Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 921–926

EFFECT OF THE AIR-JET AND THE FALSE-TWIST TEXTURING PROCESSES ON THE THERMOMECHANICAL BEHAVIOUR OF POLYAMIDE 6.6 YARNS

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Polyamide 6.6 multifilament yarns are converted to crimped fibres by texturing in order to simulate the properties of natural staple fibre yarns for textile applications. Texturing is carried out by mechanical stresses (turbulences or twisting) in different atmospheres which affect crystallinity and thermal stability of yarns. Two polyamide yarns with the same linear density but consisting of filaments of different fineness were textured by the air-jet and the false-twist procedures. The influence of texturing conditions and filament fineness on crystallinity and thermomechanical behaviour and dimensional stability were studied by TMA and DSC. The air-jet texturing procedure leads to a slight increase in crystallinity of yarns whereas the false-twist texturing procedure was more effective especially when thicker filaments were textured. The inflection point of the shrinkage curve before melting was a good estimator of the effective temperature of yarn texturing.

Keywords: *air-jet, crystallinity, DSC, false-twist, filament fineness, polyamide 6.6, shrinkage, texturing, thermal stability, TMA*

Introduction

Heat-setting is a thermomechanical process of fundamental importance to the subsequent processing of fibres and their ultimate applications. The industrial importance of heat-setting was first acknowledged when textured yarn was first produced [1]. Greer [2] demonstrated that heat-setting a material would stabilise it in a particular form by the application of heat. The imposed thermal energy would allow the material to relax into a more energetically stable configuration. For nylon 6.6 a permanent set will be achieved when fibres are heated to 180–200°C [3].

Texturing is the conversion of flat (straight) filament yarn to crimped fibres to simulate the properties of natural staple yarns of increased bulk with the benefits of thermal insulation, cover, softness and fullness, and moisture transport. In false twist texturing, the multifilament bundle is cold twisted by running the yarn over the edge of a stack of nine rotating discs on three centres in an equilateral triangle. The yarn runs through the centre of the triangle and over the edge of each disc. Twisted yarn passes the heater where it is heat plasticized and twists are heat set in a dry atmosphere close to its melting point. The yarn is subsequently cooled in the area between the heater and the spindle and untwisted after passing the spindle. Heat-set twists impart crimp, bulk and elasticity to the yarn [4]. In air-jet texturing, the multifilament bundle is fed into a jet, where it interacts with supersonic, turbulent, non-uniform air flow. Water is sprayed immediately before the jet to lubricate the yarn. Upon emerging from the jet, the filaments bend into bows and arcs, forming filament loops on the surface of the yarn. These loops are locked in the resulting textured yarn assembly because of the intermingling of the filaments. In air-jet texturing, multifilaments are textured in a humid hot atmosphere [5].

If the specimen has been rapidly crystallised, it is likely to contain many small imperfect crystals with lower melting points. At an elevated temperature, smaller crystallites would melt and re-crystallise on the larger ones. The small crystallites, which melt together with some of the molecules stretched during the fibre formation process, tend to coil up, giving rise to the observed shrinkage tension. Thus, after texturing, a new distribution of crystallite size and orientation is formed.

Thermomechanical responses of fibres depend on the inherent tendency of oriented fibres to shrink at elevated temperatures, and may be observed as shrinkage in experiments in which the temperature of the fibre is varied systematically. These experiments are useful for 'fingerprinting' fibre samples, especially for determining

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1388–6150/$20.00

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pragmatic quantities such as 'heat history' and other processing conditions in textured filament yarns [6].

A dynamic shrinkage experiment involves the monitoring of length (shrinkage) in a specimen which is exposed to a steadily increasing temperature. The experiment ends at temperatures near the crystalline melting temperature, when the specimen loses the ability to maintain internal stresses. Anton [7] reported that if a nylon 6.6 fibre is heated in a dry, relaxed state from 25 to 70°C, it begins to shrink. At around 70°C some partial crystallization reduces chain mobility. As heating is increased, the absorbed water is lost and shrinkage continues. Approximately at 160°C the crystal structure changes from a triclinic to a hexagonal form restricting further retraction. At 170–180°C the rupture of amide bonds in hexagonal crystal commences. This is the usual hot-draw temperature due to the increased mobility of the molecular chains. The most striking feature is the intermediate and complex 'structure' exhibited at temperatures between T_g and T_m. The temperature at which the maximum retraction is observed provides evidence of a crystalline order in the system, even though it is not readily detectable by conventional analysis. Dennis and Buchanan [8] proposed that the first peak was associated with relaxation and disorientation of the amorphous domains, whereas the second was associated with crystalline reorganisation phenomena, including the melting of imperfect and/or small crystals, recrystallisation, and crystallite thickening and perfection changes. If a high temperature crystal-crystal transition is included, this explanation agrees with that of Anton [7].

The first derivative of the shrinkage curve plots the variation of the shrinkage rate *vs*. temperature. Cayuela *et al*. found that the second peak of the TMA derivative curve of polyester fibres corresponds to the effective temperature of heat setting [9]. The peak of the derivative curve corresponds to an inflection point [10] of the shrinkage curve. This point marks the equilibrium between the coiling up tendency of stretched macromolecules and the relaxation for a more stable configuration.

The dry and humid thermal texturing procedures have modified the fine structure of the fibre in three ways: 1) increasing crystallinity by a secondary recrystallisation, 2) rearranging preferentially macro fibrils near the surface, which enhances the skin-core differentiation effect and, 3) enabling the polymer to form larger crystals that stabilise the fibre in the deformed state [11]. All these factors will affect the glass transition, the dimensional stability and the shrinkage behaviour of yarns with temperature.

Objective

The aim of this work is to study the effect of the texturing processes on the thermomechanical behaviour of two polyamide 6.6 multifilaments of different fineness by analyzing the change in length when the specimens are exposed to a steadily increasing temperature. Samples were subjected to periodical stresses to measure the evolution of Young's modulus at increasing temperatures. Variations in sample length, in the elastic modulus, and in thermal stability will be recorded. The relationship with filament fineness and texturing processes will be studied.

Experimental

Materials

Experiments were done on 86.67 dtex polyamide 6.6 multifilament yarns from the same producer, made up of two different types of monofilaments: Thin

Table 1 Mean values of crystallinity K, glass transition temperature T_g, Relaxation slope R of the E-modulus at T_g, linear expansion coefficient C between 50 and 200°C, temperature of maximum shrinkage rate T_s (inflection point of the dilatation curve prior to melting) maximum shrinkage rate S of 86.67 dtex multifilament yarns of filament linear density F air-jet textured and false-twist FT textured at different temperatures

Ref.	F/dtex	Texturing procedure	K/%	T_g/°C	R/MPa K^{-1}	C/nm mm^{-1} K^{-1}	T_s/°C	S/μm K^{-1}
B	1.27	raw	33.0	78.2	–85.7	530.4	163.4	7.64
B1	1.27	FT200°C	36.8	77.8	–57.7	–2.15	154.7	–1.3
B2	1.27	FT210°C	37.9	79.7	–63.0	–3.75	164.7	–1.3
B3	1.27	FT220°C	38.5	81.0	–60.1	–46.3	173.8	–2.1
B4	1.27	FT230°C	38.8	81.0	–58.7	–36.4	177.4	–2.1
C	1.27	raw	35.1	77.1	–79.7	402.6	162.8	6.26
C1	1.27	air–jet	37.6	79.9	–49.9	71.0	140.7	–0.6
E	3.77	raw	35.9	79.5	–89.0	540.3	160.0	5.14
E1	3.77	FT200°C	36.8	78.0	–61.4	176.9	153.3	1.2
E2	3.77	FT210°C	38.0	81.1	–48.2	–21.4	165.9	–1.4
E3	3.77	FT220°C	39.9	82.2	–41.1	–7.70	175.7	–1.7
E4	3.77	FT230°C	41.0	84.0	–35.8	13.25	182.5	–1.6
F	3.77	raw	35.2	79.8	–103.9	529.7	163.2	6.90
F1	3.77	air–jet	37.0	82.9	–64.8	54.2	139.3	–1.0

filaments of 1.27 dtex in fineness resulting in a 1.27 dtex×68 (R 8.67 tex/68) multifilament yarn and thick filaments of 3.77 dtex in fineness resulting in a 3.77 dtex×23 (R 8.67 tex/23) multifilament yarn.

Both yarns were thermally treated by the false-twist texturing procedure at 200, 210, 220 and 230°C and hydro thermally treated by the air-jet procedure. References which identify filament fineness and texturing conditions are included in Table 1.

Methods

Differential scanning calorimetry

Melting temperature and melting enthalpy of the substrates were determined by DSC, in a Perkin Elmer DSC-7. Filaments were cut in very short lengths using a microtome, and samples of approximately 5 mg were prepared in punched pans to guarantee good contact of the sample with the DSC sensor. DSC curves were obtained in the following operating conditions: Initial temperature 50°C, final temperature 300°C, and heating rate 20°C min^{-1}, nitrogen purging gas (2 kg cm^{-2}).

From melting enthalpy of the studied substrate (ΔH_m) and melting enthalpy of the 100% crystalline polyamide 6.6 (191 J g^{-1}), the % of crystallinity K was calculated [12] through the relationship $(\Delta H_m/191)\cdot 100$.

Thermomechanical analysis

Two samples of each reference (Table 1) 12.8 mm in length were tested in a TMA/SDTA 840 Mettler Toledo under the following conditions: Initial temperature 35°C, final temperature 250°C, heating rate 10°C min^{-1}, nitrogen purging gas 35 mL min^{-1}, periodic load between 0.1 and 0.2 N at 1/12 Hz.

Variations in length given by TMA resembled those in Fig. 1. The deformation amplitude is inversely related to Young's modulus. By analyzing the mean curve of the variations in length and the E-storage modulus evolution with temperature the following parameters were determined [13]:

E-storage modulus curve:

- T_g/°C: temperature of which the maximum relaxation in E-storage (inflection point) is observed.
- R/MPa K^{-1}: relaxation slope of the E-storage curve at T_g (maximum intensity of the glass transition effect)

Variation in length mean curve:

- C/nm mm^{-1} K^{-1}: mean linear expansion coefficient between 50 and 200°C
- T_s/°C: temperature of maximum shrinkage rate (second peak of the first derivative or inflection point of the curve prior to melting).
- S/μm K^{-1}: maximum shrinkage rate (slope at T_s).

Results and discussion

Table 1 shows the results of crystallinity K obtained by DSC, and the parameters derived from the thermomechanical analysis of the yarns: T_g and R from the E-storage curve, the linear expansion coefficient C and the shrinkage parameters T_s and S derived from the mean curve of the variation in length given by the TMA apparatus.

Glass transition

Texturing modifies the glass transition of the polyamide 6.6 yarns. Figure 2 plots the evolution of T_g according to filament fineness and the texturing procedure and conditions. T_g of the original yarns are lower than 80°C whereas the texturing process increases T_g. The air-jet texturing process increases T_g to a level reached by the false-twist texturing process at temperatures between 210 and 220°C. In false-twist texturing T_g increases with temperature, the effect being higher in thick filaments. Figure 3 shows the reduction of the intensity of the glass transition phenomenon when textured. Air-jet texturing decreases the intensity of the glass transition phenomenon

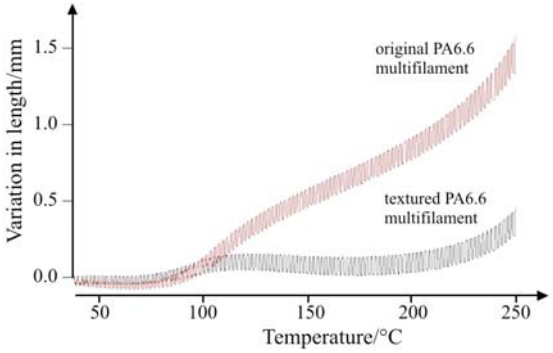

Fig. 1 Variation in length of original and textured PA6.6 multifilament samples 12.8 mm in length under periodic load between 0.1 and 0.2 N at 1/12 Hz from 35 to 250°C at 10°C min^{-1}

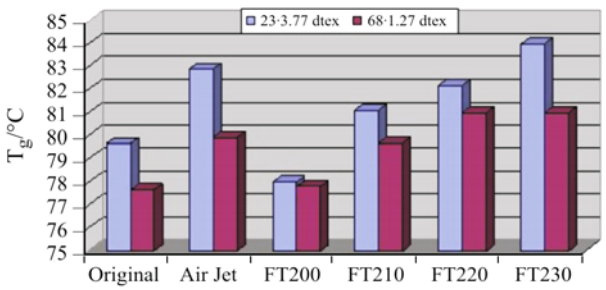

Fig. 2 Influence of the air-jet texturing and false-twist FT texturing at 200, 210, 220 and 230°C on the polyamide 6.6 glass transition temperature T_g according to filament fineness

regardless of filament fineness. By contrast the reduction of the effect of false twist texturing on glass transition in thin filaments is not affected by the texturing temperature, whereas in the case of the thicker filaments the glass transition is progressively reduced as texturing temperature is increased.

Dimensional stability

Thermal treatments are one of the most effective mechanisms that yield a permanent set. The deformed fibre, on heating, will relieve the stresses through the melting of imperfect crystals, and a new stabilised state will therefore be produced by recrystallisation [1]. The heat setting at a given temperature will be effective against subsequent treatments at lower temperatures, but can be overcome by treatments at higher temperatures [10]. Figure 4 shows the evolution of the mean linear expansion coefficient of the polyamide 6.6 multifilaments from 50 to 200°C. Texturing improves the dimensional stability of the filaments. The air-jet texturing decreases the linear expansion coefficient between 6 and 10 fold. Nevertheless, given that the maximum temperature at which filaments are subjected is lower than 200°C, the linear expansion coefficient remains positive. As regards the effect of the false-twist texturing process on the dimensional stability, it shows higher effectiveness although the thicker filaments textured at 200°C showed a positive expansion coefficient. This can be explained by the superficial incidence of thermal energy of this texturing process. Thinner filaments showed a specific surface 1.7 times higher than that of the thicker filaments, increasing the effectiveness of this texturing process [14].

Shrinkage behaviour

The thermal shrinkage curves are extremely sensitive and capable of showing structural changes that are difficult or impossible to show by other means [1]. At temperatures that are sufficiently high but lower than T_m, crystal melting and recrystallisation become important, resulting in a 'complex' structure that expands or contracts depending on whether the coiling up or the relaxing tendency of the macromolecules is dominant. The inflection point of the TMA curve T_s (Fig. 5) shows the maximum of the shrinkage tendency that can be related to the maximum recrystallisation and its slope with the intensity of the effect (Fig. 6). Cayuela *et al*. [9] identify T_s with the effective heat setting temperature of polyester. Given that the original filaments were not textured, no shrinkage occurred. These filaments show expansion coefficients between 6 and 7 μm K^{-1} at 160°C. By contrast, textured multifilaments show shrinkages at different temperatures: the air-jet textured filaments at 140°C and the false-twist textured filaments at 154, 165, 174 and 179°C

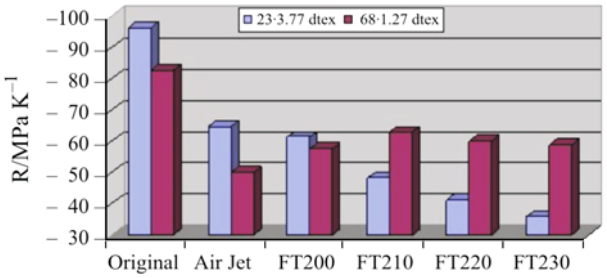

Fig. 3 Influence of the air-jet texturing and false-twist FT texturing at 200, 210, 220 and 230°C on the polyamide 6.6 glass transition intensity measured by the slope R of the elastic modulus at T_g

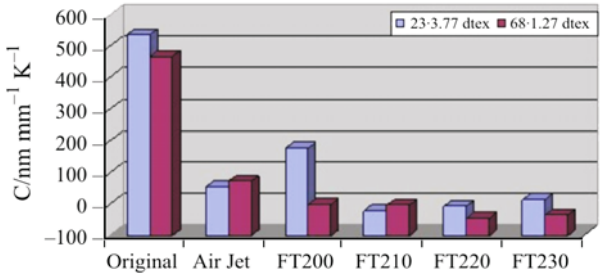

Fig. 4 Influence of the air-jet texturing and false-twist FT texturing at 200, 210, 220 and 230°C on the linear expansion coefficient C between 50 and 200°C polyamide 6.6 according to filament fineness

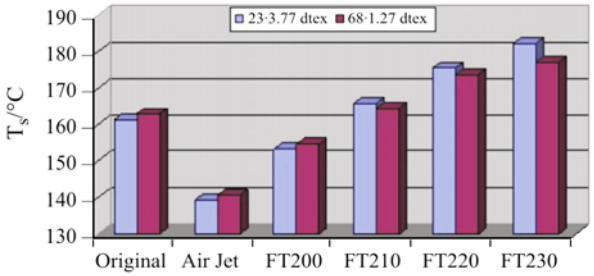

Fig. 5 Influence of the air-jet texturing and false-twist FT texturing at 200, 210, 220 and 230°C on the temperature of the maximum shrinkage rate T_s according to the filament fineness

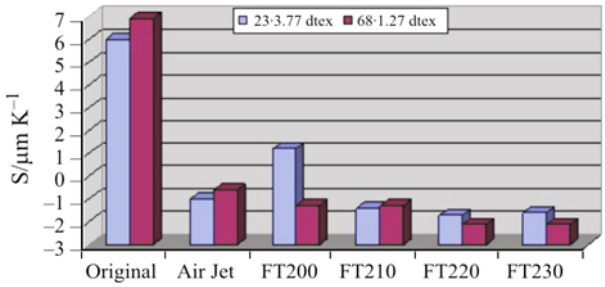

Fig. 6 Influence of the air-jet texturing and false-twist FT texturing at 200, 210, 220 and 230°C on the maximum shrinkage rate S at T_s according to the filament fineness

approximately according to the nominal false-twist texturing temperature of 200, 210, 220 and 230°C, respectively. Although the expansion coefficient of the thickest filament when false-twist textured at 200°C decreased from 6 to 1 μm K^{-1} it seems that the secondary crystallisation due to texturing is not enough to stabilise the yarn. However, the thinnest filaments reached a similar level of thermal stability at higher temperatures. As stated above, the lower effectiveness of false-twist texturing at 200°C can be attributed to the differences on the specific surface of filaments because dry heat is applied onto the surface.

There is a close linear relationship between the nominal temperature of false-twist texturing T_{ft} and the temperature T_s at which the maximum shrinkage rate S is observed. According to Cayuela *et al*. [9] T_s can be considered the effective temperature of texturing:

- 1.27 dtex×68 filaments: $T_{s\,(R\ 8.67\ tex/68)}=1.74+0.77T_{ft}$, $r=0.98$
- 3.77 dtex×23 filaments: $T_{s\,(R\ 8.67\ tex/23)}=-40.1+0.97T_{ft}$, $r=0.99$

When comparing the influence of the texturing procedures on both the linear expansion coefficients (Fig. 4) and the maximum shrinkage rate (Fig. 6) it can be seen that the effect of the false-twist texturing process on these parameters is greater on thinner filaments whereas the air-jet texturing seems to have more effect on the thicker ones. These differences can be attributed to the different procedures: false-twist texturing is a dry heat treatment that is applied onto the surface of the filaments and the effect spreads from the surface to the core of the filament. Air-jet texturing is a humid heat treatment. Owing to the presence of water the thermal energy rapidly reaches the core of the filaments regardless of its fineness. Consequently, the effect of texturing becomes apparent over the filament cross-section. The thicker the filament, the greater the effect.

Crystallinity

Air-jet texturing increases the crystallinity from 35 to 37% regardless of the filament fineness, whereas the false-twist texturing depending on the texturing temperature increased crystallinity about 5%. The influence of texturing temperature on crystallinity according to filament fineness is shown in Fig. 7: crystallinity is more developed on thicker filaments than on the thinner ones.

Crystallinity, glass transition and maximum shrinkage rate of false-twist textured filaments

The development of crystallinity due to false-twist texturing exerts an influence on both the glass transition temperature and on the temperature at which the maximum

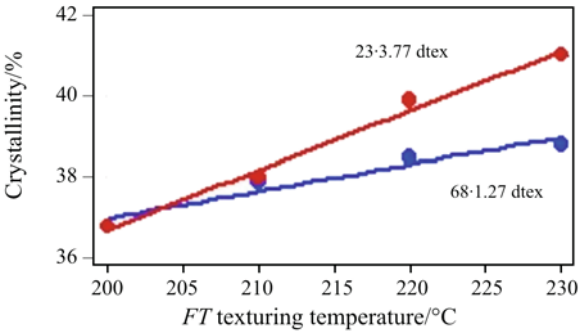

Fig. 7 Effect of the false-twist texturing temperature on the increase of crystallinity measured by DSC according to the filament fineness

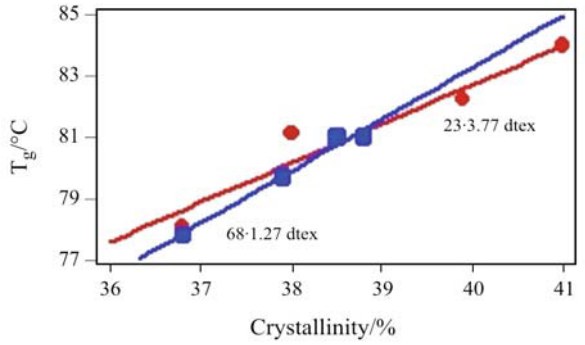

Fig. 8 Effect of the increase in crystallinity due to false-twist texturing on the glass transition temperature T_g according to the filament fineness

shrinkage rate T_s is observed. This temperature can be regarded as the effective temperature of heat setting. T_g increases with crystallinity (Fig. 8) at a slightly faster rate for thin filaments than for the thicker ones. The mean ratio of increase in T_g due to texturing recrystallisation is 1.4°C per 1% of increase in crystallinity. As regards the temperature of maximum shrinkage rate T_s this was increased with the amount of recrystallisation. As in the case of T_g, the thinner the filaments the greater the influence of recrystallisation on T_s increments (Fig. 9). This is due to the way in which this texturing procedure applies heat to the filaments. Heat transmission produced in dry atmosphere reaches the filament surface and is then progressively diffused to the core of them. The greater texturing efficiency observed in thin filaments can be explained by the larger specific surface, which is 1.7 times that of the thicker ones. Considering the relationship between T_s and crystallinity the linear regressions [15] obtained according to the filament fineness were the following:

- 1.27 dtex×68 filaments: $T_{s\,(R\ 8.67\ tex/68)}=-266.1+11.41K$, $r=0.99$
- 3.77 dtex×23 filaments: $T_{s\ (R\ 8.67\ tex/23)}=-89.9+6.67K$, $r=0.99$

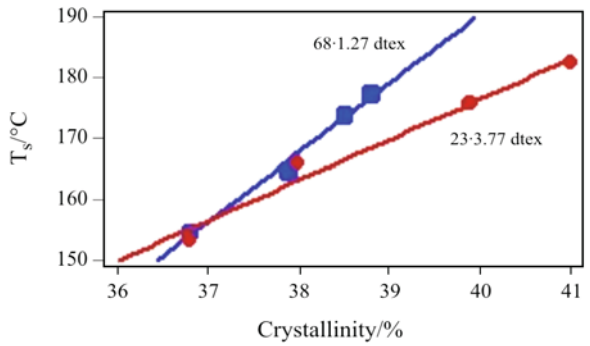

Fig. 9 Effect of the increase in crystallinity due to false-twist texturing on the maximum shrinkage rate temperature T_s according to the filament fineness

Conclusions

Based on the results of the thermomechanical analysis at steadily increasing temperatures and on differential scanning calorimetry of polyamide 6.6 air-jet and false-twist textured yarns, the following conclusions can be drawn:

- Texturing increases the glass transition temperature and broadens the glass transition region of the polyamide 6.6 multifilaments. The effect of the air-jet texturing is greater on thin filaments whereas the effect of the false-twist texturing is more effective on thicker filaments, the effect of which increases with texturing temperature.
- The dimensional stability of textured filaments measured by the linear expansion coefficient between 50 and 200°C shows that the air-jet texturing is less effective than false-twist procedure on yarn setting although the effectiveness of this procedure depends on the filament fineness. The effectiveness of the false twist texturing increases with filament fineness.
- The inflection point of the TMA curve before melting, which corresponds to a maximum of the first derivative curve, shows the temperature at which the maximum of the shrinkage tendency of the yarns is observed. This can be considered as the effective temperature T_s of yarn setting, and the slope S will correspond with the maximum shrinkage rate of the yarn. The T_s of the air-jet textured filaments was 140°C whereas the values of the false-twist textured filaments were 154, 165, 174 and 179°C for yarns textured at 200, 210, 220 and 230°C, respectively.
- Air-jet texturing favours a slight increase in yarn crystallinity regardless of filament fineness, whereas false-twist texturing induces higher increments in crystallinity especially in thicker filaments.
- Highly significant linear relationships were observed between the increase in crystallinity and the increase in T_g and T_s when false-twist textured yarns were considered according to their fineness. The increase in crystallinity exerted a stronger influence on the increase of T_s than on T_g.

Ackowledgements

Authors are indebted to the Spanish Project MAT2004-04981-C03-03 for its financial contribution. They recognise the contribution of the GRICES/CSIC 2005PT0051 Project helping the elaboration of the paper, and they are also indebted to Ms. R. Mateu, A. Lopez and C. Martínez for its contribution to the experimental work and to Mr. George von Knorring for his technical support.

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Received: May 3, 2007
Accepted: March 17, 2008
OnlineFirst: June 25, 2008

DOI: 10.1007/s10973-007-8556-z