so that crystallisation processes start with a small number of spherolites, growing to large size. Contrary to the results in melt processed material, no spherolitic structures have been detected by light microscopy in solid-state extruded PHB. The micrograph in figure 10 shows only small birefringent regions with preferential orientation. It is assumed therefore, that the brittleness of the melt crystallized PHB is related to the coarse spherolitic structure of the material.

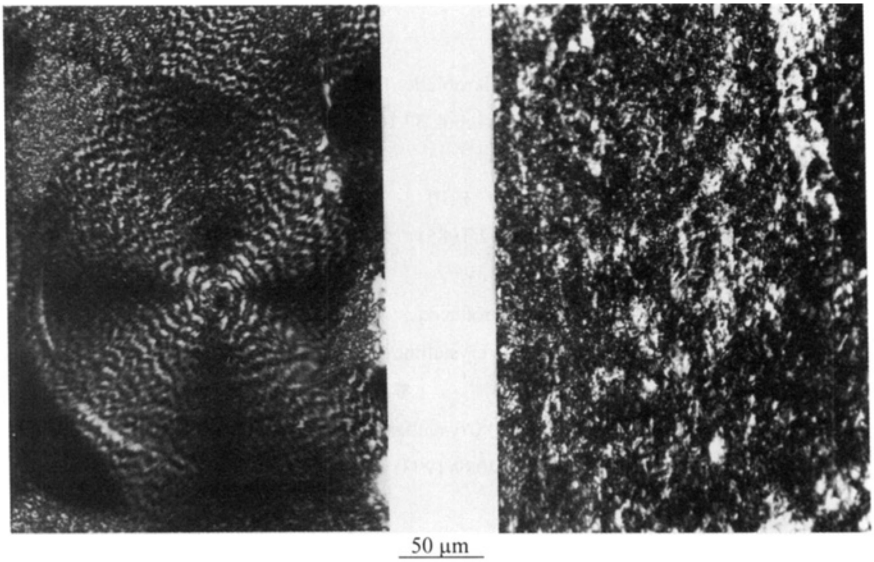


Figure 10: Polarized light micrographs of melt processed (left) and solid-state extruded (right) PHB 7

4. CONCLUSION

“Green“ polymers have a lot of special properties which open new fields of application. But also processing characteristics of these materials differ from those of “petro“ polymers. Biodegradability, a characteristic feature of “green“ polymers, often correspondents with poor thermal stability. Melt processing has to be limited therefore to a small temperature window and alternative processing technologies have to be established.

Solid-state processing offers a good possibility to minimize thermal exposure so that thermal destruction can be prevented. Furthermore, this technology allows to shape the initial polymer powder without complete reconstruction of the supermolecular structure as in the case of conventional melt processing. This leads to products with improved mechanical properties.

The advantages of solid-state processing have been demonstrated for poly(3-hydroxybutyrate). However, this technology should be valuable also for other polymers.

5. REFERENCES

(1) W.Babel, V.Riis, E.Hainich, "Mikrobielle Thermoplaste: Biosynthese, Eigenschaften und Anwendung", Plaste und Kautschuk **37**,109(1990)

(2) P.A. Holmes, "Applications of PHB - a Microbially Produced Biodegradable Thermoplastic", Phys.Technol.**6**,32(1985)

(3) P.A. Holmes, "Biologically produced (R)-3-Hydroxyalkanoate Polymers and Copolymers", in :Development in crystalline polymers-2, Elsevier, London 1988

(4) G.J.M. de Konig, P.J.Lemstra, "Crystallization phenomena in bacterial poly[[R)-3-hydroxybutyrate]", Polymer, **34**,4089(1993)