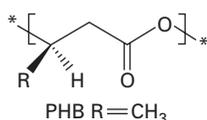


## Poly(hydroxyalkanoates) and poly(caprolactone)

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### 7.1 Introduction

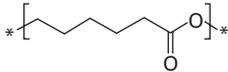
Bacterial polyesters poly(hydroxyalkanoates) (PHAs), with poly(hydroxybutyrate) (PHB) (7.1) as the first homologue, belong to the most interesting, but also the most controversial, group of biodegradable polymers. Advantages include production from fully renewable resources, rather fast and complete biodegradability, biocompatibility, and excellent strength and stiffness, which favours this material as a polymer of the future.<sup>1</sup> However, several serious drawbacks hinder its wider application, including rather high susceptibility towards thermal degradation, difficult processing related partially to thermal instability as well as to low melt elasticity, brittleness of the material resulting in low toughness (which increases further during storing due to an interesting phenomenon of physical ageing), and rather high price. These are the main reasons for low production volume and unsatisfactory number of applications.<sup>2</sup>



### 7.1

The low number of applications up to now seems to be also partially the reason for the high price of the polymer creating a vicious circle where the applications are not developing because of too high a price, while the price is not decreasing due to a low volume of produced polymer. Since fibres can be considered as a new prospective product, successful development of PHA fibres would also contribute significantly to the general spread of products from PHAs. Moreover, it is generally believed that after drawing, the properties of poly(hydroxyalkanoates) will improve including the increase of toughness.

Poly(caprolactone) (7.2) is a synthetic polymer prepared mainly by ring opening polymerisation of caprolactone. The polymer is, similar to PHAs, fully biodegradable, although the rate of biodegradation is lower compared to PHAs. This, together with a low melting temperature (of about 60°C), is a reason that the polymer is used mainly either as a component of polymer blend or as a matrix for biodegradable composites. Among the latter, its mixture with starch is possibly best known under the trademark *MaterBi* produced by Novamont, Italy.<sup>3</sup> Nevertheless, poly(caprolactone) has a number of interesting properties, such as good processability, high toughness and deformability, and good thermal stability. Therefore its wider application is expected in the future.



## 7.2

### 7.2 PHA-based oriented structures

#### 7.2.1 Materials and techniques available

Poly(hydroxyalkanoates) represent a number of materials with a broad range of properties. Generally all types described in scientific literature are produced by bacteria, although synthetic routes are also known and used.<sup>4</sup> About 40 roots of bacteria exist able to produce polyester-type polymers.<sup>5</sup> Although various bacteria differ in the conditions and the efficiency of the PHA production, they produce more or less the same products. The variation in the polymer produced is reached more by changes in the production conditions than by changing the root of bacteria; the most important from this point of view is the substrate for feeding the bacteria.<sup>6</sup> By sophisticated selection of the substrate, PHB homopolymer, its copolymers with higher PHAs,<sup>7</sup> even polyesters with branching<sup>8</sup> functional groups (epoxy,<sup>9</sup> aromatic structures<sup>10</sup> chlorine,<sup>11</sup> double bonds<sup>12</sup>) in the chain may be produced.

The properties of the first homologue, poly(hydroxybutyrate) are similar to polypropylene, as seen in Table 7.1.<sup>2</sup> While strength parameters (tensile strength, Young's modulus) and the most physical properties (crystallinity, melting temperature, and glass transition temperature) are basically the same, the important difference consists in elongation at break and, consequently, toughness. While the ductile polypropylene breaks at elongation around 700%, PHB hardly exceeds 10%, with typical values between 1 and 3%; PHB copolymers with higher PHAs have higher elongation at break mainly due to much lower crystallinity. However, the preparation of these, while well mastered in laboratory conditions, results in much more expensive materials if industrial, large-scale production is considered. From this point of view, only PHB

Table 7.1 A comparison of physical properties of PHB, copolymers of PHB with higher PHAs, polypropylene (PP), and low-density polyethylene (LDPE)

Property	PHB	20V <sup>1</sup>	6HA <sup>2</sup>	PP	LDPE
Melting temperature (°C)	175	145	133	176	110
Glass transition temperature (°C)	4	-1	-8	-10	-30
Crystallinity (%)	60	ng <sup>3</sup>	ng	50	50
Density (g cm <sup>-3</sup> )	1.25	ng	ng	0.91	0.92
E modulus (Mpa)	3.5	0.8	0.2	1.5	0.2
Tensile strength (MPa)	40	20	17	38	10
Elongation at break (%)	5	50	680	400	600

<sup>1</sup> poly(3-hydroxybutyrate-co-20 mol % hydroxyvalerate)

<sup>2</sup> poly(3-hydroxybutyrate-co-6 mol % hydroxyalkanoates) = 3% 3-hydroxydecanoate, 3% 3-hydroxydodecanoate, < 1% 3-hydroxyoctanoate, < 1% 5-hydroxydodecanoate

<sup>3</sup> ng = negligible

copolymer with poly(hydroxyvalerate) (7.1 R = CH<sub>2</sub>CH<sub>3</sub>) could be considered to be suitable for some applications.

Considering fibres based on poly(hydroxybutyrate) or higher PHAs, no successful process was reported for preparation of PHB fibres by conventional fibre processing technology, i.e. melt or gel spinning with subsequent hot drawing. Therefore, more sophisticated procedures have to be developed to achieve reasonable draw ratios, resulting in production of anisotropic material with important improvement of properties.

To prepare fibres, it is usually advantageous to start with a polymeric precursor with molecular weight within certain limits. The molecular weight values should be as high as possible to achieve good drawability and high draw ratio. On the other hand, it should increase only to the values acceptable from the point of view of processing (spinning); in the case of very high molecular weights, extremely high draw ratios can be reached resulting in ultra-high modulus, e.g. for polyethylene,<sup>13</sup> however, rather sophisticated preparation techniques, e.g. dry gel technology,<sup>14</sup> have to be applied.

In the case of PHB and generally PHAs, polymers with high molecular weight are also important concerning the rather high susceptibility of the polymer towards thermal degradation. Thus, starting with a polymer with high molecular weight may result in a polymer having the molecular weight still well above certain limits, even after rather demanding thermal treatment during processing and resulting decrease in the molecular weight due to thermal degradation. Fortunately, by a sophisticated selection of bacteria and preparation conditions, PHB or its copolymers with high M<sub>w</sub> can be produced. Kusaka *et al.*<sup>15</sup> reported a preparation of P(3HB) with a final average molecular weight of between 1.1 to 11 million produced by *Escherichia coli* XL-1 Blue (pSYL105)<sup>16</sup> containing a stable plasmid harbouring the *Alcaligenes eutrophus*

H16 (ATCC 17699) PHB biosynthesis geneoperon phaCAB. Two-step cultivation of the recombinant *E. coli* was applied for the production of high molecular weight P(3HB).<sup>17</sup> Molecular weight of PHB produced within the cells was strongly dependent on the pH of the culture medium.<sup>17</sup>

Apparently, as mentioned above, the most important reason to synthesise high molecular weight PHB seems to be a high susceptibility of PHAs towards thermal degradation. When starting with HMW material, even after a substantial decrease in molecular weight, the polymer still has  $M_w$  high enough to be processed to secure a product with acceptable properties. Another option to avoid these shortcomings might be to develop modified processing procedures, leading to a thermal treatment as short as possible or proceeding at a processing temperature below the degradation limits. Thus, solid state processing was suggested as a viable alternative for PHB processing with low thermal degradation.<sup>18</sup> An extrusion of PHB powder at temperatures well below melting temperature was successfully preformed to products with improved mechanical properties. Compared to melt processed PHB, the ductility (and consequently toughness) improved significantly.

## 7.2.2 Processing/preparation

Generally, fibre-forming polymers can be processed either by drawing the preformed amorphous material at temperatures above, but near, the glass transition temperature ( $T_g$ ) or by drawing a crystalline material below but near melting temperature. Thus, the easiest way to produce fibres should be melt spinning and, consequently cold or hot drawing. More sophisticated procedures involve so called gel-spinning, which was successfully applied for a production of ultra-high modulus polyethylene fibres<sup>13</sup> and later for other polymers.<sup>19</sup> These basic techniques have been tested and modified also for preparation of PHA fibres; other procedures have been suggested and investigated. Although the number of scientific papers dealing with PHB or other PHA fibres is much smaller compared to important synthetic polymers, the information on various spinning/drawing processes deserves reviewing, especially regarding differences between different processes and between properties of fibres prepared by different research teams.

### *Melt spun fibres*

PHB melt spinning is from several points of view not as straightforward a process as for many other fibre-forming polymers. The problems include rather rapid thermal degradation of PHB at temperatures just above melting temperature, low melt elasticity, and slow crystallisation after spinning (which results in a formation of large crystallites leading to extremely brittle material). The brittleness increases during storing due to an interesting phenomenon of

physical ageing; some improvements can be achieved by an addition of plasticisers and nucleating agents; boron nitride was reported to be one of the most efficient nucleating agents for PHB.<sup>20</sup>

An important problem consists in the fact that crystalline PHAs and especially PHB are rather brittle materials, though the brittleness can be partially removed by compression moulding. The cold rolling of PHB at room temperature results in an increase in elongation at break from 8% up to 200%, if measured in tensile mode in the rolling direction, while no change (elongation 8%) was observed if measured in the perpendicular direction.<sup>21</sup> Such pre-deformed material could be drawn at 125°C leading to an increase in tensile strength by a factor of 5. A patent from 1984<sup>21</sup> claims the procedure of cold rolling and subsequent drawing at temperature in the range of 50 to 150°C below the melting temperature of the respective polymer.

Melt spinning may lead to an improvement of some of the features mentioned above. Gordeyev *et al.* reported already in 1977 that melt spinning followed by a pre-orientation may prevent the ageing process.<sup>22</sup> However, the melt spinning is not so easy; several methods have been developed and described, differing in many details of the process. Yokouchi *et al.*<sup>23</sup> and Nicholson *et al.*<sup>24</sup> reported the procedure of the melt quenching below  $T_g$  and subsequent drawing. A more successful process seems to be the drawing of melt spun PHB immediately after spinning while the material is still hot, to obtain pre-oriented material. These pre-oriented fibres can be drawn to high draw ratios (DR) even after few weeks of storing at room temperature, under conditions when bulk PHB would turn to be extremely brittle as a result of physical ageing.<sup>22</sup>

A successful procedure leading to melt spun fibres with good properties was described by Gordeyev and Nekrasov.<sup>25</sup> The authors suggested dissolving PHB with a molecular weight of about 300,000 and  $T_m = 180^\circ\text{C}$  (determined by DSC) in chloroform and filtering the solution before spinning to remove impurities as well as high molecular weight portions, although it is not explained why higher molecular weight portions are recommended for removal nor what portion, if any, of what molecular weight was actually removed. The spinning and pre-drawing step (DR = 2) was performed in an extruder heated in four regions between 170 up to 182°C. Hot drawing proceeded at 110°C and the DR achieved was about 8. Although only a modest rise of Young's modulus was achieved, an increase in tensile strength by a factor 4 to 5 was found when compared to undrawn bulk PHB. Moreover, the fibres were rather elastic showing an elongation at break of about 50%, as seen in Table 7.2.

More detailed study on the melt spinning/hot drawing of PHB was published by Yamane *et al.*<sup>26</sup> Filaments, about 0.3 mm in diameter, were obtained by extruding. These fibres were drawn at 110°C immediately after melt spinning; the maximum draw ratio achieved was about 6. The drawing immediately

Table 7.2 Mechanical properties of melt spun PHB fibres

Sample	Draw ratio	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
As spun	2	109	2.2	160
Hot drawn 110°C	8	127	3.5	95
Annealed 155°C, 1 h	8	190	5.6	54

after melt spinning is important since after even short storing periods, PHB turns to a brittle material which is impossible to draw. A further requirement seems to be a presence of nucleating agents to increase the originally low nucleation rate of PHB. Boron nitride can be used as an additive; contaminants such as remnants of proteins and lipids from the culture media can also act as efficient nucleating agents.<sup>26</sup> The authors refer to further improvement of mechanical properties of the fibres by annealing after drawing.

It seems that to achieve the drawability, a certain structure of the polymer must be formed. The material has to be in crystalline form, but crystals must not be too large to be able to be deformed during drawing. Thus, the basic requirement for melt spinning/drawing seems to be the presence of nucleating agent on the one hand and the drawing or at least pre-drawing while the material has not developed a fully crystalline structure on the other.

#### *High speed melt spinning and spin drawing*

Certainly, a demonstration of an ability to draw fibres is of primary importance for further development. The possible industrial production depends not only on procedures enabling spinning and drawing the polymer producing fibres with good properties, but also on efficiency of the production, which is limited mainly by a development of a procedure for high speed melt spinning. Such a process was described by Schmack *et al.*<sup>27</sup> A spinning line consisted of an extruder, spinning pump, heated godets, and two winders, enabling the speed in a range of 2000–6000 m min<sup>-1</sup>, comparable with the speed of production of synthetic industrial polymeric fibres. Exceptional attention was paid to a thorough drying of the PHB powder prior to spinning to minimise hydrolytic degradation. In spite of the extreme care regarding the moisture removal, the viscometric molecular weight of the PHB being 540,000 for virgin powder dropped down to 175,000 after spinning; this has to be attributed to thermal chain scission since the water content of dried pellets was only 0.01%. The process described seems to be fast enough to be considered for an efficient production of PHB fibres, especially since the mechanical properties of the fibres are satisfying, as seen in Table 7.3. The paper deals with the procedure in rather a detailed way, so that the effect of

**Table 7.3** Mechanical properties (tensile strength ( $\sigma$ ), elongation at break ( $\epsilon$ ) and sonic modulus (E)) of PHB fibres in dependence on spinning speed ( $v$ ) and draw ratio (DR)<sup>27</sup>

$v$ (m min <sup>-1</sup> )	$\sigma$ (Mpa)	$\epsilon$ (%)	E (Gpa)	
2000	228	72	5.8	
3000	281	48	7.1	
3500	250	26	7.6	

DR (m min <sup>-1</sup> )	$\sigma$ (Mpa)	$\epsilon$ (%)	E (Gpa)	T <sub>1</sub> /T <sub>2</sub> * (°C)
4.0	52	10	n.a	40/50
4.5	108	60	n.a	40/50
5.0	220	53	n.a.	40/50
5.4	178	71	5.2	45/60
5.5	263	60	5.6	40/50
6.4	310	45	6.8	45/60
6.9	330	37	7.7	45/60

\* temperature of the first and second godet in the production line

changing preparation conditions on the ultimate properties of the fibres can be estimated.

### *Gel spun fibres*

Gel spinning is an example of a special technique for preparation of fibres with unique properties. The well-known commercially available fibres prepared by this method are those of ultra-high molecular weight polyethylene.<sup>19</sup> The gel spun material can be drawn to very high draw ratios, well above 100; fibres exhibit extremely high stiffness and strength, reaching the values of 3 to 6 GPa and 150 GPa for tensile strength and modulus, respectively.<sup>13</sup>

The typical procedure leading to gel spun PHB fibres is described by Gordeyev *et al.*<sup>28</sup> It involves dissolving the PHB in a suitable liquid (1,2-dichloromethane is recommended as the best solvent); a solution with a PHB concentration as high as possible should be prepared, which depends on the original molecular weight and is about 20 wt % for PHB with  $M_w$  about 300,000 g mol<sup>-1</sup>. Then a solid gel is prepared by evaporation of a part of the solvent; at this stage the concentration of the polymer is about 30 wt %. The gel was extrudable at about 170°C. The extruded gel is consequently processed in three stages.<sup>28</sup> For the first, so-called pre-conditioning stage, the fibre was wound on a speed-controlled drum – the optimal pre-conditioning draw ratio was estimated by comparing Tex values of the extruded and drawn fibres, respectively. For further efficient drawing the optimal draw ratio of the pre-conditioning step was found to be around 2. Continuous hot drawing between

two rollers was performed at 120°C as the second step – the total draw ratio was around 10. Finally the fibres were stretched at room temperature to 180% of the length after the second step – they were fixed and annealed at 150°C for 1 hour.

‘As-spun’ fibres from the stage 1 could be drawn via the necking process both at as well as above room temperature; the necking begins at a strain about 6–7%. The mechanical properties of the drawn fibres are shown in Table 7.4.

Table 7.4 Tensile properties of gel spun fibres at room temperature<sup>28</sup>

Sample	Draw ratio	Tensile strength (MPa)	Static modulus (GPa)	Dynamic modulus (GPa)	Strain at break (%)
As spun	2	103	2.0	4.6	250
Hot drawn	10	332	3.8	5.8	104
Annealed	10*	360	5.6	7.5	37

\* after hot drawing

The drawability depends on drawing temperature to a certain extent, manifesting the highest draw ratio (about 5) at 120°C. Although the first step (pre-conditioned drawing after spinning) has to be performed soon after spinning, the pre-conditioned fibres, once drawn, can be stored for several months without losing the ability to be drawn at stage 2. Surprisingly, the drawn material exhibited rubber-like elastic behaviour. Presumably, drawing may introduce changes to the brittle bulk PHB similar to those of cold rolled polyester,<sup>29</sup> the effect on drawing is much more pronounced, obviously as a result of a much higher degree of chain orientation.

It was reported that tensile strength of gel spun fibres is about double that of melt spun material of similar parameters.<sup>28</sup> This behaviour was attributed to a lower degree of thermal degradation due to lower thermal treatment during three-stage processing. However, this assumption was not directly proved, e.g. by comparison of changes in molecular weights. Comparison of mechanical properties of gel spun fibres from<sup>28</sup> with melt spun fibres prepared by the high spin procedure shows certain differences, but generally the properties are similar, being dependent mainly on the draw ratio. In the latter case the original molecular weight of powder 550,000 dropped down to 175,000 after processing; similar molecular weight of the fibres can be expected after the less detrimental gel spinning process from the original molecular weight around 330,000. These considerations suggest that the procedure itself does not affect the ultimate properties of the fibres if the draw ratio and molecular weight of the fibre-forming polymer is the same; the effect of the process consists in secondary phenomena, mainly the extent of thermal

treatment which is less detrimental in the case of gel spinning compared with melt spun material. It must be stressed also that for gel spun fibres annealing leads to a certain increase in stiffness while tensile strength does not change.<sup>28</sup> It is important to note that mechanical properties do not change significantly during storing as demonstrated by strength and modulus values measured during a period of 120 days. The modulus increased by a factor of less than 1.2 while a decrease in tensile strength was observed to about 82% of the original value.<sup>28</sup>

Besides fibre formation, oriented PHB can be prepared also in the form of films. A patented procedure<sup>30</sup> refers to PHB with  $M_w$  higher than 500,000, which can be oriented at temperature 144–180°C. As an example, PHB with  $M_n = 6 \times 10^6$  was treated at 160°C at draw ratio 6.2 to produce oriented film with  $T_m = 186^\circ\text{C}$ ,  $T_g$  value 2.2°C, crystallinity higher than 90%, Young's modulus 1.7 GPa, tensile strength 80 MPa, and 70% elongation. The strength parameters are not extraordinarily impressive, but reasonable elongation indicates that the material may form a flexible foil which could be considered for packaging. In that case, strength and modulus are similar to polypropylene foils and are substantially higher compared to common foil-forming material such as low density polyethylene.

#### Other procedures

Kusaka *et al.*<sup>15</sup> described a preparation of PHB fibres with a draw ratio higher than 6 via stretching solution-cast high molecular weight films in a silicon oil bath at 160°C. PHB with molecular weight well above  $10^6$  was used. The mechanical properties of the fibres are shown in Table 7.5. Compared with solution-cast isotropic undrawn films, drawing results in higher tensile strength while modulus is the same or slightly lower. Elongation at break is substantially higher and it is almost unaffected by ageing, especially if annealing

Table 7.5 Physical properties of solution cast drawn UHMW poly(3-hydroxybutyrate) films with original molecular weight  $M_n = 6,000,000$ ;  $M_w = 16,000,000$

DR	$t_{\text{anneal}}$	$t_{\text{ageing}}$ (days)	C (%)	$\sigma$ (MPa)	$\epsilon$ (%)	E (GPa)
0	0	7	65 ± 5	41 ± 4	7 ± 3	2.3 ± 0.5
0	1 sec	7	65 ± 5	41 ± 3	6 ± 3	2.4 ± 0.3
6.5	1 sec	7	80 ± 5	62 ± 5	58 ± 1	1.1 ± 0.1
6.5	1 sec	190	75 ± 5	88 ± 8	30 ± 1	2.5 ± 0.2
6.5	2 hrs	7	> 85	77 ± 10	67 ± 1	1.8 ± 0.3
6.5	2 hrs	190	> 85	100 ± 10	67 ± 2	2.5 ± 0.2

DR = draw ratio;  $t_{\text{anneal}}$  = annealing time at 160°C;  $t_{\text{ageing}}$  = ageing time at RT; C = crystallinity (X-ray);  $\sigma$  = tensile strength;  $\epsilon$  = elongation at break; E = Young's modulus

of the fibre is performed after drawing. The elongation values, the absence of the ageing phenomenon as well as a certain decrease in modulus seem to be of interest especially considering a clear increase in crystallinity due to drawing and a further rise resulting from annealing. Obviously, high crystallinity is not necessarily a reason for the high stiffness/low toughness of PHB; the changes in crystal morphology and also changes in the supramolecular structure of the amorphous phase seem to be much more important. Some authors reported a conformational transformation as a result of drawing (e.g. Orts *et al.* for PHBV stretched films);<sup>31</sup> however, reflections indicative for helix to planar conformation were not observed for UHMW PHB by Kusaka *et al.*<sup>15</sup> A centrifugation spinning process of PHB fibres preparation was also demonstrated<sup>32</sup> to be an alternative of gel spinning. An entangled fibrous material was produced which resembles 'cotton wool'. The fibres were found to possess various surface irregularities such as pores with a diameter in the range 1–15  $\mu\text{m}$ .

*Copolymers of poly(hydroxybutyrate) with higher poly(hydroxyalkanoates)*

Most of the papers on PHA fibres deal with poly(hydroxybutyrate). Although sometimes a copolymer of PHB with a low amount of poly(hydroxyvalerate) is also referred to as PHB; in the literature quoted in this review such inconsistency is not expected. The reason for not using PHBV may consist in the fact that the copolymer has a much lower crystallinity and consequently, also, modulus is lower compared to PHB. Thus, the processing to fibres may be more difficult because of low crystalline content and also the properties of the fibres may be expected to be less impressive. Moreover, PHBV itself is much tougher compared to PHB, but also more expensive, so that the need of an improvement of toughness via drawing is not crucial while the price may be prohibitive if the expected modest improvement in the properties of fibres is considered.

The procedure of preparation of fibres based on a copolymer of PHB with higher PHA is described by Fischer *et al.*<sup>33</sup> A copolymer PHB with hydroxyhexanoate (PHBH) shows high elongation but low tensile strength; cold drawing is believed to improve the strength behaviour. Solvent cast films of PHB copolymer with 5 or 12% of hydroxyhexanoate were melted in a hot press and subsequently quenched in ice water. The more or less amorphous films were oriented by cold drawing to DR 2 to 5 and annealed at various temperatures (23–140°C), then further drawing was applied at RT before annealing. PHBH films were easily drawn at low stress to DR = 5. Similar to PHB drawn fibres, also PHBH stretched films showed an elastic behaviour after the sample was released from the clamps of the stretching equipment.<sup>33</sup> Therefore an annealing procedure was required for a fixation of the extended polymer. It is interesting to note that no changes in the molecular weight

were observed as a result of the drawing procedure: this may be attributed partially to rather mild thermal treatment as well as to higher thermal stability of PHBH as a result of steric hindrance of the chain scission due to a presence of the propyl side chains.<sup>34</sup>

Considering mechanical properties of the copolymer PHBH with 5% of H, an increase of tensile strength was observed from 25 MPa for isotropic film up to 75 MPa for DR 5. In the same range of DR, modulus increased from 400 MPa up to about double value, while elongation at break decreased from an original 250% (isotropic sample) down to less than 100 % for DR 2 and then a monotonic increase back to the original 250% at DR 5 was observed. The increase in the H-copolymer content to 12% leads to a substantial increase in elongation of isotropic film and a certain decrease in tensile strength, while the decrease in modulus is substantial (from 400 down to 100 MPa). Monotonous dependences of all parameters with rising draw ratio were observed (a decrease in elongation at break and increase in tensile strength and modulus values). The two-step drawing resulted in continuing tendencies for all parameters as seen in Table 7.6. Crystallinity changes (Table 7.6) correspond with the trends in mechanical properties of drawn films.

*Table 7.6* Mechanical properties (tensile strength ( $\sigma$ ); elongation at break ( $\epsilon$ ); and modulus (E)) and crystallinity (C) of drawn PHBH films and dependence on the content of hydroxyhexanoate (H) and draw ratio (DR)

H content (%)	DR	$\sigma$ (MPa)	$\epsilon$ (%)	E (GPa)	C (%)
5	1	32 $\pm$ 2	267 $\pm$ 30	480 $\pm$ 70	42 $\pm$ 5
	5	80 $\pm$ 1	258 $\pm$ 10	870 $\pm$ 40	47 $\pm$ 5
	10	140 $\pm$ 20	116 $\pm$ 10	1480 $\pm$ 150	65 $\pm$ 5
12	1	23 $\pm$ 4	871 $\pm$ 70	90 $\pm$ 3	31 $\pm$ 5
	5	53 $\pm$ 4	204 $\pm$ 18	30 $\pm$ 1	35 $\pm$ 5

### *Oriented blends of PHAs*

Besides drawing of PHB or its copolymers with other PHAs, several attempts were made to prepare fibres from blends of PHAs with other polymers. These attempts are mainly aimed to obtain fibres with different properties or lower price; the latter being connected with either a less expensive second component of the blend or with easier processing.

Park *et al.*<sup>35</sup> investigated preparation and properties of fibres made from poly(L-lactic acid) (PLLA) and PHB of two different molecular weights. The two polymers are immiscible in the whole concentration range. The films of the blend after preparation by solvent casting were uniaxially drawn at either 2°C for PHB-rich blends (close to PHB's  $T_g$ ) or 60°C for PLLA-rich blends (around PLLA's  $T_g$ ). It is of interest to note that while blends based on the

PHB matrix were impossible to draw above  $T_g$  of the matrix due to rapid stress relaxation, PLLA-rich blends have to be drawn above  $T_g$  of the matrix polymer. Although PLLA domains in normal molecular weight PHB matrix (600,000) remained almost unstretched during cold drawing, good interfacial adhesion was suggested considering good mechanical properties and the reinforcing effect of the PLLA presence. On the other hand, PLLA was found to be oriented if ultra-high molecular weight PHB ( $M_w$  almost 6,000,000) was used as the matrix. Interfacial entanglements, which are much more numerous in blends with UHMW PHB, are suggested to be responsible for the differences in orientation of the minor component. As a result, the mechanical properties of blends with UHMW PHB matrix improved considerably with increasing PLLA content, as seen also in Table 7.7.

*Table 7.7* Mechanical properties of the blends PHB/PLLA depending on the  $M_w$  of PHB and composition of the blends (data estimated from figures in Park *et al.*)<sup>35</sup>

PHB portion	DR	$\sigma$ (MPa)		E (%)		E (GPa)	
		NMW	UHMW	NMW	UHMW	NMW	UHMW
1	1	22	21	22	12	0.65	0.72
	5	25	41	60	45	0.88	1.18
0.9	1	22	23	30	13	0.65	0.73
	5	28	70	48	75	1.05	1.22
0.7	1	22	24	30	16	0.63	0.73
	5	34	102	39	102	1.12	1.55
0.5	1	24	30	18	33	0.70	0.81
	5	72	151	50	150	1.31	1.54
0.3	1	30	31	28	35	0.82	0.81
	5	165	158	92	158	1.80	2.05
0	1	44	44	22	22	1.12	1.12
	5	170	168	90	167	1.86	2.18

Oriented foils based on blends of copolymer PHB-co-hydroxyvalerate and polyalcohols are described by Cyrus *et al.*<sup>36</sup> The blends were prepared by solvent casting, and castor oil or polypropylene glycol were used as the polyalcohol component. Dynamic mechanical behaviour indicates a formation of the two-phase immiscible blend. The addition of polyalcohols leads to an increase of crystallinity but lower storage modulus was observed due to an addition of the amorphous compound.

### 7.3 Poly( $\epsilon$ -caprolactone)-based fibres

Poly( $\epsilon$ -caprolactone) (PCL) is a synthetic polymer which has many advantages: biodegradability; mechanical properties similar to polyolefins; hydrolysability similar to polyesters; compatibility with many other polymers; ease of melt

processability; and high thermal stability. However, low melting point (around 60°C) and slow rate of degradation *in vivo* (2–3 years) hinder its use as a homopolymer in many cases. Therefore PCL is used more frequently as a component in blends or as a comonomer if copolymers are to be formed.

Various methods have been described and used for PCL fibre production, some of them rather unconventional. Simple melt spinning is possible to apply.<sup>37</sup> Due to low melting and crystallisation temperature of PCL, vertical direction of spinning, small distance between the die and cooling bath, and intensive cooling (ice water 5–10°C) is recommended. The spinning temperature should be kept around 85–90°C. At higher temperature (120°C) fibres with uniform diameter could still be obtained but signs of capillary instability were observed.<sup>37</sup> Fibre diameters were in the range 0.49–0.91 mm depending on the spinning conditions, e.g. ram speed, extrusion rate, take-up rate and the ratio of take-up to extrusion rate. Melt spinning of PCL with the additive content was performed to receive PCL fibres containing *N*-(3,4-dimethoxycinnamoyl)-anthranilic acid, a drug suppressing the fibroblast hyperplasia.<sup>38</sup>

An interesting method of PCL fibre preparation is described by Smith and Lemstra<sup>14</sup> as gravity spinning. The polymer is dissolved in a suitable solvent, in this case acetone to produce solutions containing 6–20 wt % of PCL. The solution was transferred into a vessel and allowed to flow out through a spinneret placed in a bottom of the vessel. The polymer solution was forced by its gravity to flow into a non-solvent (methanol) forming a fibre. The 'as-spun' fibre was taken up on a mandrel using a variable speed. At concentration 5% and lower the fibre was not formed. Within a concentration range of 6–20% the production rate varied from 2.5 to 0.9 m min<sup>-1</sup> and fibres with diameter between 0.19 to 0.15 mm were formed. Both the production rate and diameter of the fibres decreased with the increase in the solution concentration. The fibres were round in diameter and exhibited a rough, porous surface.

This procedure can be used also for preparation of fibres containing various additives. Williamson *et al.*<sup>39,40</sup> prepared PCL fibres with addition of ovalbumin as a hydrophilic macromolecule. The procedure consists in a preparation of 10% PCL solution in acetone and *in situ* formation of ovalbumin nanoparticles in the concentration 1 or 5% re PCL content. Addition of poly(vinylpyrrolidone) is recommended for obtaining better dispersion of nanoparticles. The fibres are then prepared by gravity spinning as described above. Progesterone as a lipophilic steroid was also shown to be incorporated into fibres in a concentration 0.625 and 1.25% using the above mentioned procedure.

Zeng *et al.*<sup>41</sup> investigated a preparation of ultrafine poly(caprolactone) fibres by electrospinning technique to achieve a biodegradable material with high surface area so that the rate of biodegradation could be substantially increased. The technique itself involves spinning the polymer from solution

in a strong electrostatic field through a syringe with a capillary jet outlet. When the voltage is over a certain threshold value, the electrostatic forces are higher than surface tension. As the jet moves towards a collecting metal screen it acts as a counter-electrode, the droplets of the solution split into small charged fibres or fibrils and the solvent evaporates.<sup>42</sup> Nonwoven fabric is formed from the fibres produced. Chloroform solution of PCL was used; an addition of 1,2-dichloroethane resulted in an improvement of the process.<sup>41</sup> The voltage depends on the capillary diameter and was in the range of 29 to 36 kV. The diameter of fibres was strongly dependent on the capillary thickness which was between 0.1 and 0.4 mm, while the fibre diameter was in the range 300 to 900 nm. The effect of the driving pressure in the capillary as well as ambient temperature and air flow were also investigated in detail.

The mechanical strength of melt spun fibres was very low. The fibre could be easily stretched to DR over 20 without breaking; it was suggested that the spinning process introduced very little if any orientation along the fibre axis.<sup>37</sup> After drawing to various DR (between 5 and 25) the strength and modulus increased and elongation at break decreased substantially. Unfortunately the authors do not present exact data on mechanical properties; for the highest DR = 25, the values 280 MPa and 450% for tensile strength and elongation at break, respectively, can be roughly estimated from the stress–strain curves presented.

The tensile properties of the gravity spun fibres were rather low, characterised by a tensile modulus between 10 and 100 MPa, tensile strength 1.8 to 9.9 MPa and elongation at break 175 up to 600 for 6 and 20% PCL concentration, respectively. All values are substantially lower when compared to bulk PCL, obviously due to the porosity of the samples. Cold drawing of the fibres proceeded rather easily and resulted in an increase in strength properties and a decrease in elongation. Again, the properties depended on the concentration of the PCL solution during spinning. Fibres prepared from 6% solution were possible to draw up to DR 2, while DR = 5 could be achieved with the other fibres prepared from solutions containing 10 to 20% of the polymer. The highest values reached were 320 MPa for modulus, 39 MPa for tensile strength and 136% for elongation at break. These values are not at all impressive and do not differ substantially from values for bulk PCL. Similarly, only a marginal effect was observed regarding the changes in melting temperature and crystallinity in dependence on DR.

Incorporation of additives (ovalbumin, progesterone) resulted in a decrease of tensile strength, modulus and elongation at break compared to fibres without additive. A continuous decrease in the properties was observed with increasing concentration of the additive.<sup>40</sup> Similar concentration-dependent deterioration of mechanical properties was observed also if *N*-(3,4-dimethoxycinnamoyl)-anthranilic acid was mixed into PCL fibres during melt spinning.<sup>38</sup>

As indicated, caprolactone can be used also as a comonomer for preparation of copolymers, in this case, transesterification reactions can also be considered. Poly(ethylene terephthalate) copolymers with poly(caprolactone) were prepared by reactive extrusion. In the presence of stannous octoate, ring opening polymerisation of caprolactone is initiated by hydroxyl end groups of molten PET. A block copolymer with rather low portion of transesterification was formed in twin screw extruder as a result of fast distributive mixing of caprolactone into high melt viscosity PET and short reaction time. The copolymer was directly fed into a spin pot and extruded filaments were spun and drawn to DR = 6.6. The interactions between PET and PCL segments may result in a formation of miscible phase with a single  $T_g$  being around 45°C.

## 7.4 Structure of drawn fibres

Isotropic PHB crystallises in an orthorhombic lattice crystalline structure ( $\alpha$ -form) with the chains in the left-handed 2/1 helix, as reported by Yokouchi *et al.*<sup>23</sup> and Pazur *et al.*<sup>43</sup> X-ray diffraction patterns indicating an orthorhombic crystal structure ( $\alpha$  modification, 2/1 helix) were also described by Yamamoto *et al.*<sup>44</sup> Changes in the crystalline structure may be expected as a result of drawing. Frequently, an additional crystal structure is observed, assigned to a zigzag conformation of a hexagonal  $\beta$  modification.<sup>31</sup> Thus, appearance of both helical and planar conformation and their ratio depend on preparation conditions, mainly on draw ratio. A paper of Yamane *et al.*<sup>26</sup> describes an appearance of higher crystalline orientation with increasing draw ratio with c-axis parallel to the fibre axis, which seems to be the most preferential orientation direction. A reflection at  $2\theta = 19.7^\circ$  was assigned to a reflection of the pseudohexagonal phase as proposed by Furuhashi *et al.*<sup>45</sup> Using high speed spinning procedure, Schmack *et al.*<sup>27</sup> reported no signs of hexagonal modification for high speed spinning up to draw ratio 4.0 and proposed lack of stress-induced crystallisation at that degree of orientation. However, an increase to 4.5 leads to WAXS patterns indicating a presence of both crystal structures. The observed effects are generally in accordance with mechanical properties, but the effect of extrusion speed is not clear from this study, i.e. whether stress-induced crystallisation would be sufficient for a formation of hexagonal modification if the DR would stay low at higher speed of extrusion.

Similar orthorhombic structure was observed also for drawn fibres based on a copolymer PHB-co-hydroxyhecanoate.<sup>33</sup> It was concluded that the higher hydroxyalkanoate units were excluded from the crystal structure.

The surface of melt spun fibres consists of many large spherulites, as indicated by SEM observations.<sup>46</sup> After drawing to DR = 6, the fibres have a fibrillar structure and their surface is fairly smooth. This fibrillar structure is formed mainly in surface areas of the fibres as indicated by the appearance

of fibres observed by SEM after various periods of enzymatic degradation. The annealing results in a higher portion of fibrillar structure which is formed also in core parts of the fibres. Annealing under tension leads to a formation of a more perfect fibrillar structure in the core and this effect seems to be increasing with the rising tension load during annealing.<sup>46</sup>

A similar structure was observed also for melt spun poly(caprolactone) fibres. SEM observations showed spherulites in the undrawn fibres which change to fibrillar stripes along the fibre axis in drawn fibres.<sup>47</sup> Differences in the crystal structure were observed also with rising draw ratio.

## 7.5 Thermal properties

Generally thermal properties of polymers change after drawing. Melt temperature of PHB determined by DSC depends to certain extent on the material itself as well as on the measuring conditions; Yamane *et al.*<sup>26</sup> reported  $T_m = 171^\circ\text{C}$  (second run) and  $T_c = 91^\circ\text{C}$  at cooling rate  $5^\circ\text{C min}^{-1}$ , while  $T_m$  of virgin powder was found to be  $177^\circ\text{C}$ .<sup>27</sup> Melting temperature depends also on the molecular weight, as revealed by Park *et al.*<sup>35</sup> who determined  $T_m$  to be around 165 and  $177^\circ\text{C}$  for PHB with molecular weight  $M_w$  590,000 and 5,300,000, respectively. Equilibrium melting temperature was determined to be around  $186^\circ\text{C}$ .<sup>48</sup> 'As-spun' fibres showed a melting temperature of  $176^\circ\text{C}$  irrespective on draw ratio,<sup>26</sup> drawing results in a significant increase in the  $T_m$ . An increase from  $177^\circ\text{C}$  for virgin PHB powder up to 181.6, and even to  $188.9^\circ\text{C}$ , was reported,<sup>27</sup> depending on the draw ratio being between 4.5 and 6.9. It is interesting that melt spinning/drawing at DR = 4 does not lead to any increase in  $T_m$ ; also mechanical properties are not improving due to drawing, although a little higher DR, namely 4.5, was reached. It has also to be mentioned that fibres drawn to DR around 6 have a melting temperature higher than that reported for equilibrium temperature of isotropic PHB.<sup>27</sup> Thorough drying itself leads to a substantial increase in the melting temperature, namely from  $177.2^\circ\text{C}$  for virgin PHB powder up to  $189.9^\circ\text{C}$  for pellets dried for 16 hours at  $120^\circ\text{C}$ .<sup>27</sup> Thorough drying may have certain effects on the melting temperature, changes in the supramolecular structure occurs after several hours treatment at  $120^\circ\text{C}$ , even without the effect of losing moisture.

Annealing leads to changes in thermal behaviour of drawn fibres. DSC melting peaks of annealed fibres are larger and tend to be sharper compared to unannealed fibres;<sup>26</sup> both effects are more pronounced with rising annealing temperature. Annealing under tension results in even sharper peaks, the results indicate<sup>26</sup> that annealing without tension leads to a recrystallisation of the material to more perfect  $\alpha$ -form, while the molecules between  $\alpha$ -form lamellae crystallise into  $\beta$ -form if tension is applied during annealing; the effect is more pronounced at higher annealing temperatures.

## 7.6 Enzymatic and hydrolytic degradation

Yamane *et al.*<sup>46</sup> investigated the enzymatic degradation of melt spun fibres, PHA depolymerase from *Comamonas testosteroni* in potassium phosphate buffer was used at 37°C for this study. The enzymatic degradation of PHB occurs on the surface of the material and the rate of degradation strongly depends on the structure.<sup>46</sup> SEM observations of 'as-spun' fibres indicate that enzymatic degradation begins on the surface, preferentially in less-ordered regions between spherulitic crystals. At the same time, the fibre diameter decreases as the degradation proceeds to the core of the fibre, similarly, degradation of drawn fibres started in less-ordered regions leaving the fibrillar structure to resist for longer time. Clear difference in the morphology of fibres drawn to various DR (4, 5, and 6) was not observed. After four days of enzymatic degradation, the drawn fibres changed to aggregates of small fibrous fragments while 'as-spun' fibres retained their fibre shape with a spongy structure, although the diameter significantly decreased. This difference was attributed mainly to the original thickness of the 'as-spun' fibres being thicker compared to drawn fibres while the degree of crystallinity was similar. It has to be noted that both the 'as-spun' as well as drawn fibres decomposed rather fast so that mechanical properties could not be measured after 24 hours of degradation. However, the annealed fibres (DR = 6) kept their consistency longer, so that the mechanical tests could be performed even after 50 hours of degradation. The resistance of fibres against enzymatic degradation increases with increasing temperature of annealing; higher tension during annealing has a retarding effect on degradation.<sup>46</sup> WAXS study revealed that disordered  $\beta$  form is attacked by PHB depolymerase more rapidly than the more ordered  $\alpha$  form.

Similar tests were done with an oriented copolymer PHB-poly(hydroxyhexanoate) using PHB depolymerase purified from *Ralstonia picketti* T1.<sup>33</sup> It was found that the rate of enzymatic degradation of two-step drawn films decreased with increasing DR, i.e. with increasing crystallinity, as expected. However, the decrease in the rate for one-step films was irrespective on draw ratio 3 or 5 and much more pronounced compared to the two-step drawn films even though the DR was significantly higher in the latter case (DR up to 10). The authors admit having difficulties with offering a reasonable explanation for this behaviour.

Special centrifugally spun fibres as an alternative for gel spun fibres were tested regarding hydrolytic degradation (pH 10.6, 70°C).<sup>32</sup> Fibres degraded by gradual fragmentation and erosion to fibre fragments, particles and eventually monomer. Mammalian and human epithelial cells were used to investigate the cellular interactions with the fibres. To achieve good cell adhesion, the surface of the fibres has to be treated by alkali or acids; the introduction of hydroxyls or carbonyls on the surface is suggested as an

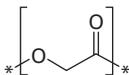
explanation of the effect. Neither cell line exhibited any cytotoxic response to the fibres.

Although no more detailed studies were found on the environmental degradation of PHB fibres, the above-mentioned effects may be considered to be generally valid for the anisotropic materials depending on the draw ratio, structure parameters (content of  $\alpha$  and  $\beta$  phase, etc.).

The rate of enzymatic degradation by lipase of poly(caprolactone) fibres drawn to various ratios was dependent on draw ratios, suggesting that crystallinity and orientation degree are important parameters affecting the degradation kinetics.<sup>49</sup> Degradation behaviour of fibres differing in details of the preparation procedure revealed the changes in degradation kinetics on supramolecular structure of the material. From SEM observation it is observed that enzyme preferentially attacks amorphous or less ordered regions.<sup>47</sup> Differences in crystal structure were revealed by SEM consisting mainly in a portion of spherulites and fibrilles depending on the drawing conditions, these structural parameters affect the enzymatic degradation kinetics. However, in spite of different degradation rates in amorphous and crystalline regions, the crystalline part is also attacked by the enzymes and biodegrades.<sup>47</sup> It is interesting to note that when investigating enzymatic degradation of films made from butylene succinate-co-ethylene succinate copolymer it was found that the rate of degradation depends on the crystallinity rather than on the primary chemical structure. Thus, the crystallinity degree seems to be the major rate-determining factor of biodegradation of solid polymers, while the crystalline structure seems to be an additional parameter.

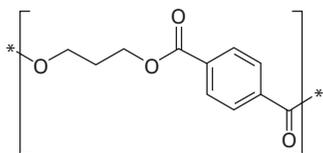
## 7.7 Other biodegradable and sustainable polyesters

Poly(glycolic acid) (PGA; 7.3) is an aliphatic polyester that has been widely used in biomedical applications since the early 1970s<sup>50-54</sup> and degrades via a simple hydrolysis mechanism (bulk degradation). However, the homopolymer has found little application as a fibre outside medicine, but such fibres do offer potential for the future and maybe an area worth further research.



### 7.3

Poly(trimethylene terephthalate) (PTT; 7.4) was first synthesised in the 1940s by Whinfield and Dickson,<sup>55</sup> but has only recently received attention as a viable textile fibre as it can be synthesised via a more economical process.<sup>56</sup> PTT is desirable because it has several unique properties, such as



#### 7.4

its force-elongation behaviour, resilience, and dyeing properties. It has outstanding elastic recovery; the fibre recovers 100% from approximately 120% strain.<sup>57</sup>

Although PTT is not a biodegradable fibre, it is worth mentioning as a fibre which offers a level of sustainability in the form of Sorona<sup>®</sup>. In 2004, DuPont and Tate & Lyle PLC announced a joint venture (DuPont Tate & Lyle BioProducts, LLC) to create products from renewable resources such as corn for numerous applications including clothing, interiors, engineered polymers and textile fibres. The company uses a proprietary fermentation and purification process to produce 1,3-propanediol (PDO), one of the two base chemicals for producing PTT. Rather than using PDO from petrochemical sources, in this process it is derived from renewable sugar. The resultant fibre formed from polymerisation of renewable PDO and terephthalic acid is Sorona<sup>®</sup>.<sup>57</sup> However, the polymer is not fully sustainable due to the non-renewable sources of terephthalic acid, so cannot be compared to poly(lactic acid) in terms of its sustainability. Nevertheless, this fibre is a demonstration of positive moves by multinational companies to reduce demands on fossil fuels.

### 7.8 Application of polyester-based biodegradable fibres

PHA fibres are frequently aimed at medical applications; a combination of biodegradability, hydrophobicity and biocompatibility seems to be of importance for many medical applications. Poly(hydroxybutyrate) fibres were considered to be mainly used for production of scaffolds.<sup>58</sup> From the point of view of medical applications, an interesting paper of Schmack *et al.*<sup>59</sup> deals with the effect of electron irradiation on properties and degradation of PHB fibres with the aim of estimating the consequences of sterilisation of medical devices via electron beam irradiation. In this paper, melt spun PHB fibres were drawn to DR 7 and textiles with a mesh size of 0.5 mm were produced using embroidery technology.<sup>60</sup> Irradiation resulted in a decrease in tensile strength, while changes in modulus and elongation at break were negligible, as seen in Table 7.8; the changes can be attributed to a decrease in molecular weight, which is quite substantial. Hydrolytic degradation in a Sorensen buffer of irradiated fibres was found to be only a little more pronounced if

**Table 7.8** The effect of irradiation dose on changes in average number  $M_n$  and molecular  $M_w$  weights, tensile properties (strength ( $\sigma$ ), elongation ( $\epsilon$ ), modulus (E)) and relative change of  $M_w$  after *in vitro* degradation

Dose (kGy)	$\sigma$ (MPa)	$\epsilon$ (%)	E (GPa)	$M_n$ (kg mol <sup>-1</sup> )	$M_w$ (kg mol <sup>-1</sup> )	$M_n^{84*}$	$M_w^{84*}$
0	307	41	4.5	77	157	0.87	0.84
5	295	41	4.3	65	145	–	–
10	248	39	4.3	61	126	–	–
15	257	39	4.1	53	111	–	–
25	236	39	4.4	44	92	0.82	0.74

\* relative molecular weight ( $M_t/M_o$ ) after 84 days in Sorensen buffer

the fibres were irradiated by a 25 kGy dose compared to non-irradiated fibres.<sup>59</sup>

Application as scaffolds was suggested also for centrifugally spun fibres.<sup>32</sup> Although almost no cell adhesion was observed for unmodified fibres investigated by SEM, subsequent acid or alkali treatment resulted in a cell-adhesive material which may have a potential value as wound scaffold.

In fact, most biodegradable polyester-type fibres are intended for medical purposes, although the application is not limited to scaffolds. Poly(caprolactone) gravity spun fibres were found to attach fibroblasts and myoblasts. Due to high fibre compliance and a potential for controlling the fibre surface architecture, the fibres can be recommended to be used as compliance-matched implants for soft tissue engineering.<sup>39</sup>

Poly(caprolactone) gravity spun fibres were used also as a carrier for ovalbumin or progesterone.<sup>40</sup> The delayed drug release was observed; the rate depends on several factors, e.g. concentration and size of the protein particulates, which enables a programmed delivery of drugs or supporting agents for tissue engineering.

Poly(caprolactone) was used as a matrix for a composite with poly(lactic acid) and poly(glycolic acid) long fibres. The composite was prepared by *in situ* polymerisation of caprolactone with dispersed fibres, and bioabsorbable composite material was obtained which is investigated for an application for craniofacial bone reconstruction.<sup>61</sup> PCL fibres containing *N*-(3,4-dimethoxycinnamoyl)-anthranilic acid can release the agent which suppresses the fibroblast hyperplasia.<sup>38</sup> The drug release rate was found to decrease with increasing draw ratio, obviously as a result of increased crystallinity of the polymeric matrix.

An industrial application was suggested for copolymers of poly(caprolactone) and poly(ethylene terephthalate) as a material for elastic seat belts. In this case the impact on the passenger was damped by the increased elasticity of the belt, compared to the belt made of pure PET, decreasing the extent of injuries caused by contact with the seat belt.<sup>62</sup>

## 7.9 Future trends and concluding remarks

It can be said that the research on PHA fibre techniques is in quite an advanced stage so that a feasible technology could be designed if a request for a high amount of fibres arose. The high volume production, however, depends on two factors, the quality of the fibres and the ultimate price of the product. At the moment, apparently, the quality improvement resulting from drawing does not compensate for the rather high price of the fibre, caused mainly by the price of the poly(hydroxyalkanoates) as the parent materials. The reason for the high price consists partially in the low volume of production of PHAs; it can be hardly expected that a production of fibres can influence the volume of production to such an extent that the price would fall substantially. Thus, in the near future, the PHA fibres can be expected to be applied mainly as low volume special materials. From this point of view, an application in medicine is the most obvious. The biodegradability of the fibres is certainly considered in many applications outside of medicine, but at the current material price it can hardly be expected to be a decisive factor regarding the high volume applications of PHA fibres.

Electrospinning may play a role in a spread of biodegradable fibres, especially if feasible ideas for an application of nonwoven biodegradable textiles would appear.<sup>63</sup> Electrospinning of poly(caprolactone) was successfully accomplished at laboratory scale as mentioned above; poly(hydroxyalkanoate) electrospinning should be investigated as well, especially regarding PHB, electrospinning could bring some interesting, possibly surprising, results.

Considering oriented biodegradable bacterial polyesters, attention should be paid to foils. Manufacturing the oriented or even biaxially oriented biodegradable foils could result in a material with high application potential in packaging. In this case the volume of the biodegradable plastics could be rather high so that also the price of the polymer could be affected. Thus, the success in this direction may have a positive influence on the future of biodegradable polyesters.

The potential of oriented poly(caprolactone) seems to be lower compared to PHAs. Apparently it will be an important special polymer, but high volume applications are less probable. The main problem consists in its low melting temperature, although it can be improved to a certain extent via various modifications, especially transesterifications with poly(caprolactames)<sup>64</sup> or other polymers. However, even in this case the consumption will stay at low level. The most promising way seems to be Novamont's (Italy) attitude of mixing PCL with starch or other biodegradable species to prepare composites. This material (MaterBi) is used routinely for production of biodegradable foils of good quality.<sup>3</sup> At the moment no data are available on drawing of the composites to produce fibres; neither does a need for such fibres seem to exist. Poly(caprolactone) can be used in quite high volume as a modifying

component in blends with other biodegradable plastics, including PHAs and PLA. In this case, its role consists in an improvement of toughness and the increase in drawability. The significance of such blends for biodegradable fibre production is obvious.

In any case, biodegradable fibres based on polyesters while investigated and developed by researchers, should be considered seriously by industry and consumers. A knowledge concerning the properties and new techniques of production of the fibres should bring new ideas for applications of these materials followed by development of production technology.

## 7.10 References

1. Sudesh, K. Abe, H. and Doi, Y., *Progr. Polymer Sci.*, 2000, **25**, 1503.
2. Chodak, I., *Degradable Polymers Principles and Applications*, 2nd edn, editor: G. Scott, Kluwer Acad. Publ. Dordrecht, Boston, London 2002, chapter 9.
3. Bastioli, C. and Facco, S., *Biodegradable Plastics 2001 Conference*, Frankfurt, November 26–27, 2001.
4. Hori, Y., Hongo, H. and Hagiwara, T., *Macromolecules*, 1999, **32**, 3537.
5. Braunegg, G., *Degradable Polymers Principles and Applications*, 2nd edn editor: G. Scott, Kluwer Acad. Publ. Dordrecht, Boston, London 2002, chapter 8.
6. Braunegg, G., *ICS UNIDO Workshop Environmentally Degradable Plastics*, Seoul September 19–22, 2000, 181–200.
7. Kunioka, M., Nakamura, Y. and Doi, Y., *Polymer Commun.*, 1988, **29**, 174.
8. Fritsche, K., Lenz, R.W. and Fuller, R.C., *Int. J. Biol. Macromol.*, 1990, **12**, 92.
9. Bear, M.M., Leboucherdurand, M.A., Langlois, V., Lenz, R.W., Goodwin, S. and Guerin, P., *React. Funct. Polymers*, 1997, **34**, 65.
10. Kim, Y.B., Lenz, R.W. and Fuller, R.C., *Macromolecules*, 1991, **24**, 5256.
11. Doi, Y. and Abe, C., *Macromolecules*, 1990, **23**, 3705.
12. Fritsche, K., Lenz, R.W. and Fuller, R.C., *Int. J. Biol. Macromol.*, 1990, **12**, 85.
13. Chodák, I., *Progr. Polymer Sci.*, 1998, **23**, 1409.
14. Smith, P. and Lemstra, P.J., *Makromol. Chem.* 1979, **180**, 2983.
15. Kusaka, S., Iwata, T. and Doi, Y.J., *Macromol. Sci. Pure Appl. Chem.*, 1998, **A35**, 319.
16. Lee, S.Y., Lee, K.M., Chang, H.N. and Steinbuechel, A., *Biotechnol. Bioeng.* 1994, **44**, 1337.
17. Kusaka, S., Abe, H., Lee, S.Y. and Doi, Y., *Appl. Microbiol. Biotechnol.*, 1997, **47**, 140.
18. Luepke, T., Radusch, H.J. and Metzner, K., *Macromol. Symp.*, 1998, **127**, 227.
19. Bastiaansen, C.W.M., *Mater. Sci. Technol.*, 1997, **18**, (Chapter 11) 1373, eds: Cahn, R.W., Haasen, P. and Kramer, E.J.
20. Liu, W.J., Yang, H.L., Wang, Z., Dong, L.S. and Liu, J.J., *J. Appl. Polymer Sci.* 202, **86**, 2145.
21. Barham, P.J. and Holmes, P.A., *US Patent* 4,427,614, 1984, Jan. 24.
22. Gordeyev, S.A., Nekrasov, Yu, P. and Ward, I.M., *IVth Int Symposium on Polymer for Advanced Technologies*, Leipzig, 1977, PVII.10.
23. Yokouchi, M., Chatani, Y., Tadakoro, K., Teranishi, K. and Tani, H., *Polymer*, 1973, **14**, 267.

24. Nicholson, T.M., Unwin, P.A. and Ward, I.M., *J. Chem. Soc. Faraday Trans.*, 1995, **91**, 2623.
25. Gordeyev, S.A. and Nekrasov, Yu, P., *J. Mater. Sci. Letters*, 1999, **18**, 1691.
26. Yamane, H., Terao, K., Hiki, S. and Kimura, Y., *Polymer*, 2001, **42**, 3241.
27. Schmack, G., Jehnichen, D., Vogel, R. and Tändler, B., *J. Polymer Sci., B Polymer Phys.*, 2000, **38**, 2841.
28. Gordeyev, S.A., Nekrasov, Yu, P. and Shilton, S.J., *J. Appl. Polymer Sci.*, 2001, **81**, 2260.
29. Barham, P.I. and Keller, A., *J. Polymer Sci., Polymer Phys. Ed.*, 1986, **24**, 69.
30. Doi, Y., Iwata, T. and Kusaka, S., *Eur. Pat. Appl.* EP 849311.
31. Orts, W.J., Marchessault, R.H., Allegrezza, Jr A.E. and Lenz, R.W., *Macromolecules*, 1990, **23**, 5368.
32. Foster, L.J.R., Davies, S.M. and Tighe, B.J., *J. Biomaterials Sci., Polymer Ed.*, 2001, **12**, 317.
33. Fischer, J.J., Aoyagi, Y., Enoki, M., Doi, Y. and Iwata, T., *Polymer Degrad. Stability*, 2004 **83**, 453.
34. Asrar, J., Valentin, H.E., Berger, P.A., Tran, M., Padgette, S.R. and Garbow, J.R., *Biomacromolecules*, 2002, **3**, 1006.
35. Park, J.W., Doi, Y. and Iwata, T., *Biomacromolecules* 2004, **5**, in press.
36. Cyras, V.P., Fernandez, N.G. and Vazquez, A., *Polym. Int.*, 1999, **48**, 705.
37. Charuchinda, A., Molloy, R., Siripitayananon, J., Molloy, N. and Sriyai, M., *Polymer Int.*, 2003, **52**, 1175.
38. Yamane, H., Inoue, A., Koike, M., Takahashi, M. and Igaki, K., *Sen-I-Gakkaishi*, 1999, **55**, 261.
39. Williamson, M.R. and Coombes, A.G.A., *Biomaterials*, 2004, **25**, 459.
40. Williamson, M.R., Chang, H.-I. and Coombes, A.G.A., *Biomaterials*, 2004, **25**, 5053.
41. Zeng, J., Chen, X., Xu, X., Liang, Q., Bian, X., Yang, L. and Jing, X., *J. Appl. Polymer Sci.*, 2003, **89**, 1085.
42. Reneker, D.H., *J. Appl. Phys.*, 2000, **87**, 4531.
43. Pazur, R.J., Hocking, P.J., Raymond, S. and Marchessault, R.H., *Macromolecules*, 1998, **31**, 6585.
44. Yamamoto, T., Kimizu, M., Kikutani, T., Furuhashi, Y. and Cakmak, M., *Int. Polymer Process*, 1997, **12**, 29.
45. Furuhashi, Y., Kikutani, T., Yamamoto, T. and Kimizu, M., *Sen i Gakkaishi*, 1997, **53**, 356.
46. Yamane, H., Terao, K., Hiki, S., Kawahara, Y., Kimura, Y. and Saito, T., *Polymer*, 2001, **42**, 7873.
47. Mochizuki, M., Hirano, M., Kanmuri, Y., Kudo, K. and Tokiwa, Y., *J. Appl. Polymer Sci.*, 1995, **55**, 289.
48. Organ, S.J. and Barham, P.J., *Polymer*, 1993, **34**, 2169.
49. Mochizuki, M. and Hiram, M., *Polymers for Advanced Technologies*, 1997, **8**, 203.
50. Uhrich, K., Cannizzaro, S.M., Langer, R. and Shakesheff, K.M., 1999, *Chem. Rev.*, **99**: 3181–3198.
51. Langer, R. and Vacanti, J.P., 1993, *Science*, **260**: 920–926.
52. Wong, W.H. and Mooney, D.J., 1997, in: Atala, A., Mooney, D.J., Vacanti, J.P. and Langer, R. (eds) *Synthetic biodegradable polymer scaffolds*. Boston, Birkhäuser, 51–82.
53. Frazza, E.J. and Schmitt, E.E., *J. Biomed. Mater. Res. Symp.*, 1971, **1**: 43–58.

54. Kimura, Y., 1993, in: Tsuruta, T., Hayashi, T., Kataoka, K., Ishihara K. and Kimura, Y. (eds) *Biomedical applications of polymeric materials*. Boca Raton, CRC Press, 163–190.
55. Whinfield, J.R. and Dickson, J.T., BP 578,079; 1941; USP 2,465,319; 1949.
56. Chuah, H.H., *Chem. Fibers Int.*, 1996, **46**, 424.
57. <http://www.dupont.com/sorona/home.html>
58. Patent EP 0567 845 B1 1998.
59. Schmack, G., Kramer, S., Dorschner, H. and Gliesche, K., *Polymer Degrad. Stability*, 2004, **83**, 467.
60. Schmack, G., Gliesche, K., Nitschke, M. and Werner, C., *Biomaterialien*, 2002, **3**, 21.
61. Corden, T.J., Jones, I.A., Hudd, C.D., Christian, P., Downes, S. and McDougall, K.E., *Biomaterials*, 2000, **21**, 713.
62. Tang, W., Murthy, S., Mares, F., McDonnell, M.E. and Curran, S.A., *J. Appl. Polymer Sci.*, 1999, **74**, 1858.
63. Dzenis, Y., *Science*, 2004, 1917.
64. Bernášková, A., Chromcová, D., Brožek, J. and Roda, J., *Polymer*, 2004, **45**, 2141.