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High performance poly(ethylene terephthalate) fibre properties achieved via high speed spinning with a modified liquid isothermal bath process

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A liquid isothermal bath (LIB) was used in the spinline to produce high performance poly(ethylene terephthalate) (PET) fibres at high speed melt spinning in a one step process. The take-up stress was measured under various spinning conditions. It was found that maximum applicable take-up stress was determined by the state or morphology of the filament before entering the liquid bath. To render the filament more amenable to a preferred morphological texture prior to its entry into the liquid bath, a small amount of hot liquid was applied to the running filament at a position upstream of the liquid bath. The results show that rapid cooling leads to a non-uniform fibre structure and the loss of subsequent filament deformability. However, the prolongation of attenuation, attendant the heating of the filament before entering the liquid bath, induced uniform radial structure and an increase of deformability. Then the maximum operable liquid depth within the LIB could be attained. Furthermore, the delay of attenuation in the upper portion of the liquid bath and the attendant increase of stress within the liquid bath also resulted in an increase of the tensile properties. The modified LIB process was suggested as a further control of the temperature profile upstream of the liquid bath. High tenacity (9.7 g d^{-1}), high modulus (>120 g^{-1}) and high load at a specified elongation of 5% (LASE-5) (>4 g d^{-1}) PET of as-spun fibres are achievable using the modified LIB one step process. The as-spun fibres produced with the modified LIB process have high amorphous orientation, low crystallinity and relatively large crystallite size. After drawing and annealing, the fibres exhibit desirable characteristics of high tenacity (>11 g d^{-1}), high modulus (>140 g d^{-1}), high LASE-5 (5.8 g d^{-1}), and low shrinkage (<6%). © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(ethylene terephthalate); high performance fibre; threadline modification)

INTRODUCTION

High tenacity, high modulus poly(ethylene terephthalate) (PET) fibres are used in various industrial applications, such as reinforcements for rubber articles (i.e. tyres and hoses), geotextiles, ropes and cordage. To obtain high performance PET fibres, much effort has been expended in spin–draw processes[1,2], high speed melt spinning[3,4], zone drawing/zone annealing[5,6], solid state extrusion[7,8], and solution spinning[9,10]. However, only the first technique has been used in a commercial production process, wherein the as-spun fibres were made by relatively low speed spinning (<1500 m min^{-1}), followed, in a separate step, by drawing and heat setting. Recently, a liquid isothermal bath (LIB) spinning process was developed by Cuculo and coworkers[11,12]. This process makes possible formation of high tenacity, high modulus PET fibres via melt spinning at high speeds (up to 5000 m min^{-1}). For the LIB process, the spinline stress within the liquid bath was enhanced by friction between the filament and the liquid. This leads to 'super-deformation' in the liquid bath, i.e. a neck-like deformation[12].

In our previous work[13], the effect of the processing parameters on structure and properties has been widely studied, such as take-up speed, liquid bath position, depth, and temperature. However, methods to respectively control the stress and temperature profiles of the filament before entering the liquid bath in order to further improve the tensile properties of PET fibres are still undefined. It is well known that the stress and temperature (together with time) are the most important parameters in melt spinning. In this paper, the effects of stress and temperature on the properties of PET fibres have been considered separately. Also, a modified liquid bath process was used instead of the normal liquid bath process to further modify the threadline parameters upstream of the liquid bath.

EXPERIMENTAL

Spinning process

The PET resins used in this study had an intrinsic viscosity (IV) of 0.97 dl g^{-1}. Prior to spinning, each PET chip was dried in a vacuum oven at 140°C for at least 14 h. A hyperbolic spinneret with a round orifice having a diameter of 0.6 mm, as described by Ihm and Cuculo[14], was employed in this work. The LIB used is described

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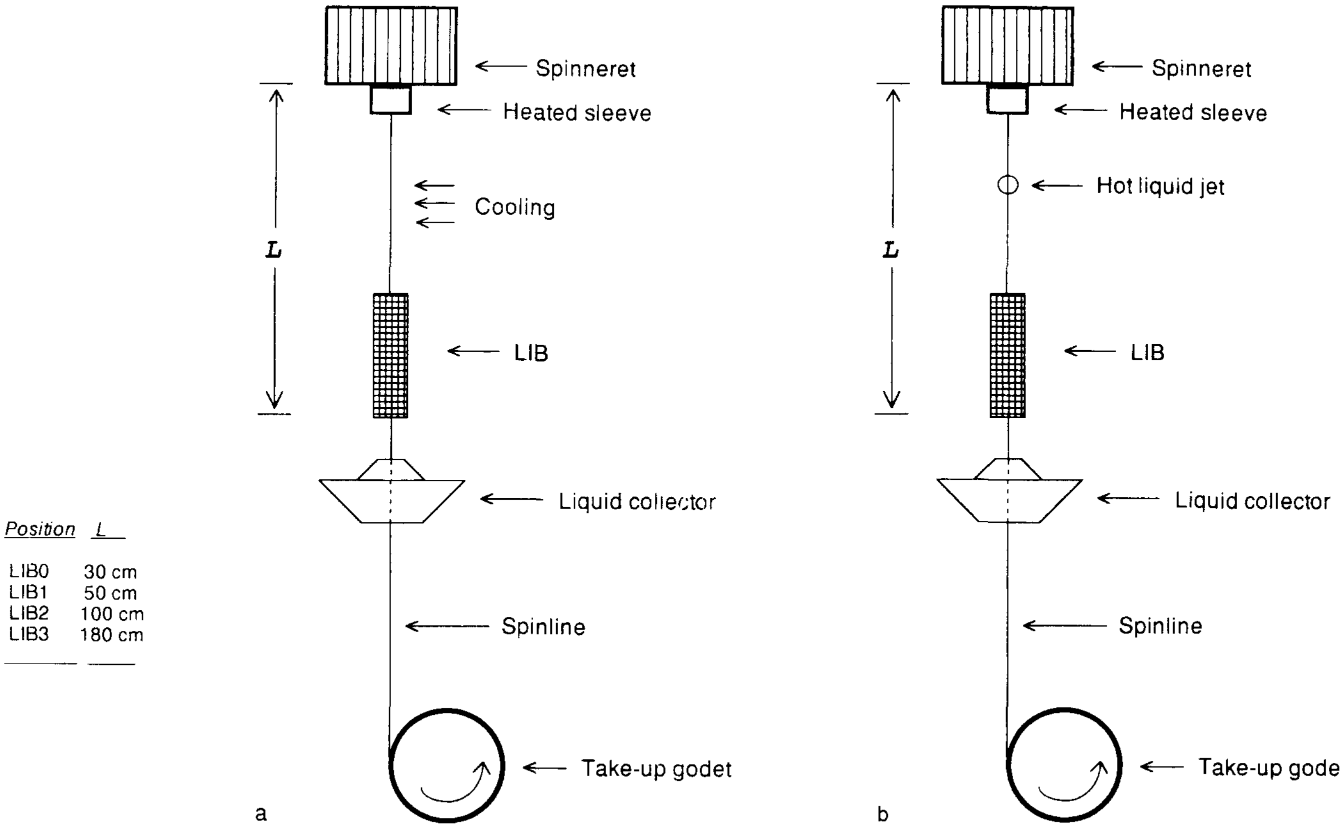

Position	*L*
LIB0	30 cm
LIB1	50 cm
LIB2	100 cm
LIB3	180 cm

Figure 1 Schematic diagram of melt spinning with liquid isothermal bath. (a) The normal LIB process. (b) The modified LIB process

elsewhere[11]. For the normal liquid bath process, the liquid bath was placed in the threadline at LIB position 3, that is 150–180 cm from the spinneret (*Figure 1a*). The modified LIB process was developed with the intention of increasing the filament temperature prior to its entry to the liquid bath (*Figure 1b*). The liquid bath was still located at LIB position 3 as in the normal LIB process. However, in the modified process, a hot liquid was applied at a suitable location. The hot liquid encased the filament resulting in a reduction of its cooling rate.

Tensile properties

A table model 1122 Instron tensile tester was used to measure tenacity, ultimate elongation, and initial modulus, in accordance with ASTM D3822-82. The fibre sample was tested at a gauge length of 25.4 mm and at a constant crosshead speed of 20 mm min^{-1}. The load at a specified elongation of 5% (LASE-5) was measured from the load–elongation curves.

Thermal shrinkage

Thermal shrinkage was determined under a tension of 0.05 g d^{-1} at 177°C. Measurements were taken at equilibrium, in accordance with ASTM D855.

Polarizing microscopy

A Nikon polarizing microscope equipped with a Leitz tilting compensator was used to measure the birefringence of the fibres. The average birefringence was based on the mean value of five individual values.

Density and crystallinity

Fibre density was measured at 23°C using a density gradient column filled with sodium bromide solution in the density range of 1.335–1.415 g cm^{-3}. The sample preparation and density measurement were in accordance with ASTM standard D1505-68. The volume fraction crystallinity was calculated from the equation:

$$X_c = \frac{\rho - \rho_a^o}{\rho_c^o - \rho_a^o} \qquad (1)$$

where ρ is the density of the fibre, and ρ_c^o and ρ_a^o are the respective densities of the crystalline and amorphous phases. The values of ρ_c^o and ρ_a^o used in the calculation for PET are 1.455 and 1.335 g cm^{-3}, respectively[15].

Wide-angle X-ray scattering

A Siemens type-F X-ray diffractometer system equipped with a nickel-filtered CuKα ($\lambda = 1.54$ Å) radiation source and a proportional counter was used in the analysis of the crystalline structure of PET samples.

The apparent crystalline size was determined according to the Scherrer equation:

$$L_{\mathrm{hkl}} = \frac{K\lambda}{\beta\cos\theta} \qquad (2)$$

where β is the half width of the diffraction peak, K is taken to be unity, θ is the Bragg angle, and λ is the wavelength of X-ray used. The crystalline orientation factor, fc, is related to $\langle\cos^2\phi_{c,z}\rangle$ as follows:

$$fc = [3\langle\cos^2\phi_{c,z}\rangle - 1]/2 \qquad (3)$$

where ϕ is the angle between the c crystallographic axis and the fibre axis. For PET, the $(\bar{1}05)$ plane is used to determine f_c. The value of $\langle\cos^2\phi_{c,z}\rangle$ is determined from azimuthal intensity measurement on the reflection of

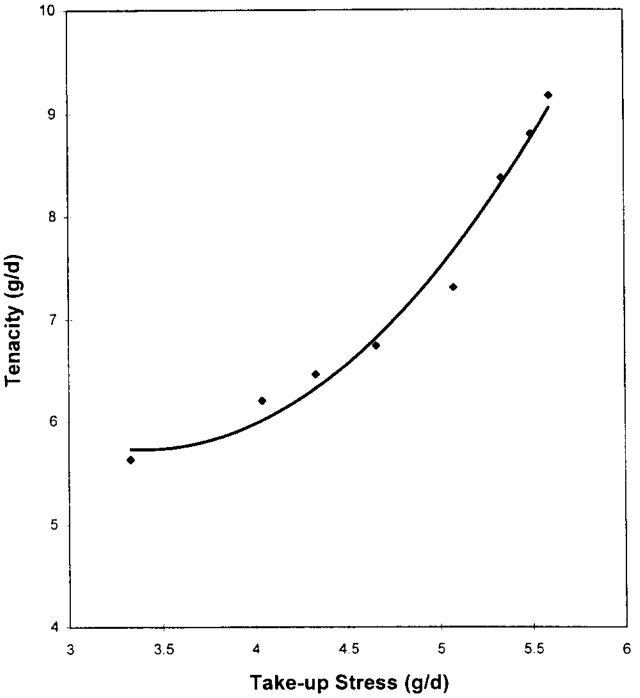

Figure 2 Effect of take-up stress on tenacity of as-spun fibres with the normal LIB process

($\bar{1}05$) using the following equations:

$$\langle \cos^2 \phi_{\bar{1}05,z} \rangle = \left[\int_0 \mathrm{I}(\phi) \sin\phi \cos^2 \phi d\phi \right] \Big/ \left[\int_o I(\phi) \sin\phi d\phi \right] \quad (4)$$

$$\langle \cos^2 \phi_{c,z} \rangle = \langle \cos^2 \phi_{\bar{1}05,z} \rangle / \cos^2 \alpha \quad (5)$$

Where $\phi_{\bar{1}05,z}$ is the angle between the ($\bar{1}05$) reflection plane normal and the fibre axis and α is the angle between the ($\bar{1}05$) reflection plane normal and the c crystallographic axis.

Amorphous orientation

The amorphous orientation factor, fa, was determined using the following relationship:

$$\Delta n = \Delta n_c^o f_c X_c + \Delta n_a^o f_a (1 - X_c) \quad (6)$$

Where Δn is the total birefringence of the fibre, X_c is the volume fraction crystallinity, and Δn_c^o and Δn_a^o are the respective intrinsic birefringences of the crystalline and the amorphous regions. The values of Δn_c^o and Δn_a^o are 0.22 and 0.275[16].

RESULTS AND DISCUSSION

The effects of take-up stress on properties

Take-up force was measured at a point near the take-up device using a Rothschild Tensometer. The take-up stress was calculated according to the final denier of the fibres. *Figures 2* and *3* shows that tenacity and modulus increase with increase of the take-up stress. Take-up stress, grammes per dernier (gd^{-1}), for the normal cooling process has been measured and is reported to be within the range 0.2–0.4 g d^{-1}, for take-up speed from 3000 m min^{-1} to 5000 m min^{-1}. The take-up stress of the normal cooling process is considerably lower than the take-up stress using the liquid bath process. This implies that the air drag contribution to the development of spinline stress is essentially negligible when compared with that contributed by the liquid drag. Therefore, the take-up stress may be considered as a first approximation to the stress experienced within the liquid bath, which in turn is directly related to the depth of the liquid bath.

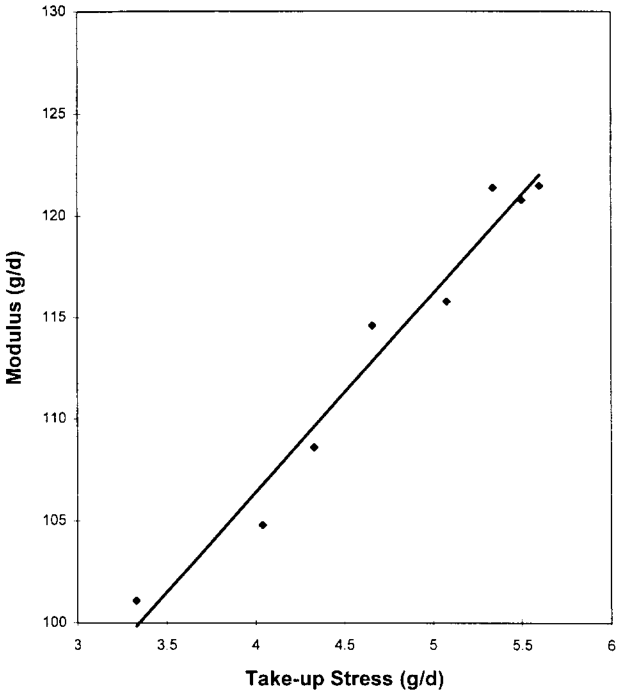

Figure 3 Effect of take-up stress on modulus of as-spun fibres with the normal LIB process

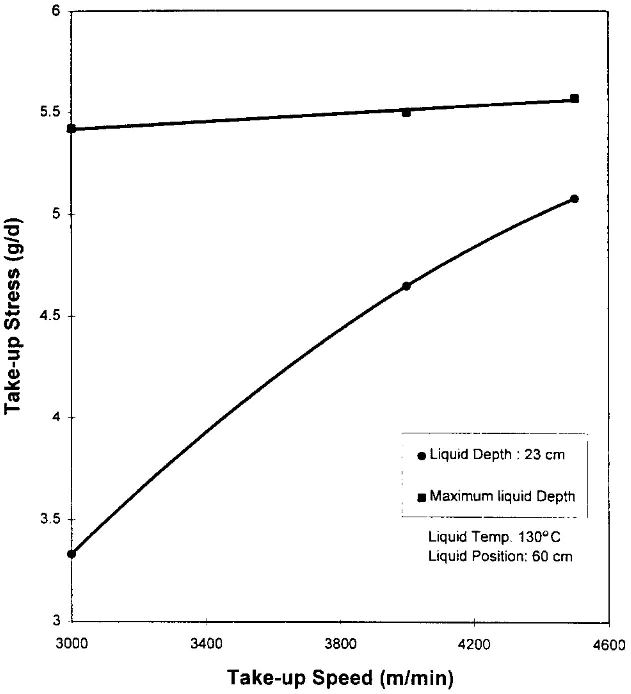

Figure 4 Relationship between take-up speed and take-up stress at a given liquid depth and the maximum liquid depth

Figure 4 plots take-up stress as a function of the take-up speed. The liquid bath, maintained at 130°C, was

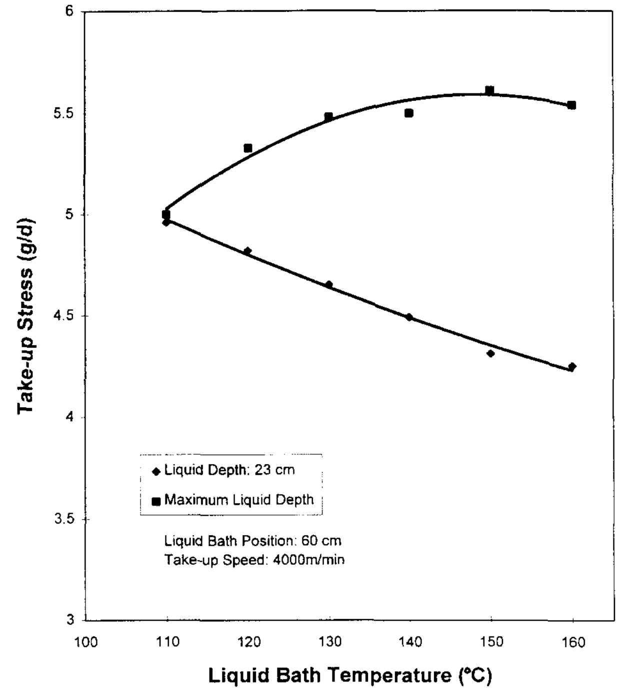

Figure 5 Relationship between the liquid temperature and take-up stress at a given liquid depth and the maximum liquid depth

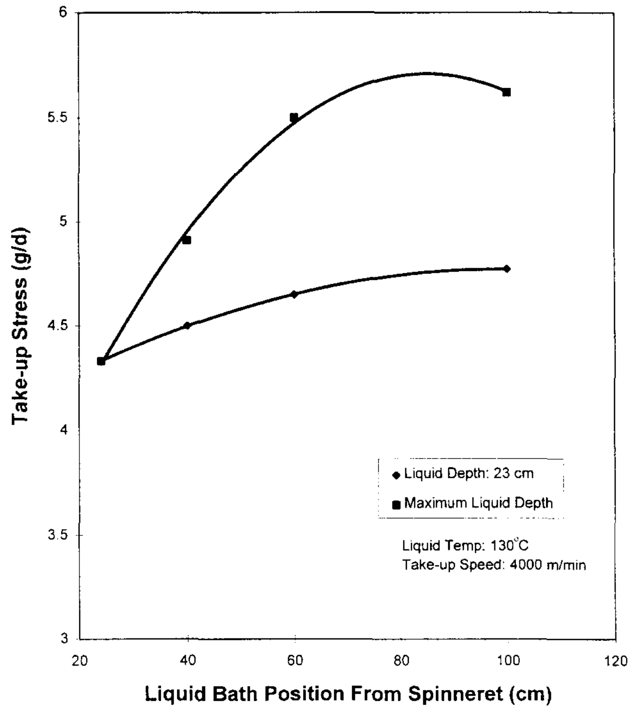

Figure 6 Effect of the liquid bath position on take-up stress at a given liquid depth and the maximum liquid depth

positioned 60 cm from the spinneret face. As predicted, the take-up stress increased with increasing take-up speed at a given depth of liquid bath (23 cm). However, take-up stress showed no significant difference with the change of take-up speed, when the maximum applicable liquid depth was used for each take-up speed at the given temperature and position.

Figure 5 plots take-up stress as a function of the liquid temperature at a take-up speed of 4000 m min^{-1}. The liquid bath was still located 60 cm from the spinneret. The take-up stress decreased as the liquid temperature was increased from 110 to 160°C when the liquid depth was held constant at 23 cm. However, by increasing the liquid temperature, the liquid viscosity drops, and the maximum liquid depth which can be achieved increases. Also shown in *Figure 5* is how the take-up stress changes with increasing liquid temperature as the corresponding maximum liquid depth is simultaneously maintained. However, it should be noted that the take-up stress does not show any further increase for the liquid temperatures greater than 130°C. As seen in *Figures 4* and *5*, the maximum applicable take-up stress is *ca* 5.5 g d^{-1} regardless of take-up speed used for a given liquid bath position and liquid temperatures above 130°C. This implies that the filament can tolerate or bear only a limited stress within the liquid bath at a given liquid bath position. However, this stress limit is related to the temperature of the filament prior to entering the liquid bath. It has been reported[11] that under the particular extrusion conditions, the filament temperature at 60 cm from the spinneret is above 130°C. Thus, the filament is cooled if the liquid temperature is lower than that of the filament. This increased cooling may be the cause of the lower maximum stress levels for liquid temperatures below 130°C, as shown in *Figure 5*.

Figure 6 shows the relationship between take-up stress and liquid bath position. It was found that take-up stress changed only slightly with alteration of liquid position at a given fixed liquid depth, liquid temperature and take-up speed. However, if the maximum applicable liquid depth was used in each run, take-up stress was lower for the liquid position closest to the spinneret. In fact, spinning operability for the liquid bath position closest to the spinneret was poor. Only low liquid depth could be used in this case, which resulted in low take-up stress. In addition, when close to the spinneret, the threadline appears to be weak because, we believe, the filament was quickly cooled by the liquid bath due to the lower temperature of the liquid bath (130°C). It has been reported[13] that non-uniform structure was obtained in the fibres which were spun at the liquid bath position closest to the spinneret. Actually, the radial distribution of molecular orientation is related to the temperature distribution and if rapid cooling of the fibre surface occurs, the radial variation of temperature produces a distribution of viscosity in the spinline cross section. Tensile spinning stress along the spinline is given simply by $\sigma = \eta_T (\mathrm{d}V/\mathrm{d}x)$, where the velocity gradient $\mathrm{d}V/\mathrm{d}x$ is assumed to be uniform in the cross section, η_t is elongational viscosity of the polymer at a given temperature. The viscosity in the skin is higher than that of the core and this situation induces non-uniform tensile stress and an orientation distribution in the cross section. The higher the cooling rate, the higher the degree of radial variation. Therefore, a non-uniform structure was formed as the filament was quickly cooled. Hence, only a relatively lower maximum take-up stress could be applied in this case. However, a uniform structure was observed in the fibres when the liquid bath was located at the positions more distant from the spinneret where the filament had nearly solidified[13] (LIB2 in *Figure 1*) or completely solidified (LIB3 in *Figure 1*) prior to entering the bath. The results suggest that the maximum applicable take-up stress was also strongly affected by the state or morphological characteristics that the filament exhibited before

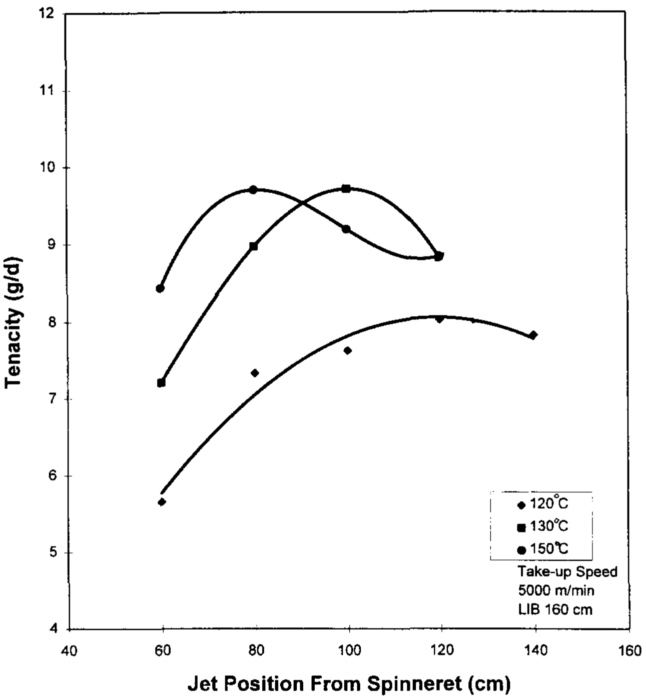

Figure 7 Effect of the hot liquid jet position on tenacity of PET fibre from the LIB process

entering the liquid bath. In *Figure 6*, it was noted that take-up stress did not show a significant change when the liquid bath was located beyond 80 cm from the spinneret, when the maximum liquid depth was used. It has also been found that the tensile properties of fibres spun under the above conditions did not show significant change as a function of the maximum applicable liquid depth. This result also suggests that similar morphologies may exist in all of the filaments which enter the liquid bath, when the liquid bath is located at positions beyond 80 cm from the spinneret. In fact, preliminary on-line measurements have indicated that the filament has nearly solidified, or completely solidified before entering the bath when located at these more distant positions. After combining the results shown in *Figures 4*, *5* and *6*, the constancy of the take-up stress becomes evident when the maximum liquid depth is maintained, the bath position is greater than or equal to 80 cm, and the temperature held above 130°C, regardless of what take-up speed is applied.

Effects of temperature of hot liquid jet

As discussed above, the maximum applicable take-up stress was affected by the filament temperature and morphological character of the developing threadline before entering the liquid bath. Therefore, the relationship between the temperature of the fibre upstream of the liquid bath and take-up stress will be discussed in this section. It has been reported[13] that the optimum temperature of the liquid bath is approximately 140–160°C. However, this conclusion was based upon experiments in which the depth of liquid bath was kept constant. In these cases, the stress was different for each temperature due to reduction of liquid viscosity with increasing temperature. To avoid this problem, the maximum liquid depth was consistently maintained and the liquid bath was placed 160 cm from the spinneret for all experiments discussed in this section. In addition, a small amount of hot liquid was applied to the running filament at a position upstream of the liquid bath. Since there was no liquid recovery device in position, the small amount of liquid that was applied to the filament upstream of the liquid bath simply ran down with the filament without developing any pool or 'depth of liquid'. The filament was then heated or cooled by the liquid jet applied upstream of the liquid bath. In this way, we can further consider how the liquid and/or threadline temperature affects threadline stress and resulting tensile properties.

Figure 7 shows the relationship between the tenacity and hot liquid application position at specific given liquid temperatures. For this series, the take-up speed was maintained at 5000 m min^{-1} and the liquid bath was located 160 cm from the spinneret. It was found that tenacity passed through two well defined maxima at the two higher jet temperatures and a less well defined maximum at the lower temperature as a function of jet position. The best hot liquid jet position is *ca* 80–100 cm from the spinneret. As mentioned above, it was assumed that the same maximum liquid depth could be applied if the same take-up speed, liquid bath position and liquid temperature were respectively used for each run. However, the maximum applicable depth was found to be lower when the hot liquid jet was moved closer to the spinneret. This means that the modified temperature profile prior to the liquid bath in some manner affects the maximum applicable take-up stress and the tensile properties of the resulting fibres. As we know, the filament temperature decreases gradually after leaving the spinneret. As seen in *Figure 7*, the highest tenacities are attained at the higher jet temperatures at distances *ca* 80–100 cm from the spinneret. The low tenacity and low achievable liquid depth are believed to be a consequence of the cooling effect and its negative impact on structure uniformity that the liquid jet likely has on the filament when located relatively closer to the spinneret.

Figure 8 shows the relationship between the tenacity and the temperature of the hot liquid jet at the hot liquid jet position of 80 cm. It was found that the optimum liquid temperature is *ca* 130–150°C. *Table 1* shows the maximum liquid depth, birefringence and crystallinity of fibres for each run at a take-up speed of 5000 m min^{-1}. *Table 1* also shows how the maximum achievable liquid depth varies with the liquid temperature. The maximum liquid depth increases quickly with increasing liquid temperature until reaching a liquid temperature of *ca* 130°C. Above this temperature only slight increases in liquid depth are attainable. The birefringence shows a similar type of response with the maximum value being achieved at a temperature of 140°C. One reason for the lower maximum achievable liquid depth at lower liquid temperatures is most likely the increased liquid viscosity associated with these lower temperatures. However, it must be noted that the maximum liquid depth at liquid temperature of 130°C is more than twice that at 110°C. *Figure 5* shows the variation in take-up stress with liquid temperature for both a fixed liquid depth condition and a variable liquid depth condition in which the maximum achievable liquid depth was maintained. For a fixed liquid depth condition the measured take-up stress as a function of liquid temperature should be considered proportional to the variation in liquid viscosity. The magnitude of the variation of take-up stress with liquid temperature for the fixed liquid depth condition clearly shows that the

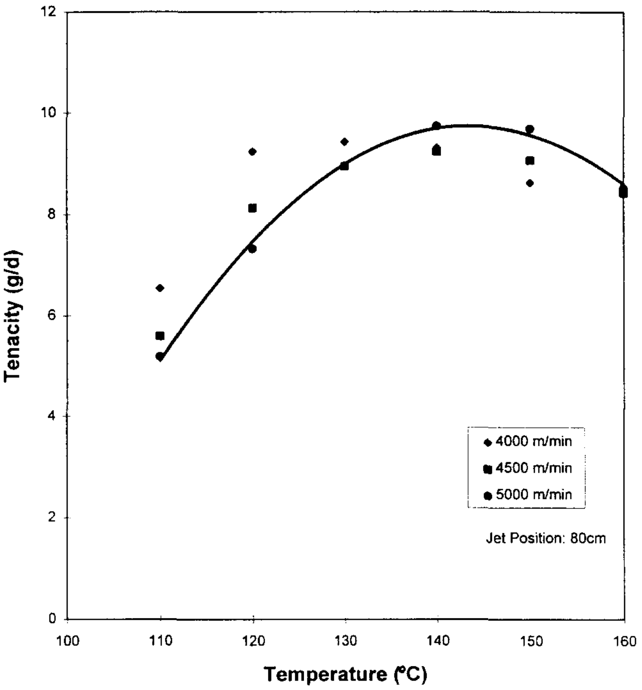

Figure 8 Effect of the hot liquid jet temperature on tenacity of PET fibre from the LIB process

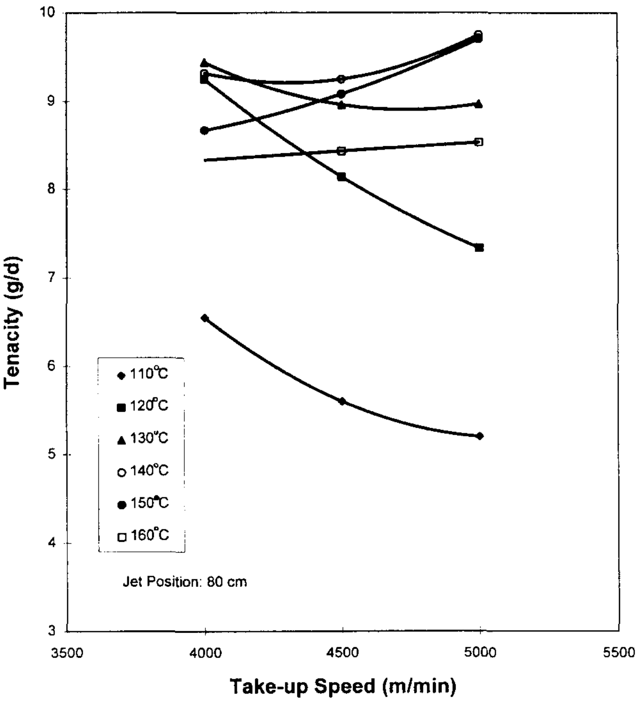

Figure 9 Effect of take-up speed on tenacity of PET fibre from the LIB process with a hot liquid jet

increase in viscosity with decreasing liquid temperature is, on its own, not enough to account for the large drop in the maximum achievable liquid depth. As stated previously, non-uniform structures can be generated when the filament is prematurely cooled by the liquid bath. The development of this type of non-uniform structure may be another, more predominant, reason that only a very low maximum liquid depth could be applied at low liquid temperature. It has been previously confirmed[13] that a uniform radial structure was observed in the resulting fibre when the liquid bath was located at LIB position 3 (180 cm from spinneret). It has also been emphasized[11] that the attenuation of the filament prior to the liquid bath is delayed when the LIB is located in this distant position. This prolongation of the attenuation or draw-down process might result in a filament with a uniform structure, which could then bear a much higher stress within the liquid bath. It is also being suggested that the temperature of the liquid jet should be higher than that, or at least very near to that, of the filament in order to obtain high tenacity fibres. On the other hand, it was noted that the tenacity of fibre spun at the liquid temperature of 160°C had been reduced even though the maximum achievable liquid depth was highest in this series. As shown in *Table 1*, the fibre spun at a liquid temperature of 160°C possessed relatively higher crystallinity and lower birefringence. Previously reported findings have shown that the use of such high liquid temperatures typically results in enhanced crystallization[13]. However, as might be anticipated, this enhanced crystallization almost always comes at the expense of reduced amorphous orientation. While these two parameters have not yet been determined for these particular fibres, this same type of structural balance (high crystallinity and low amorphous orientation) is believed to be present and to be the main reason for the reduction in tenacity occurring at the higher liquid temperatures. Finally, the structure of the resulting fibre will undoubtedly also be strongly affected by the temperature profile upstream of the liquid bath.

Figure 9 illustrates an interesting finding, namely, the effect of take-up speed on tenacity of fibres at various liquid temperatures. In the liquid temperature range 110–120°C, the tenacity decreased with increasing take-up speed at a given hot liquid jet position. But, the tenacity increased with increasing take-up speed in the liquid temperature range of 130–150°C. From *Figures 7* and *8*, it has been concluded that the filament is cooled by the liquid jet when the hot liquid jet was placed 80 cm from the spinneret and liquid temperature is lower than 130°C. It has also been mentioned in the last section that rapid cooling may lead to a non-uniform structure and suppress

Table 1 Characterization data from fibres at various liquid temperatures

	Sample no.					
	1	2	3	4	5	6
Take-up speed ($m\,min^{-1}$)	5000	5000	5000	5000	5000	5000
Temp. of liquid jet (°C)	110	120	130	140	150	160
Depth of liquid (cm)	13	19	28	30	32	33
Tenacity of fibres ($g\,d^{-1}$)	5.21	7.33	8.97	9.75	9.7	8.53
Modulus of fibres ($g\,d^{-1}$)	94.5	108.9	121.8	125.6	126.0	125.1
Birefringence, Δn	0.1764	0.1986	0.2146	0.2244	0.2219	0.2108
Crystallinity, X_c	0.209	0.221	0.234	0.266	0.282	0.333

Table 2 Characterization data from the normal LIB and the modified LIB processes

Sample no.	Take-up speed ($\mathrm{m\,min^{-1}}$)	Liquid temperature (°C)	Liquid jet (cm)	Tenacity ($\mathrm{g\,d^{-1}}$)	Modulus ($\mathrm{g\,d^{-1}}$)	Elongation (%)	LASE-5 ($\mathrm{g\,d^{-1}}$)	SAR (%)	Δn	X_c	f_c	f_a	L105 (Å)
1	4000	130	–	8.95	100.0	11.2	3.03	60.6	0.208	0.156	0.922	0.761	28.81
1a	4000	130	80	9.44	121.1	10.6	4.11	67.9	0.219	0.143	0.924	0.806	43.82
2	4000	140	–	9.14	101.3	11.5	3.10	61.2	0.212	0.171	0.929	0.777	33.24
2a	4000	140	80	9.32	121.7	11.5	4.20	69.0	0.221	0.157	0.932	0.814	49.95
3	5000	150	–	8.72	113.5	11.3	3.82	67.3	0.218	0.238	0.934	0.807	–
3a	5000	150	80	9.75	125.6	11.0	4.36	69.4	0.224	0.221	0.932	0.834	–

Note: Samples 1a, 2a, and 3a were spun from the modified LIB process

the maximum deformability of the filament in the spinline. On the other hand, based on diameter profile measurements above the liquid bath, which will be discussed in detail in a forthcoming publication, attenuation in the upper portion of the threadline prior to the liquid bath was delayed with increasing take-up speed, when the liquid bath was placed in the same position. It is clear that the temperature difference between the filament and the liquid jet is larger for a high take-up speed than for a low take-up speed at liquid temperatures of 110–130°C. Hence, the filament was quickly cooled by the liquid jet at high take-up speed, resulting in poor deformability and low tenacity.

As concluded earlier, when the respective maximum liquid depths were used with a given liquid bath position beyond 80 cm and temperature above 130°C, the take-up stress remains essentially constant regardless of the take-up speed. In *Figure 9*, the tenacity increased with increasing take-up speed in the liquid temperature range of 130–150°C. The question is what is responsible for the improvement in the tensile properties with increasing take-up speed. Actually, the attenuation in the upper portion of the liquid bath was delayed with increasing take-up speed according to diameter profile measurement. In addition, at the liquid temperatures of 130–150°C, the temperature of the liquid jet was higher than or approaching the filament temperature. These two conditions might imply that delay of the attenuation process may result in the formation of a more uniform structure and an increase of filament deformability in the spinline. This change in the mechanism of the morphology development is accompanied by property improvements in the fibres. These considerations generated the suggestion to modify the temperature profile of the fibre upstream of its entry into the liquid bath.

Comparison between the modified LIB process and the normal LIB process

The properties and morphology of fibres spun from the modified LIB process and the normal LIB process will be compared in this section. For a modified LIB process, a small amount of hot liquid was applied to the running filament at a position upstream of the liquid bath. Since there was no liquid recovery device in position, the liquid that was applied to the filament simply ran down with the filament without developing any pool or 'depth of liquid'. The filament was heated by the hot liquid applied prior to the liquid bath. Therefore, the attenuation process was delayed if other spinning parameters were unchanged from the normal LIB process. The mechanical properties of the fibres are listed in *Table 2*. It is clear that relatively higher tenacity, initial modulus and LASE-5 were achieved by using the modified LIB process, however, the elongations were almost the same as those achieved using the normal LIB process. The tenacity and initial modulus of the samples made by the modified LIB process showed an average increase of 6 and 20%, respectively. LASE-5 values are one method of quantifying differences in dimensional stability at room temperature. Therefore, the higher LASE-5 value is representative of higher fibre dimensional stability at lower temperatures. The LASE-5 value of each sample made by the modified LIB process is over $4.0\,\mathrm{g\,d^{-1}}$. The average increase of LASE-5 compared with those of the normal liquid bath process under the same spinning parameters is 30%. A stress-amplification ratio (SAR) is defined as the secant modulus at 5% elongation (i.e. LASE-5/0.05) divided by the initial modulus. As indicated in *Table 2*, SAR vales of as-spun fibres spun from the modified LIB process are larger than that of fibres spun from the normal LIB process.

To analyse further the different effects the two processes on the as-spun fibres, representative stress–strain curves of three different samples are depicted in *Figure 10*; as-spun fibre spun from the normal LIB process (fibre I), as-spun fibre spun from the modified LIB process (fibre II), and drawn fibre made from the modified LIB process (fibre III). Although the final tenacity and elongation are similar for the two types of as-spun fibres, the tenacity of fibre II at the same strain as fibre I is much higher. This means that the modulus of fibre II at the same strain as fibre I is greater. *Figure 11* shows the instantaneous modulus–strain curves. It is clear that the instantaneous modulus of fibre II is larger than that of fibre I at all strains tested up to 8.7%. In fact, fibre II has an 80% higher modulus than fibre I at 2.36% strain. From LASE-5 values, SAR, stress–strain curves, and modulus–strain curves, it was found that fibre II has relatively higher yield resistance. In general, this is a desirable characteristic in reinforcement materials.

An unexpected result of the LIB process with a hot liquid jet was an increase in the maximum liquid depth within the liquid bath if the temperature of the hot liquid was higher than that of the filament at the point of application of the liquid jet. *Table 3* shows the maximum operable liquid depth for both the normal liquid bath process and the liquid bath with a hot liquid jet. In both cases, all other spinning conditions were kept identical with the liquid bath positioned 160 cm from the spinneret. At a liquid temperature of 140°C and take-up speed of $4000\,\mathrm{m\,min^{-1}}$, the maximum depth obtained was 40 cm, compared to 36 cm obtained with the normal liquid bath

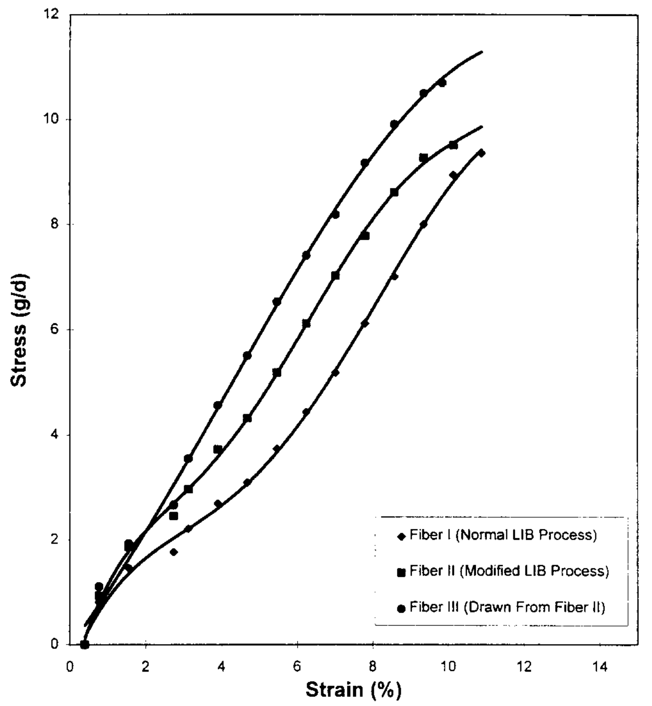

Figure 10 Comparison of the stress–strain behaviour for fibre I, fibre II and fibre III

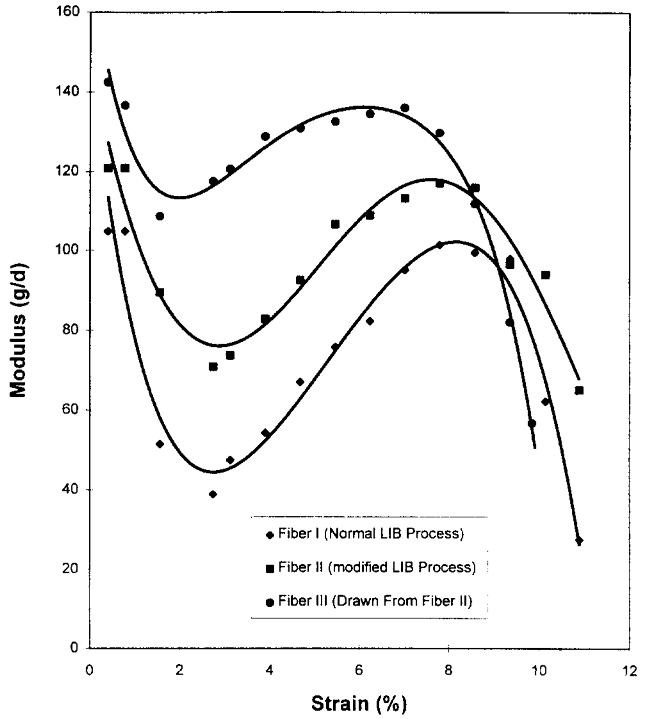

Figure 11 Comparison of the modulus–strain behaviour for fibre I, fibre II and fibre III

set-up. The increase in liquid depth results in an increase in the threadline tension within the liquid bath, which is desirable and considered to be very important in improving the final properties of the fibres. This unexpected result suggests that threadline stress within the liquid bath may be further controlled by modifying the temperature profile of the fibre upstream of the liquid bath.

It has been hypothesized[12] for the LIB process that the filament deformation within the liquid bath occurs in a neck-like fashion. As we know[17], the most important parameter, in terms of morphology development region in the threadline, is the neck-like region. During the neck-like deformation process, the molecules become oriented along the filament axis. It has been reported[12] that attenuation of the filament stops at 80 cm from the spinneret. The calculated velocity at that point is only *ca* 700–800 m min^{-1}. As is known[18], only low amorphous orientation can be achieved at such low speeds. It would seem that most of the structure orientation must be developed within the liquid bath. Ziabicki[19] suggested that amorphous orientation was closely related to the threadline stress and strain rate. The higher the respective stress and strain rate, the higher the amorphous orientation that can be achieved in the spinline. As previously stated, it was also illustrated that a delay in the attenuation process and a high stress within the liquid bath would favour the formation of high tenacity PET fibres. Actually, the first experiments were conducted with hot air[20], but it was confirmed that the filament could be more effectively heated by a flowing liquid than by hot air. The attenuation was delayed by reducing the elongational viscosity of the filament, which produced a uniform radial structure in the filament before entering the liquid bath. The uniform structure along the cross section could then bear a higher level of stress within the liquid bath. Indeed, the stress in the liquid bath region was increased because a greater depth of liquid in the bath could be used in the modified process (*Table 3*), which may have resulted in high amorphous orientation of the fibres.

Table 2 shows the super-molecular structure parameters of as-spun fibres. The as-spun fibres made by the modified LIB process have a higher birefringence, higher amorphous orientation, and larger crystalline size when compared with the normal liquid bath process. Apparently, higher amorphous orientation was indeed achieved by the modified LIB process. These data supported our hypothesis of the formation mechanism of the modified process. To confirm this mechanism, further investigation is needed. However, the crystallinity and orientation in the crystalline region do not show any apparent differences between the two as-spun fibres. Therefore, it may be concluded that the higher LASE-5 and higher modulus of as-spun fibre made from the

Table 3 The maximum operable liquid depth for both LIB processes

Sample no.	Remark	Take-up speed (m min^{-1})	LIB temperature (°C)	LIB depth (cm)
1	Normal LIB process	4000	140	36
2	Modified LIB process	4000	140	40
3	Normal LIB process	4500	140	30
4	Modified LIB process	4500	140	33
5	Normal LIB process	5000	140	28
6	Modified LIB process	5000	140	31

Table 4 Characterization data of as-spun fibres and drawn fibres from the modified LIB

Sample no.	Take-up speed (m min^{-1})	Draw temperature (°C)	Draw ratio	Tenacity (g d^{-1})	Modulus (g d^{-1})	Elongation (%)	LASE-5 (g d^{-1})	HAS (%)	Δn	X_c	f_c	f_a	L105 (Å)
1	4000	–	–	9.44	121.1	10.6	4.11	13.5	0.219	0.143	0.924	0.806	43.82
2	4000	180	1.12	10.7	141.9	9.01	5.87	5.78	0.236	0.407	0.951	0.925	62.41
3	5000	–	–	9.75	125.6	11.0	4.36	12.4	0.224	0.221	0.932	0.834	–
4	5000	180	1.12	11.1	142.9	9.1	5.60	5.4	0.237	0.461	0.956	0.945	–

Note: Samples 2 and 4 are the drawn fibres from samples 1 and 3, respectively

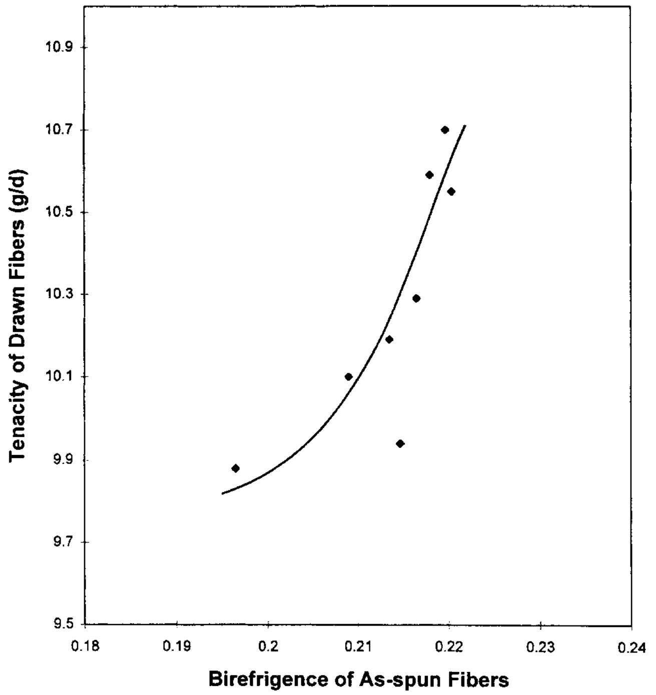

Figure 12 Relationship between the tenacity of drawn fibres and birefringence of as-spun fibres produced by the LIB process

modified LIB process are very likely due to the higher amorphous orientation. Rim and Nelson[21] have reported that LASE-5 of a fibre increased with increasing amorphous orientation. For both processes, the fibres showed a very low level of crystallinity, around 15–22%. It has been reported[12] that the crystallization was suppressed by high stress in the LIB process, resulting in the low crystallinity.

Hot-drawing and annealing

As seen in *Table 4*, the thermal shrinkages of as-spun fibres made from the modified LIB process have high values (12.4–14%). This means that the dimensional stability of as-spun fibres is poor at high temperatures although it does show good dimensional stability at low temperatures. As may be seen in *Table 2*, the as-spun fibre has high amorphous orientation and low crystallinity, which obviously results in high shrinkage at a temperature higher than the glass transition temperature. To overcome this, the as-spun fibres made by the modified LIB process were heat-treated under certain conditions. The mechanical properties of drawn fibres are also shown in *Table 4*. It is clear that the tenacity of drawn fibres is over 11 g d^{-1} and the modulus of drawn fibre is over 140 g d^{-1}. After post treatment, the tenacity and modulus increase 13.6% and 17%, respectively. The LASE-5 increases 38% after drawing and annealing, near to 6 g d^{-1}. The thermal shrinkage decreases over 50%.

On the other hand, fibre III (drawn fibre made from modified LIB process) in *Figure 11* shows the desired feature of a more nearly constant modulus at low strains. The modulus of fibre III is 60% higher than that of the as-spun fibre spun from the modified LIB process (fibre II) at a strain of 2.36–3.15%. Meanwhile, the modulus of the drawn fibre retains a high value (>100 g d^{-1}) at a relatively wide strain range (0–8.6%). Therefore, the drawn fibres exhibit desirable characteristics of high tenacity, high modulus, high LASE-5, and low thermal shrinkage.

Table 4 shows the structural parameters of both the as-spun fibres and drawn fibres. After hot-drawing and annealing, the crystallinity, amorphous orientation and crystallite size increase to a very high level, which results in the low thermal shrinkage. It is known that a relationship exists between the mechanical properties and both crystallinity and orientation. Generally, the higher the crystallinity and orientation, the higher are the modulus and tenacity. The particular combination of fine structural features certainly plays a dominant role in producing drawn fibres with high tenacity, modulus and low thermal shrinkage. Thus, it is necessary to draw and heat-treat the as-spun fibres to make them competitive with current industry standards. Note, however, the low maximum draw ratio which is effective.

Figures 12 and *13* show the relationships between the mechanical properties of drawn fibres and the birefringence of as-spun fibres. The as-spun fibres were spun at different liquid depths at a take up speed of 4000 m min^{-1}, which resulted in different birefringences. It is clear that the higher the birefringence of the as-spun fibres, the higher the tenacity and modulus attainable after drawing and annealing. As stated above, a higher birefringence means that there is a higher amorphous orientation due to similar crystalline orientation and low crystallinity of as-spun fibres. In the drawing process, a high crystallinity is easily formed if the as-spun fibres have high amorphous orientation. Thus, the mechanical properties of the final fibres are determined by the as-spun fibres. On the other hand, if a crystalline structure has already been formed, it will be difficult to destroy and reform. The high crystallinity would affect the deformability of the as-spun fibres and also the amorphous structure development. Therefore, for high tenacity and high modulus fibres to be formed, the as-spun fibres should have higher amorphous orientation and low crystallinity.

CONCLUSIONS

A LIB was used in the spinline to produce high

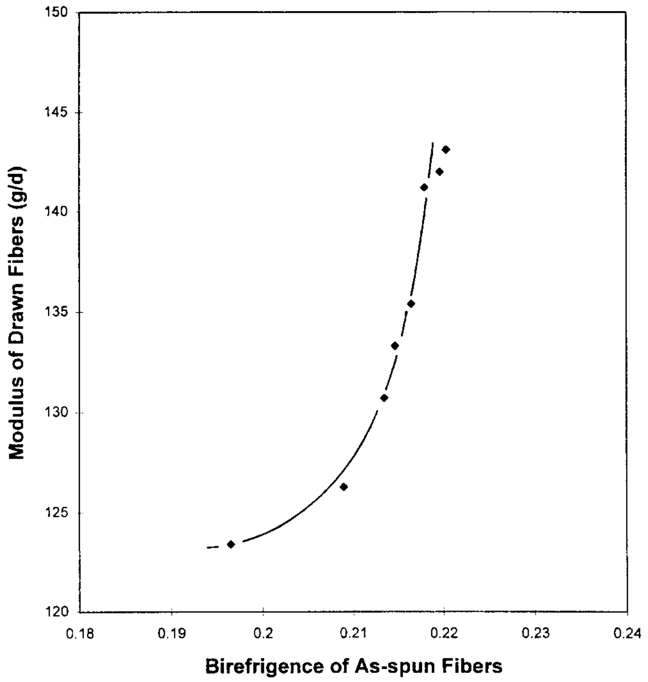

Figure 13 Relationship between the modulus of drawn fibres and birefringence of as-spun fibres produced by the LIB process

performance PET fibres under conditions of high speed melt spinning. The take-up stress was measured at various spinning conditions. It was found that maximum applicable take-up stress was determined by the state of the filament upstream of the liquid bath. To alter the morphological state of the filament before entering the liquid bath, a small amount of hot liquid was applied to the running filament at a position upstream of the liquid bath. The temperature profile of the spinline was changed by heating or cooling the filament with this liquid jet. The results show that quick cooling leads to a loss of filament deformability and formation of a non-uniform radial structure in the fibres. However, a delay of the attenuation process by heating the filament before it enters the liquid bath induces a uniform radial structure and an increase of deformability. An increase in the maximum allowed liquid depth was also found to occur in this case. Furthermore, the delay of attenuation in the upper portion of the threadline just prior to the liquid bath and the attendant increase of stress within the liquid bath also resulted in an improvement of the tensile properties. These considerations gave birth to the modified LIB process. High tenacity (9.7 g d^{-1}), high modulus (>120 g d^{-1}) and high LASE-5 (>4 g d^{-1}) PET as-spun fibres are achievable using the modified LIB process in one step. The as-spun fibres produced with the modified LIB process have high amorphous orientation, low crystallinity and relatively large crystallite size. Since the as-spun fibres have a large thermal shrinkage, as-spun fibres must be drawn and heat-treated to increase the thermal dimensional stability. After drawing and annealing, to an unprecedented low maximum attainable draw ratio of 1.12, the fibres exhibit desirable characteristics of high tenacity (>11 g d^{-1}), high modulus (>140 g d^{-1}), high LASE-5 (5.8 g d^{-1}), and low shrinkage (<6%). The mechanical properties of drawn fibres are determined primarily by the morphological characteristics of as-spun fibres, which should have higher amorphous orientation and lower crystallinity prior to post-treatment. The modified LIB process makes it possible to obtain this type of as-spun fibre, which results in high tenacity, high modulus and low shrinkage fibres after drawing and annealing.

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