Front. Chem. China 2008, 3(4): 445–450
DOI 10.1007/s11458-008-0079-z

RESEARCH ARTICLE

Long CHEN, Peng WANG, Yanmo CHEN, Yu ZHANG, Meifang ZHU

Study on formation of poly(β-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) fiber

Abstract In this paper, the crystallization behavior, thermal degradation properties, rheological behavior and the spinnability of poly(β-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) fiber were studied. Experimental results indicated that the spherulite growth rate of PHBV was very slow and its size was very large. PHBV began to degrade above 170°C. The flowing curve indicated that the processing temperature and the residential time had important effects on PHBV melts. When the equipment of melting spinning was improved and processing conditions were strictly controlled, the mechanical properties of the PHBV filament can comply with the requirements of the American Pharmacopoeia.

Keywords poly(β-hydroxybutyrate-*co*-hydroxyvalerate) fiber, crystallization behaviour, thermal degradation properties, rheological behaviour, spinnability

1 Introduction

Among synthetic biodegradable polyester fibers, poly (lactic acid) (PLA) fiber, aliphatic polyesters and their copolyesters fibers have attracted more attention recently. Applications of fibers obtained from the polycondensation of aliphatic diacids (or their derivatives) and diols, are very limited in the synthetic fiber industry because it is difficult to get high molecular weight polyesters. It makes the melting point very low and the mechanical performance very poor. A promising biodegradable fiber is poly(hydroxy alkanoates) (PHA) fiber. It is a kind of aliphatic polyester involved in procaryotic microbe cells as carbon and energy reservoir. Poly(hydroxybutyrate) (PHB), a kind of PHA biopolyester which exists widely in bacteria, was found first and has been studied extensively. The research with PHB was done by British company ICI which named the compound Biopol. It was then transferred to the U.S. Monsanto Company. Biopol is a random copolymer of 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV) (PHBV) containing 0–30% HV. Biopol involving 5 mol%–10 mol% HV can be melt spun into fibers. The copolymer with 5 mol% HB can also be melt spun into fibers. In China, an industrial project of annual output of 1 000 tons PHBV has been set up in Tian'an Biomaterials Company of Ningbo in Zhejiang Province with the support of the National High-Tech Research and Development Plan. It is now is the largest PHBV manufacturer in the world. PHBV is often bio-synthesized with more than 5% HV monomer. This, however, reduces the efficiency of PHBV fermentation and increases the cost of PHBV production. In addition, the final product with about 5% residual impurities will cause heavy oxidation in the melt spinning process. Decomposition in melt spinning at high temperature also causes the failure of spinning. Until now, no PHBV biodegradable fiber has been successful marketed due to high cost and numerous technical problems.

In this paper, the crystallization behavior, thermal degradation properties, rheological behavior and the spinnability of PHBV were studied. A kind of biodegradable fiber which can conform to the requirements of the American Pharmacopoeia was prepared under optimal processing conditions in the laboratory.

2 Experimental

2.1 Sample preparation

The PHBV powder was supplied by Zhejiang Biological Materials Company. Its basic properties are listed in Table 1.

Translated from *Journal of Donghua University* (*Natural Science Edition*), 2007, 33(4): 425–430

Long CHEN, Peng WANG, Yanmo CHEN, Yu ZHANG, Meifang ZHU (✉)
State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 200051, China
E-mail: happyjack@dhu.edu.cn

Table 1 Characteristics of PHBV samples

sample	HV mole rate/mol%	M_w	M_n	T_g/°C	T_c/°C	T_m/°C
PHBV	10	467 309	244 702	7.5	67.7	169.15

The HV mole rate was determined by NMR in Changchun Institute of Applied Chemistry. T_g, T_c and T_m were determined by DSC in our laboratory. M_w and M_n were measured by GPC in Wuhan University.

2.2 Crystallization behavior

2.2.1 Polarized light microscopy (PLM)

The crystallization morphology of PHBV was observed on a polarized light microscope (Leitz 44XI, Germany) with the magnification of 2.5, 10, 40, and 100.

2.2.2 Polarized optical microscopy

The instrument was a DLI-1 polarized optical microscope designed by Donghua University. The instrument consisted of the power supply regulator, temperature controller, recorder, the crystallization of furnace, the detection system of polarized light and projection light intensity compensation circuit.

The operating condition was set at 190°C and the crystallization temperatures were selected at 05, 95, 85, 75, 65, 55, 45°C, respectively.

2.3 Thermal degradation properties

Thermal degradation properties of samples were tested with a Thermo Gravimetric Analyzer (TGA 7, Perkin-Elemer Company). The test was carried out with an air flow rate of 20 mL/min, a heating rate of 10°C/min and a temperature range of 100°C–500°C.

2.4 Rheological properties

Rheological behavior was investigated using an Instron 3211 rheometer (Britain) at 178°C, 184°C, 189°C, 195°C, 200°C, respectively with a capillary aspect ratio *L*/*D* of 40 and a capillary length *L* of 5.54 cm. The operating pressure ranged from 20 to 200 N and the piston speed was 20, 6, 2, 0.6, 0.2 or 0.06 cm/min.

2.5 Melt spinning of PHBV

The melt spinning was performed on a Fuji MST-C400 (Japan) spinner instrument with a spinneret containing 4 orifices. The capacity of the pump is 10 r (0.3 cm^3/r).

3 Results and discussion

3.1 Crystallization properties

3.1.1 Crystallization morphology

The photograph of the big PHBV spherulite crystal observed with polarized light microscope at 90°C is shown in Fig. 2. There is a clear black cross extinction pattern of the PHBV crystal. The spherulite is so large that it is even observable by the naked eye. In the present work, PHBV possesses high purity. Therefore, it is easy for homogeneous nucleation and the spherulite crystal can grow completely.

3.1.2 Crystallization rate

Two methods were used for calculating the crystallization rate of PHBV. Through the image processing software, the spherulite diameter was measured directly to calculate the spherulitic crystal diameter growth, as shown in Fig. 3. The results indicate that PHBV spherulite crystal diameter has a good linear relationship with the crystallization time as shown in Fig. 4. The correlation coefficient R is 0.99983 and standard deviation SD is 2.37×10^{-8} m/s. The slope represents spherulitic crystal radial growth rate. The spherulitic crystal radial growth rate of PHBV at 90°C was found to be to be 2.53×10^{-6} m/s, which means a very slow growth.

Another method to calculate the crystallization rate of PHBV was by using the intensity of polarized light transmission. The crystallization rate parameter is represented by half-crystalline time ($t_{1/2}$), that is, the time required for crystallization to be half complete. Figure 5 shows half-

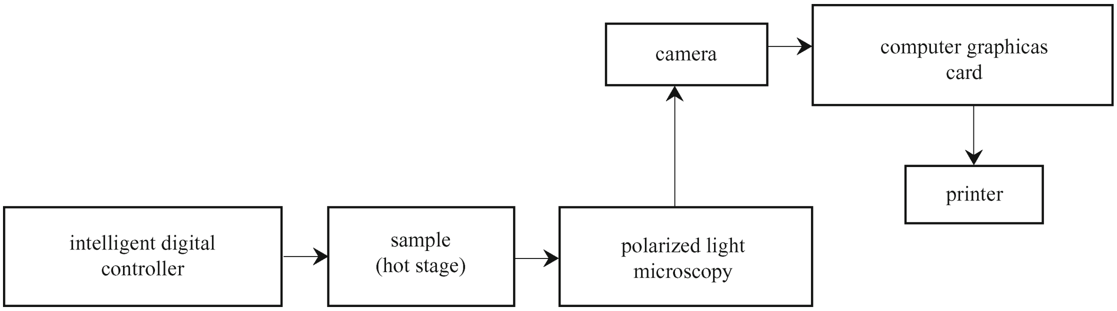

Fig. 1 Polarized light microscopy (PLM)

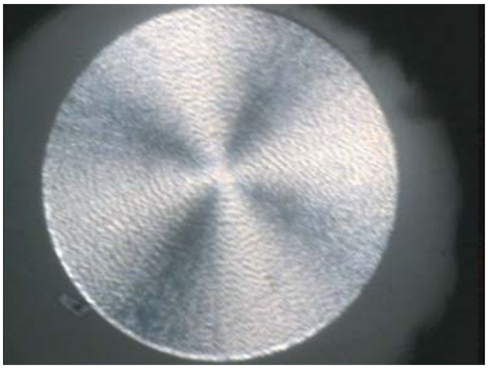

Fig. 2 Crystalline Morphology photographs taken from PHBVat 90°C by PLM

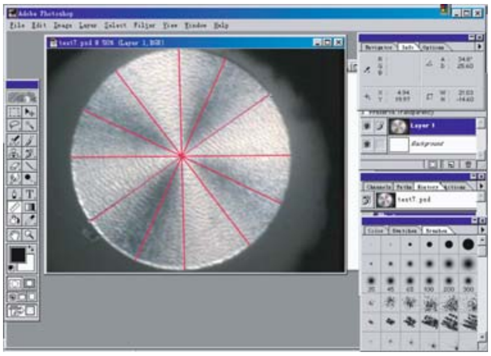

Fig. 3 The measurement of PHBV spherulite diameter

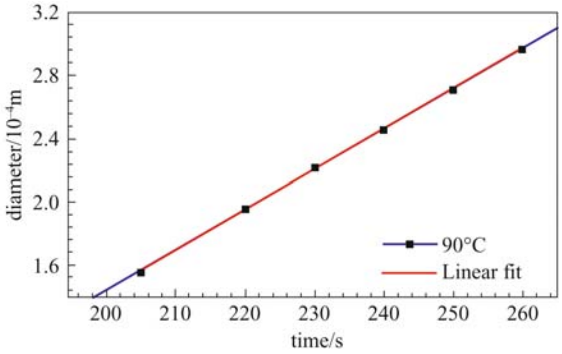

Fig. 4 The linear fit for PHBV spherulite growth

crystalline time of PHBV at different crystallization temperatures. It indicates that semi-crystalline time is shortest between 65°C–75°C. The crystallization of PHBV is fastest in this temperature range.

3.2 Thermal degradation properties

3.2.1 Static thermal degradation properties

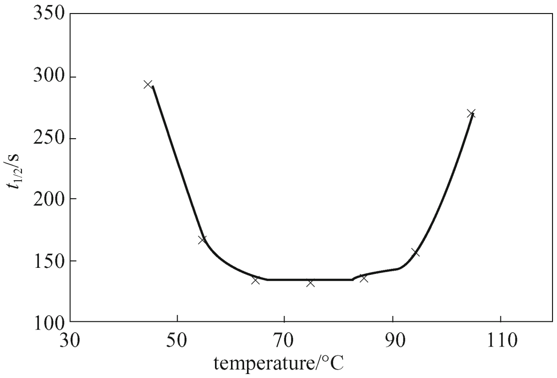

Fig. 5 Half crystallization time of PHBV at different temperatures

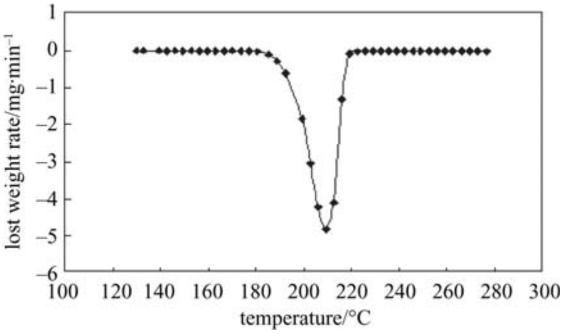

Fig. 6 The weight loss rate curve of PHBV

The static thermal degradation properties were investigated by TGA. Fig. 6 provides the weight loss rate curve of PHBV. It indicates that PHBV begins thermal degradation at 180°C, and thermal degradation is greatest at 210°C. PHBV degrades completely at 230°C in the absence of shear force. It can be concluded that PHBV degrades very easily at high temperature and the degradation speed is very high even in the absence of shear stress.

3.2.2 Dynamic thermal degradation

1) The change of fluid type

In the fluid type experiment, PHBV stayed for some time in the rheometer cylinder and then was pressed out. Due to thermal degradation, the extruded melt changed from a stream into small droplets and the viscosity also decreased significantly. Table 2 lists the residential time when the PHBV melt changed at different temperatures. PHBV degraded into very dilute black liquid after about 24 min at 200°C but changed into black fluid after almost 60 min at 180°C. This indicates that the change of the flow type will not influence the PHBV processing if the temperature is lower than 180°C with a short time but it will influence the PHBV processing when temperature exceeds over 190°C.

Table 2 The need time of the different HV% PHBV changing from streamlet to drop at different temperatures

temperature/°C	170	180	190	200	210
change time/min	–	> 60	32	24	18

2) The influence of residential time and the shear force on apparent viscosity

In order to get more data on the PHBV thermal degradation during melt processing, the thermal degradation of PHBV in the melt flow was investigated using a capillary rheometer. Figure 7 and 8 show the curve of apparent viscosity under different residential times and different temperatures when the shear rate is set at 1200, 120 s^{-1} respectively. At different temperatures, no matter what the shear rate is, the apparent viscosity decreases when the residence time increases. Meanwhile, the apparent viscosity at 190°C–210°C decreases greatly with the residential time more than at 180°C–170°C. In addition, compared with the static thermal degradation, the beginning of PHBV thermal degradation temperature decreases in the presence of shear force. It is therefore necessary to control the temperature in the PHBV spinning processing. Comparing Figs. 7 and 8, it can also be concluded that the decline rate of apparent viscosity increases when the shear rate increases. It also implies that the shear force would accelerate the thermal degradation. Moreover, the increase of thermal degradation rate at low temperature (under 180°C) is larger than that at higher temperature of 180°C. Shear rate has a great influence on the PHBV thermal degradation rate in the actual processing stage.

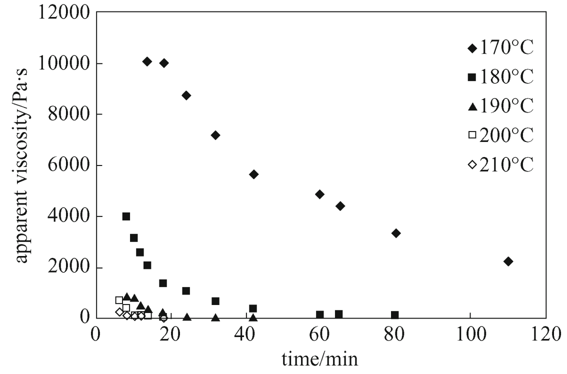

Fig. 7 The curve of apparent viscosity with the change of the residential time (shear rate: 1200 s^{-1})

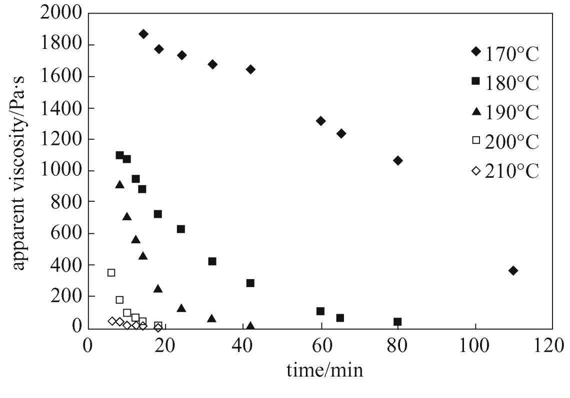

Fig. 8 The curve of apparent viscosity with the change of the residential time (shear rate: 1200 s^{-1})

3.3 Rheological behavior

3.3.1 The influence of temperature on rheological properties

Figure 9 shows the flow curves of PHBV at different temperatures (the residential time is 14 min). It shows that the apparent viscosity of PHBV at the same shear rate decreases significantly with an increase in temperature. These results are consistent with the fact that the temperature improves the free volume of PHBV melt, the chain activity ability and the polymer mobility.

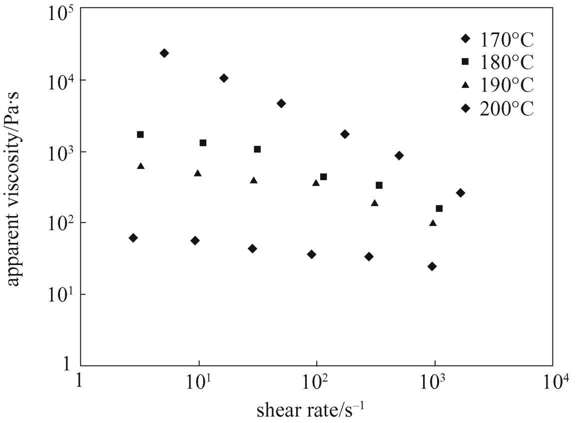

Fig. 9 The flow curves of PHBV at different temperatures

In addition, it can be concluded from Fig. 9 that the shear rate has little effect on the apparent viscosity at high temperature. This result is contrary to the shear shinning of polymer melts. On the other side, due to high thermal degradation, it was found that PHBV pressed out from the capillary rheometer changes from a stream into small droplets at high temperature in the rheological experiments. Hence, for the same reason, the rheological behavior of PHBV seems to be that of a low-molecular-weight non-Newtonian fluid at high temperature and shear shinning could not be observed at high temperature.

3.3.2 The influence of residential time on the rheological properties

As mentioned before, PHBV would degrade at high temperature after a certain time. In order to investigate the degradation time, the effect of the residential time on the apparent viscosity was studied. The flow curves of PHBV with different residential time at 180°C are provided in Fig. 10. As the residential time increases, the apparent viscosity exhibits a sharp drop at low shear rate and a smaller drop at high shear rate. These are due to the quick degradation at high shear rates and high temperatures. The apparent viscosity decreases significantly after about 65 min and reaches about 100 P. In addition, it also found that the flow curve changed more gently with increasing residential time which is same as the influence of temperature on the flow curve.

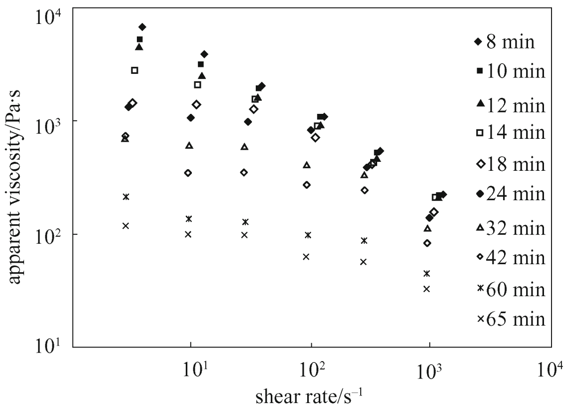

Fig. 10 The flow curves of PHBV at the different residential time

3.3.3 Analysis of PHBV structure viscosity index

The structural viscosity index is an empirical parameter to evaluate the spinnability. The structure viscosity index is calculated using Eq. (1).

$$\varDelta\eta = -\left(\frac{d\log\eta_a}{d(v)^{1/2}}\right)\times 10^2 \qquad (1)$$

Generally, the more the structure viscosity index increases the better the spinnability is. From Fig. 11, there is no order for the change of structure viscosity index over time and temperature but it can be concluded that when residential time is less than 20 min, PHBV has minimal structure viscosity index at 190°C. Structure viscosity index would increase above or below this temperature. In addition, the structure viscosity index corresponding to 200°C is also small but the sample degrades very quickly at that temperature. Thus, the temperature between 180–190°C is optimal for the fiber spinning process. Actually, in the present work, the spinning experiment was carried out in this temperature range. This is in agreement with the conclusion obtained from the flow curve.

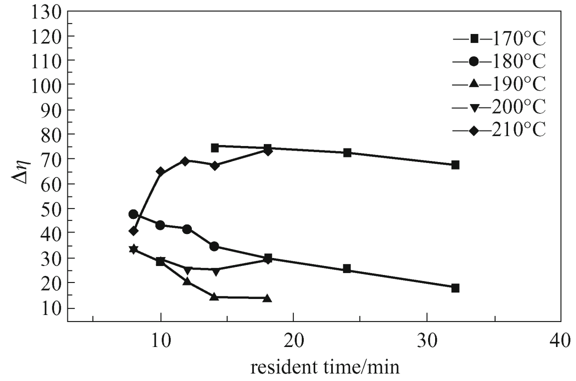

Fig. 11 The structure viscosity index ($\Delta\eta$) of PHBV at different temperatures and different residential times

3.4 Spinnability

PHBV with 10 mol% HV was selected in the fiber spinning process because it is more pure and is more stable. In the PHBV rheological experiments, it was found that the PHBV flow surface is tacky and rough. So, in order to prevent fiber from becoming sticky and adhesive, PHBV should solidify very quickly and very early in the spinning process.

The spinning of PHBV was carried out in two ways. The first is to draw down only at high-speed spinning (method I). Another is to draw down together with continued drawing (method II). Table 3 lists an adhesion and an unwinding situation of PHBV in different spinning conditions. Because PHBV materials crystallize very slowly, the as-spun fiber has low crystallization orientation under low take-up velocity speed in method I or the low draw ratio in method II. Meanwhile, the final result is the tackiness of the fiber and difficulty in unwinding. In conclusion, using method I, with the winding speed increasing, the adhesion level decreases and the unwinding improves; Using method II, with increasing take-up speed or later draw ratio, the level of adhesion decreases and the unwinding property improves.

As engineering materials, PHBV fiber requires good mechanical properties. The mechanical properties of fiber mainly referred to are tensile strength and elongation at

Table 3 Spinnability of PHBV at different spinning conditions

spinning method	draw down ratio	later draw ratio	traction speed/(m·min^{-1})	take-up speed/ (m·min^{-1})	tackiness level*	unwinding condition
method I	10	–	–	1046	3	+
	11	–	–	1124	2	+
	12	–	–	1176	2	+
	13	–	–	1307	1	++
method II	3	1.3	313	392	2	+
	3	1.7	313	523	2	++
	3	1.8	313	575	1	++

* Tackiness level is denoted by number, that is, “0” represents no tackiness and the bigger the number, the higher the tackiness level.
“+” indicates general spinnability and “++” represents the better spinnability.

Table 4 The physical-mechanical properties of PHBV

spinning method	take-up speed/m·min^{-1}	fineness/dtex	breaking strength/cN·dtex^{-1}	elongation at break/%
method I	1307	33	1.85	47.9
	1176	36	1.79	51.1
	1046	49	1.38	56.2
	523	96	1.03	164
method II	523/313	102	1.11	19.1

break. The stress-strain curve of PHBV fiber provides the dependence of tensile stress (load) upon elongation when the fiber is extended with force until it breaks. Table 4 lists the tensile properties of PHBV multifilaments.

Fiber strength and elongation at break are influenced by various factors, such as fiber orientation, crystallinity, etc. From Table 4, as the speed of the spinning increases in method I, the fiber strength improves markedly and the elongation at break decreases. However, the fiber strength and elongation at break of the fiber in method II are lower and that is mainly due to low crystallization orientation and low crystallization degree. Under optimal spinning conditions, the mechanical performance of PHBV fiber conforms to the requirement of the United States Pharmacopoeia.

4 Conclusions

1) The large spherulites and low crystallinity rate of PHBV make the material brittle. The solidification rate of the fiber is slow. The fiber also has unstable internal structure.

2) The fiber will degrade quickly over its melting point under shear forces. Therefore, the processing temperature range of the fiber spinning process is very narrow and should be controlled very strictly.

3) PHBV has similar rheological properties as regular thermoplastic polymer and it is a shear-thinning fluid. Both the spinning temperature and the shear rate of the fiber have a remarkable effect on the spinning process because of the poor thermal stability of PHBV.

4) With improvement of melt-spinning equipment and optimal processing conditions, PHBV can be melt spun into biodegradable fiber to meet the requirement. This work serves as a fundamental step towards industrial production of PHGV fibers.

References

1. Yu H, Zhang Y, Zhu M F, et al. The progress of biodegradable polyester fiber. Synthetic Fiber, 1999, 28(2): 33–39(in Chinese)
2. Hirano Madoka, Murase Shigemitsu. Biodegradable conjugate monofilament and its production. JP7278965, 1995-10-24
3. Kang Sub Yim, Sang Yup Lee, Ho Nam Chang. Synthesis of poly-(3-hydroxybutyrate-*co*-3-hydroxyvalerate) by recombinant Escherichia coli. Biotechnology and Bioengineering, 1996, 49(5): 495–503
4. Tian J S, Song H C, Wu B H, et al. High and stable yield Polyhydroxyalkanoates reorganization of the Construction of E. coli. Journal of microbiology, 2000, 40(1): 26–40(in Chinese)
5. Suzuki T, Yamane T, Schimizu S. Mass production of poly-β-hydroxybutyric acid by fed-batch culture with controlled carbon/nitrogen feeding. Appl Microbiol Biotechnol, 1986, 24: 370–374