Fiber Spinning Behavior of a 3-Hydroxybutyrate/3-Hydroxyhexanoate Copolymer

Eric Bryan Bond

The Procter & Gamble Company, 8611 Beckett Road, West Chester, OH 45069, USA

Summary: The fiber spinning behavior of a poly(3-hydroxyalkanoate) (PHA) copolymer resin containing 11.3 mol% hexanoate copolymer (H11) was studied to determine its usefulness in fiber based applications, such as nonwovens. Monocomponent fibers were spun initially, but it was found they would not solidify in the spinline. Bicomponent (sheath/core) fibers were melt spun using a H11 core and a polylactic acid (PLA), as well as a polyethylene succinate (PES) sheath. The spinning results showed that H11 levels up to 30wt% could be incorporated with stable spinning. The incorporation of H11 was found to be limited due to the slow crystallization kinetics of the H11 in the spinline. The neat and bicomoponent fibers were found to have tensile strengths similar to polypropylene. The PES based fiber compositions were found to have elongation-at-break values similar to PP. Neat H11 copolymer fibers were found to be readily biodegradable at 25°C under aerobic conditions.

Keywords: bicomponent; biodegradable; fiber; PHA; PLA; polyethylene succinate

Introduction

In the past several years poly(3-hydroxyalkanoate) (PHA), specifically poly(3-hydroxybutyrate) or PHB, has been studied extensively for use as a biodegradable or biocompatable family of polymers[1-4]. Since these polymeric materials can often be made through a bacterial fermentation process, it is though these biofriendly polymers can be produced in large quantities at reasonable costs in order to increase their widespread use and acceptance. The present paper will present data on fiber spinning of a PHA copolymer, with the general structure:

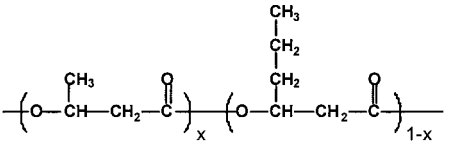

Figure 1. Chemical structure of the PHA copolymer. The x denotes the PHB polymer component, while the (1-x) component is the hexanoate copolymer.

 DOI: 10.1002/masy.200350703

This family of PHA copolymers has substantially different behavior versus PHB due to the long chain branching, which reduces the crystallinity and melting temperature. These morphological differences result in a polymer that is more ductile and processable on commercially avaliable processing equipment, such as fiber spinning equipment in the present case. The PHA copolymer in the this report is produced by bacteria and has the general structure detailed in Figure 1 with 11.3 mol% hexanoate copolymer, designated as H11. This polymeric material is part of the Nodax™ family of polymers being marketed by The Procter & Gamble Company.

One of the key points of interest that seperates the H11 copolymer from other thermoplastic biodegradable polymers is illustrated in Figure 2. Figure 2 compares the aerobic degradation behavior of regenerated cellulose (rayon or viscose) fibers, polyL-lactic acid (PLA) fibers and polyethylene succinate (PES) fibers at 25°C using an activated sludge inoculum.

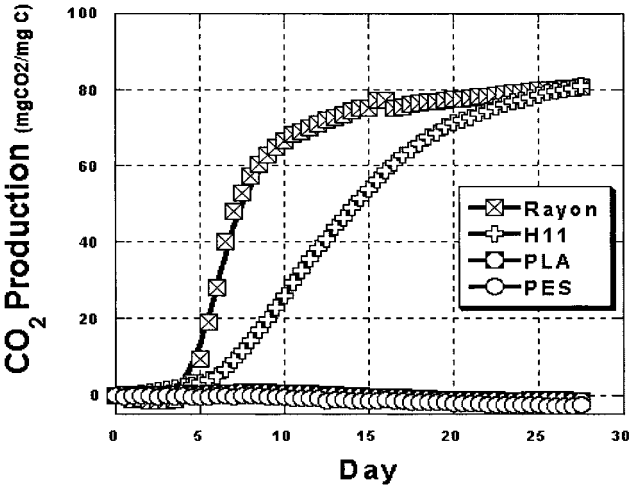

Figure 2. Aerobic degradation data of various biodegradable polymers.

The PLA and PES fibers in Figure 2 exhibit no CO_2 production under aerobic conditions during the time scale of 28days. The rayon and H11 are completely mineralized during the same time scale. For this reason, H11 has a special place in the current selection of biodegradable polymer in that it is both thermoplastic *and* aerobically degradable at room temperature. It is well known that PLA and PES do ultimately biodegrade, but under much more liberal testing conditions and specialized environments[5-7].

Materials

There are four thermoplastic polymers to be studied in this paper, three biodegradable polymers and a polypropylene (PP) resin used to compare the fiber properties of the biodegradable polymers to be compared to a commercially accepted thermoplastic polymers. Table 1 indicates the material, chemical name, supplier and source.

Table 1. Material Sourcing

Material	Chemical Name	Supplier	Product Code	Abbreviation
PLA	poly L-(lactic acid)	Biomer	L9000	PLA
Bionolle	poly (alkylene succinate)	Showa High Polymer	Bionolle 1020	PES
Nodax	polyhydroxyalkanoate	P&G/Kaneka	Nodax H11	H11
PP	polypropylene	ExxonMobil Chemical	Achieve 3854	PP

The data in Table 2 indicates some of the material properties. The molecular weights were determined by gel permeation chromotography (GPC). The PLA was measured in chloroform at 25°C, while the PES was measured in chloroform at 30°C. The H11 was measured in dichloromethane at 25°C. The PP was measured in trichlorobenzene at 135°C. The copolymer level and type was determined using carbon-13 NMR using the same solvents. The molecular weight distribution of all these materials are quite narrow, all having a polydispersity index less than 2.5. The other point of interest in Table 2 involves the M_W of the H11 resin. The initial M_W was 1911kg/mol, while the M_W after processing was found to be 1069kg/mol, a reduction of almost 50%, which must be taken into consideration when choosing the M_W of the PHA-type polymer.

Table 2. Material Properties

Material	M_z	M_w	M_n	Polydispersity	Copolymer Level	Copolymer Type
	(kg/mol)	(kg/mol)	(kg/mol)	(M_w/M_n)		
PLA	181	98.5	52.2	1.89	3.4wt%	D-isomer
PES	215	118.1	48.5	2.43	-	-
H11	3515	1911	806	2.37	14.4wt%	C6
PP	260	169	86.9	1.94	1.5wt%	Stereo/Regio

The data in Table 3 shows some of the thermal properties of these resins. The DSC was a Perkin-Elmer DSC-7. The heating and cooling rate was 20°C/min with the indicated data being determined on the 2nd heat and 2nd cool cycle. The sample is held in the melt at 230°C for 10minutes followed by the cooling cycle. The sample was annealed at –60°C for 10minutes before heating. The DMA is a TA Instruments DMA Q-800. In the DMA testing, the sample was cooled to –60°C for 10minutes before heating at 10°C/min. It is worth pointing out the Tg determined by DMA is significantly different for H11 and PES than measured by DSC, which really illustrates the fundamental difference in what each instrument measures; DSC measures the change in heat capacity while DMA measures changes in storage modulus i.e. thermodynamic vs mechanical.

Table 3. Thermal Characteristics of Resins

Material	T_m[1]	T_c[1]	T_g[1]	ΔH_f-melt[1]	ΔH_f-crystallization[1]	T_g[2]
	(°C)	(°C)	(°C)	(J/g)	(J/g)	(°C)
PLA	172.6	110.4	58.7	34.5	36.8	65
PES	112.2	96.9	-32.6	64.8	66.7	-16.7
H11	115.6	N.O.	-40.1	79.9	N.O.	-27.3
PP	150.9	100.2	-5.0	83.9	85.7	8.3

1-Determined by DSC at Heat/Cool Rates of 20°C/min
2-Determined by DMA

The other interesting piece of data in Table 3 is the behavior of H11 on the cooling cycle. The H11 resin does not exhibit a real crystallization peak during the cooling cycle, but does anneal and crystallize significantly during the following cooling and heating cycles. This annealing is very subtle and gets lost in the background, which is not easily accounted for since the entire baseline is shifted.

Experimental

Spinning Equipment and Conditions

The fibers were melt spun on an 82-hole bicomponent spinning system using Hills Inc bicomponent spinning technology. The bicomponent fibers were sheath/core (S/C) with a non-eccentric core. The S/C ratio was 70/30 by weight and is is controlled by Zenith gear pumps that deliver a constant volume at a set speed. The melt densities used were 1.05g/cm^3 for PLA, PES and H11. The PP melt density used was 0.75g/cm^3. The melt temperature used was 190°C at the entrance to the spinneret using a constant mass through-put of 0.6grams/hole-minute.

The methods for measuring the fiber properties structure and properties can be found in the author's previous papers[8,9].

In conventional melt spinning processes, fiber velocities or spinning speeds are most often calculated from the Continuity Equation:

$$V_x = \frac{4Q}{\pi \rho_{fiber} d^2} \quad (1)$$

where V_x is the total fiber velocity, Q the mass throughput per spinnerette hole, ρ_{fiber} is the density of the fiber, and d the diameter (or equivalent diameter) of the fiber. Figure 3 shows the fiber diameter versus spinning speed for the biodegradable resins melt spun in this report.

As the data in Figure 3 indicates, all of the calculations fall on what appears to be a master curve, as they should according to Equation (1). The variations are due to experimental measurement variations in Q, d and ρ. The data also shows that the bicomponent fiber in each case can be melt spun into finer fiber diameters and higher filament velocities versus the neat sheath material.

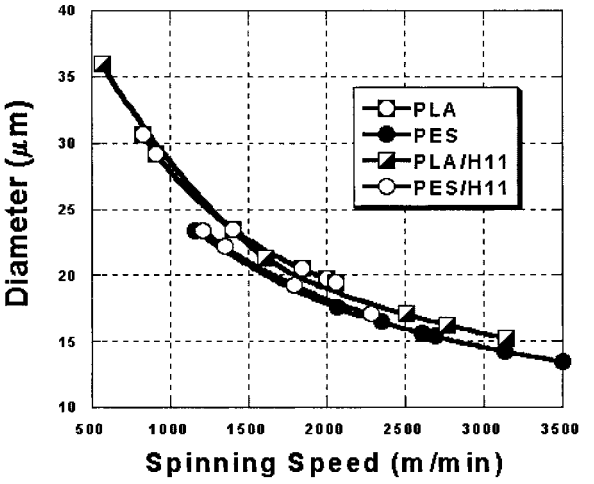

Figure 3. Filament Diameter versus Spinning Speed.

Preliminary Spinning Trials

The first spinning trials were conducted to assess the spinnability of H11 as a monocomponent fiber. It was quickly found that no matter the processing temperature and conditions, filaments were still not completely solidified when collected on a mechanical winder or through an air drag attenuation device. This observation suggests that stress induced or stress enhanced crystallization is not exhibited or is insufficient to crystallize H11 in the spinline, even when the fiber velocity exceeds 3000m/min. When the spinning results are combined with the quiescent crystallization data measured for H11 in Table 3, the results suggest that the primary nucleation rate for this PHA copolymer is very slow.

The H11 was blended with various nucleating agents to try and enhance its crystallization rate in the spinline. The nucleating agents, must notably PHB melt blended at 3 and 10wt% levels, did not enhance the crystallization rate in the spinline, but did substantially increase the solidification rate after the molten filament streams contacted the winder. It is well understood that PHB is a nucleating agent for H11, but the melt temperature exceeded the melting temperature of PHB at 180°C.

When the fused fiberous structure was studied, individual fibers could be separated. Testing indicated these fused filaments had very low crystallinities ($\Delta H_f \approx 15 J/g$) and tensile properties of 46MPa and 200% elongation-at-break.

The net result of the neat spinning studies was that this H11 resin could not be spun alone as a monocomponent fiber, so it was combined with other biodegradable resins to produce bicomponent fibers.

Results and Discussion

Structure of As-Spun Filaments

The data in Figure 4 shows the heats of fusion (ΔH_f) for the as-spun fibers containing the biodegradable polymers as a function of spinning speed. The ΔH_f can be used in fibers to approxiamate the crystallinity. (The best way to measure crystallinity in fibers is to measure the density, but no consistent values could be determined for these fibers at the time of publication.) The data for the monocomponent and bicomponent PLA based fibers shows a gradual increase in heat of fusion with increasing spinning speed. The PES based fibers show a generally flat profile as a function of increasing spinning speed. The ΔH_f for the PES compositions is significantly higher than PLA compositions, suggesting the PES compositions have higher levels of crystallinity. However, the ΔH_f (crystallinites) of the neat and bicomponent fibers are similar to one another within a given chemical species.

The data in Figure 5 shows the birefringence of the filaments as a function of spinning speed. The data indicates that the PES and PLA based fibers increase in overall molecular orientation with increasing spinning speed. The PES/H11 fiber has a slightly higher level of overall molecular orientation at equivalent spinning speed versus the neat PES. The overall molecular orientation for the bicomponent PES/H11 fibers appear to be slightly shifted to lower spinning speeds when compared to neat PES. The other noteworthy point is the slight decrease in birefringence for neat PES at the highest spinning speeds.

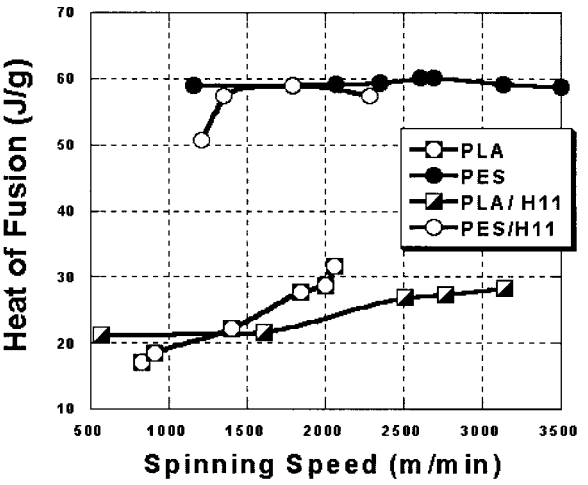

Figure 4. Heat of Fusion versus Spinning Speed for the biodegradable polymers.

According to Figure 5, the PLA based fibers generally increase in overall molecular orientation with increasing spinning speed, except at the highest velocity where there appears to be a slight decrease in overall molecular orientation. This decrease in birefringence has been observed for PLA based fibers[10]. The neat PLA fibers have slightly higher overall molecular orientation than the PLA/H11 fibers at equivalent spinning speed. However, the PLA/H11 compositon has an extended spinning speed range in which it develops higher overall levels of molecular orientation. When the ΔH_f (i.e. crystallinity) data is included with the birefringence, the data appears to indicate the neat PLA fibers have a higher level of crystallinity at equivalent spinning speeds when compared to PLA/H11, suggesting it generates more stress and more overall molecular orientation, while the bicomponent fibers crystallization is delyaed until higher filament velocities, hence stresses are developed.

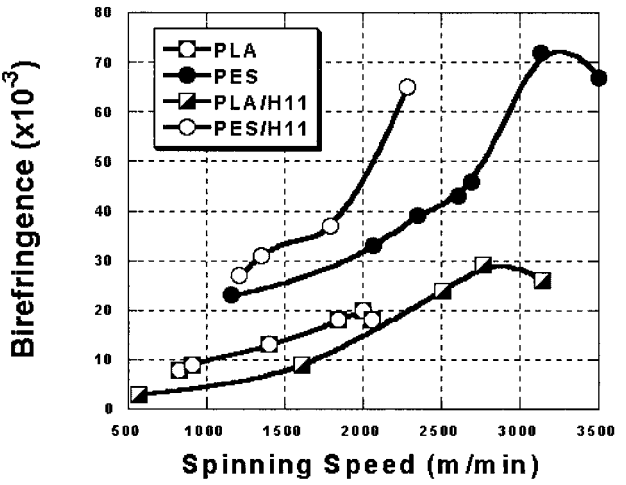

Figure 5. Birefringence versus Spinning Speed for the biodegradable polymers.

Tensile Mechanical Properties of Bicomponent Fibers

The data in Figure 6 shows the ultimate tensile strength versus spinning speed for all fiber compositions. The fiber tensile strengthes generally increase with increasing spinning speed. The lone exceptions are the neat PLA and PES at their highest spinning speed. Since PLA and PES are both polyester based polymers, they should behave as most polyesters due in that they tend to show a decrease in tensile strength at high spinning speeds[11]. This observation has been made with PLA previously[10]. It has not, to this author's knowledge been observed in a low Tg polyester based polymer such as PES.

When tensile strength profiles of the PLA and PES based fibers are compared in Figure 6, two observations are made. First, at low spinning speeds, the PLA/H11 fiber is significantly weaker than neat PLA, by as much as 100MPa. However, the PLA/H11 composition has an broader spinning speed range that allows it become stronger as the filament is further attenuated, ultimately becoming stronger as the stress is increased and filament diameter decreases.

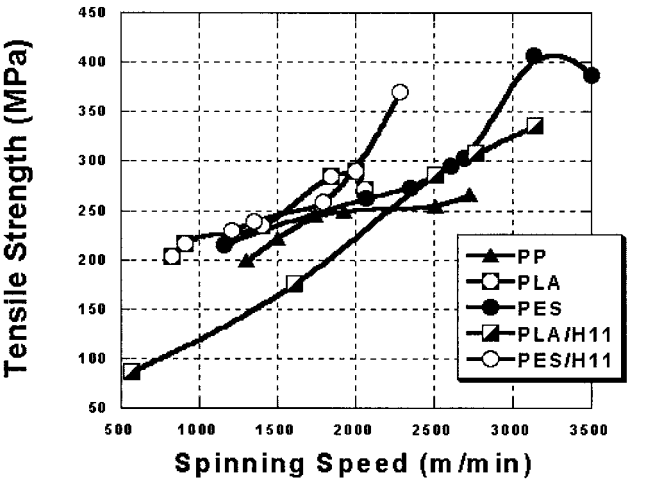

Figure 6. Fiber Ultimate Tensile Strength versus Spinning Speed.

The second trend appears when PES is compared to the PES/H11 fiber. Below 1700m/min, the two fibers have nearly identical strengthes. As the spinning speed increases further, the PES/H11 fiber has a sharp increase in tensile strength then breaks at 2250m/min, while the neat PES continues to slowly increase until 2700m/min. The PES fiber then dramatically increases in strength at 3000m/min, followed by a decrease in strength at 3500m/min. This trend is similar to the birefringence profile for PES in Figure 5. The second major point of interest is that for most all fiber compositions (except for PLA/H11 below 2000m/min), they have similar tensile strengths to PP.

The data in Figure 7 shows the fiber elongation-at-break versus spinning speed. The general trend is that with increasing spinning speed, the elongation-at-break decreases for each fiber composition. This is most often the case, since as the spinning speeds increases, overall molecular orientation (birefringence) increases, the fiber gets stronger and the residual elongation of a filament decreases. These results also indicate the PLA based fiber compositions have substantially lower elongation at break than the PES system. These lower elongations-at-break, at room temperature, are mostly attributed to the fact that PLA is well below its Tg when the fibers are tested.

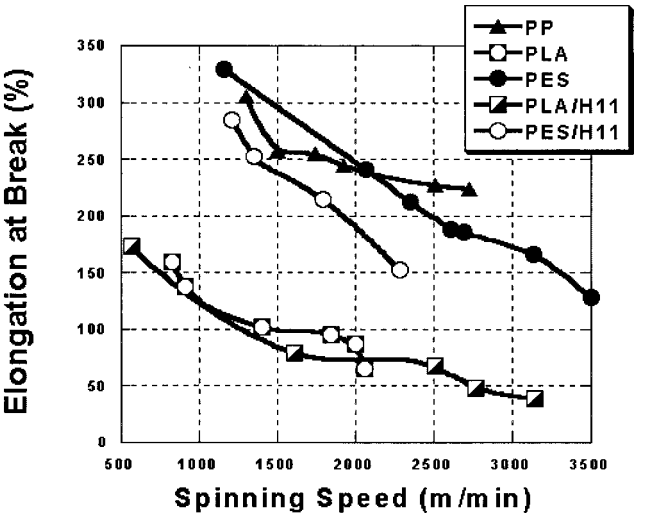

Figure 7. Fiber Elongation-at-Break versus Spinning Speed.

The data in Figure 8 shows the fiber tensile strength versus birefringence for the PLA and PES series of fibers. There are two distinct observations in this data. The first as that the PLA and PLA/H11 based fibers fall onto a similar line to one another, as do the PES and PES/H11. The second is that the two master curves are not the same, indicating the inherent birefringence of PLA and PES are different. The data also suggests the interface between the two components for both the PLA and PES bicomponent fibers appears to be at least a partially miscible and does not appear to disrupt the index of refraction measurements, upon which the birefringence is based.

When the as-spun fiber structure and properties of the biodegradable polymers are collectively studied, two general observations can be found, both related to the same experimental phenomenia. This phenomenia is the failure of the H11 core to crystallize in the spinline, resulting in a heat source being encapsulated into the core of the PLA and PES fibers. However, due to the difference in Tg of the PLA and PES, the results on the fibers properties due to the presence of the hot H11 core are very differenent for PLA and PES, respectively.

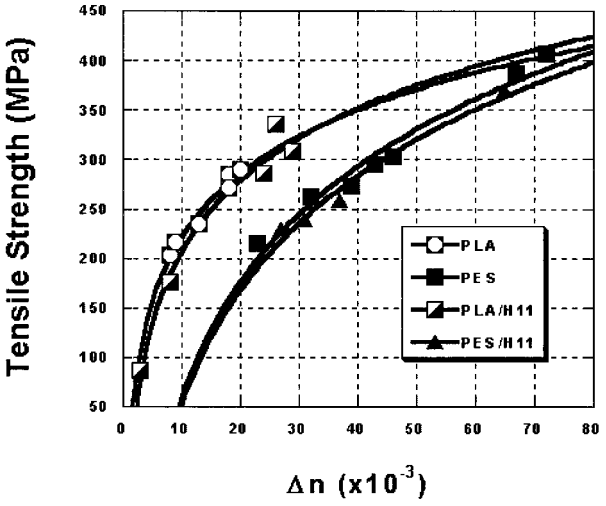

Figure 8. Fiber Tensile Strength versus Birefringence for the Bicomponent Compositions.

1) PLA: The neat PLA fibers are more highly oriented and stronger than the PLA/H11 fibers at equivalent spinning speeds. At equivalent spinning speeds, the orientation and strength is lower in the PLA/H11 fibers because the hot H11 core is relaxing or delaying the structure being developed in the sheath, which delays crystallization. For neat PLA, there is a limit to the delay in crystilization, since the PLA quickly passes through its Tg where the morphology is essentually frozen in as the filament undergoes further attentuation. However, for the PLA/H11 the delayed crystallization does result in an extended spinning speed range over the neat PLA at 190°C. The extended spinning speed range allows more molecular orientation to be developed, producing stronger filaments. This processing temperature for PLA is likely to be slightly cold, based on previous research[10].
2) PES: In the case of PES/H11 fibers, the hot H11 core also delays crystallization. The present data suggests the delay in crystallization allows the PES/H11 fiber to develop more stress, hence a more oriented fiber that is stronger with a lower elongation at break. This increased stress somewhat lowers the spinning speed range for the bicomponent PES/H11. The biggest

difference in structure development between the PLA and PES bicomponent fibers, is the PES/H11 is still able to crystallize quite significantly in the spinline after the delay in crystallization onset, based on the ΔH_f data, due in large part to its relatively low Tg.

Conclusions

Both neat and bicomponent as-spun fibers produced from PLA and PES with a core of H11 have fiber properties comparable to a standard PP. The presence of the slow crystallizing H11 core delayed crystallization in the spinline. The delay in crystallization produced PLA and PES bicomponent fibers that had opposite impacts on filament structure and properties due to the presence of the H11. In the case of PLA, the PLA/H11 fibers has lower orientation and strength versus neat PLA at equivalent spinning speeds. The PES/H11 fibers were more orientated and stronger than the neat PES fiber at equivalent spinning speeds. These differences are explained by the difference in Tg between PLA and PES.

Acknowledgements

The author wishes to thank Isao Noda and Dave Melik for conversations on PHA based polymers. Judson Haynes, Daniel Wheeler and Barb Nuck all contributed to measuring some of the properties of these polymers and fibers, their contribution is appreciated.

[1] A.J. Anderson, E.A. Dawes, *Microbiol. Rev.* 1990, **54**, 450.
[2] Y. Doi, "Microbial Polyesters", VCH Publishers, New York 1990, p6.
[3] H. Verhoogt, B.A. Ramsay, B.D. Favis, *Polymer* 1994, **35**, 5156.
[4] K.C. Berger, G. Meyerhoff, in "Polymer Handbook", 3rd ed., J. Brandup, E.H. Immergut, Eds., J. Wiley & Sons, New York, 1989, pII/67ff.
[5] M. Vert, *Angew. Makromol. Chem.*, 1989, **15**, 166/167.
[6] D.F. Williams, *Ann. Rev. Material Science*, 1976, **6**, 237.
[7] D.F. Williams, *J. Material Science*, 1982, **17**, 1233.
[8] E.B. Bond, J.E. Spruiell, *J. Applied Polym. Sci.*, 2001, **82**, 3223.
[9] E.B. Bond, J.E. Spruiell, *J. Applied Polym. Sci.*, 2001, **82**, 3227.
[10] K. Mezghani, J.E. Spruiell, *J. Polym. Sci. Polym. Phys.*, 1998, **36**, 1005.
[11] G. Perez, "High-Speed Fiber Spinning", A. Ziabicki, H. Kawai Eds., Krieger, Florida, 1991.