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DIFFERENTIAL SCANNING CALORIMETRY OF SPUN AND DRAWN POLYESTER YARN

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Polyester yarn spun over a range of wind-up speeds and subsequently drawn at 373 K has been characterized by differential scanning calorimetry. Samples that are constrained from shrinking during the thermal scan respond differently than samples that are free-to-shrink. In the region of intermediate orientation, the constrained samples typically show a lower cold crystallization temperature: In the region of high orientation, the constrained samples typically show a higher melting temperature. The results are quantitatively similar to those based on fibers in which the orientation is imparted directly by high speed spinning.

There are basically two techniques to impart orientation to a synthetic polymer fiber: spinning and drawing. Fibers may be spun to various levels of molecular orientation, most readily measured by birefringence, simply by changing the wind-up speed. Alternatively, fibers spun to any level of orientation can be readily drawn to enhance the orientation. In this paper select thermal properties of *drawn* poly(ethylene terephthalate) fibers are compared to those based on yarns *spun* to the same birefringence. The thermal properties of the spun yarns have been published previously in a note that focused on technique as well as results [1]. To obtain useful calorimetric data on oriented yarns, it is necessary to prevent the fibers from shrinking during the thermal scan. One technique, outlined in detail elsewhere [1], consists of winding single filaments loaded in tension onto small aluminum spools and fixing the ends in place with epoxy. By maintaining the fibers at constant length during thermal analysis, one measures properties that characterize the yarns per se and not the yarns undergoing dynamic shrinkage. Data thus obtained are quite useful for predicting the behavior of the fiber crystallization during processing.

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Experimental

Sample preparation

The polymer employed was a standard, textile-grade PET, which is characterized by an intrinsic viscosity of 0.64 dl/g in a 1% solution of *o*-chlorophenol, and contains delusterant (0.2–0.4% titania). The spinning was conducted by Dr. W. E. Bessey (Fiber Industries, Charlotte, NC) on full-scale equipment (33 fils/yarn) under experimental conditions. The wind-up speed was varied from 25 to 100 m/s. The spun yarn and filament denier decreased with wind-up speed, as shown in Table 1.

Table 1 Thermal data of drawn fibers

Sample		Filament denier	Δn, x1000	Cold crystallization			Melting	
				T, onset, K	T, peak, K	ΔH_c, J/g	T, peak, K	ΔH_f, J/g
A	pan	14.8	11	388	410	28	525	41
	spool			390	407	25	524	36
A1	pan	10.3	28	363	387	20	525	46
	spool			–	378	~4	524	37
A2	pan	7.4	78	359	374	13	526	53
	spool			359	372	11	526	46
A3	pan	6.2	132	364	378	5	527	53
	spool			369	378	4	530	53
A4	pan	5.2	165	365	380	3	528	54
	spool			Na	Na	Na	531	54
A5	pan	4.8	178	342	359	4	527	56
	spool			375	392	2	533	50
G	pan	8.0	48	360	381	16	527	46
	spool			358	368	8	527	41
G1	pan	6.6	98	368	380	6	527	56
	spool			367	380	5	529	53
G2	pan	5.4	128	367	381	5	528	56
	spool			367	385	15	530	53
G3	pan	4.9	158	362	378	6	529	57
	spool			366	384	9	532	61
RR	pan	5.7	112	367	381	2	537	56
	spool			369	385	2	540	54
RR1	pan	5.2	125	Na	Na	Na	537	58
	spool			371	383	2	541	53
RR2	pan	4.9	132	Na	Na	Na	537	57
	spool			371	383	2	542	48

*Drawn at 293 K

Fiber drawing was conducted on laboratory scale equipment. A 30 cm Lindberg tube oven was placed between a feed and a draw roll. Yarn was taken up on a Leesona winder at about 0.2 m/s. Thus, the residence time in the 373 K hot zone was two seconds.

The draw temperature of 373 K was selected for a number of reasons:

(1) it is sufficiently high that necking is avoided and, consequently, a range of draw ratios could be used; (one sample was drawn at room temperature to an extension that exceeded the natural draw and the data are included in Table 1).

(2) it is sufficiently low that the crystallization exotherm for unoriented PET is avoided, and

(3) it is of commercial importance.

Thermal analysis

A DuPont 1090 Thermal Analyzer coupled to a 910 Cell Base was employed for all the thermal work. Free-to-shrink samples were prepared by lightly crimping the lid on standard aluminum pans containing the fibers. Samples which were constrained from shrinking were prepared by wrapping a known length of a filament loaded with about 40 mg tensile force on a small aluminum spool and securing the fiber and with epoxy. The weight of the sample was assessed by taking the product of length and denier; usually about 2 mg were used. The spool (including fiber and cured epoxy) was placed in the Cell Base, the reference being another spool of near equal weight, and the temperature increased at 20 K/min.

Orientation

Molecular orientation was assessed by measuring birefringence. A polarizing light microscope equipped with a Berek Compensator was used to obtain retardance values and a filar micrometer eyepiece was used to obtain diameter (thickness) values [2].

Results and discussion

The results of the thermal analyses conducted on three sets of spun and drawn yarns are summarized in Table 1. ΔH_c is the heat of crystallization (cold); ΔH_f is the heat of fusion; T_c refers to the temperature of the cold crystallization exotherm; and T_m denotes the peak of the melting endotherm. "Pan" signifies that samples were prepared for thermal analysis in the conventional fashion, i.e., by encapsulation in aluminum pans, and "spool" signifies fibers were constrained on spools to constant length.

Examining the data closely, one notes there is considerable scatter in ΔH_c. This results primarily from errors in assuming the position of the baseline. In addition, the values of cold crystallization temperature become increasingly inaccurate as the orientation increases. This stems from the fact that crystallization accompanies orien-

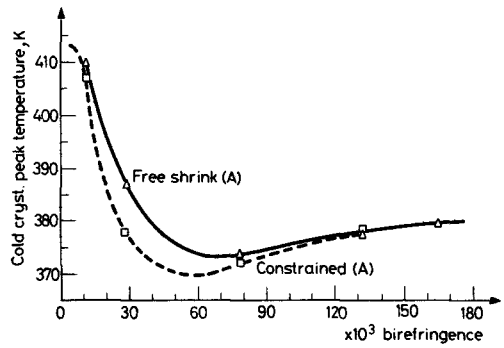

Fig. 1 Crystallization-birefringence plots of drawn PET fibers

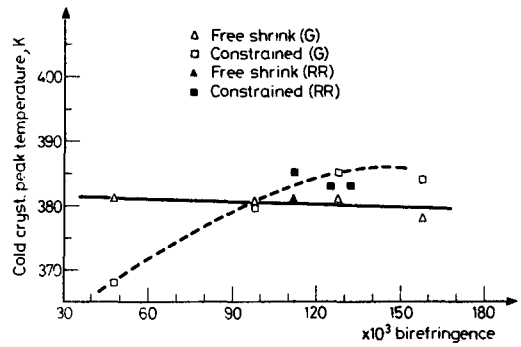

Fig. 2 Crystallization-birefringence plots of drawn PET fibers. + free shrink (G), □ constrained (G), ◇ free shrink (RR), ○ constrained (RR)

tation and, consequently, the fraction of the sample that crystallizes in the DSC decreases with orientation (and is reflected by the decreasing values of ΔH_c). Also, T_g and T_c approach each other as orientation increases.

The effect of draw-induced orientation on the peak cold crystallization temperature of sample A, spun at 25.6 m/s, is shown in Fig. 1. In the birefringence range of about 0.020–0.080, samples constrained to constant length are characterized by a lower T_c than are free-to-shrink samples. Similar data are shown in Fig. 2 for samples G and RR1 spun at 56.4 and 97.4 ms respectively. These data may be usefully compared to those presented in a previous publication [1] and reproduced in Fig. 3 after transposition of the abscissa to birefringence units and adding the data point for sample RR. The curves are quite similar, suggesting that, as a first approximation, the *origin* of the molecular orientation is inconsequential to the kinetics of cold crystallization.

Melting temperature data are shown in Fig. 4. At high birefringence only, the samples that are constrained from shrinking are characterized by a higher melting

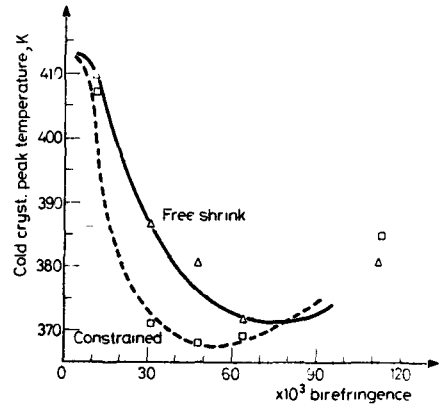

Fig. 3 Crystallization-birefringence plots of spun PET fibers

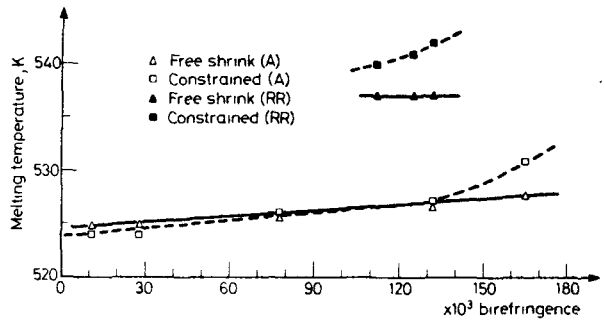

Fig. 4 Melting-birefringence plots of drawn PET fibers. △ free shrink (A), □ constrained (A), ◇ free shrink (RR), ▫ constrained (RR)

temperature than are the free-to-shrink samples. This behavior is as one would expect in light of the behavior of oriented crystalline PET fibers in dynamic shrinkage: Unlike fibers of low crystallinity, highly crystalline (oriented) fibers are characterized by the occurrence of primary shrinkage just prior to T_m, rather than subsequent to T_g.

It is important to note that the onset of crystallization occurs much before the peak exothermic temperature. To be more precise, when $\Delta n \geqslant 0.025$, the onset of crystallization is about 363 K. Consequently, fibers, either spun or drawn to a birefringence in excess of 0.020, tend to crystallize below 373 K, a temperature of commercial importance. To predict drawing behavior, however, other parameters such as strain rate and heat generated from deformation must be assessed.

Summary

Polyester yarns, spun to various levels of molecular orientation and subsequently drawn at 373 K, have been analyzed by differential scanning calorimetry. In one series of thermal scans, fibers were allowed to shrink whereas in the other set of scans, fibers were constrained to constant length. As is the case of spin-oriented yarns, the results show that the cold crystallization temperature is lower in constrained than in free-to-shrink samples, particularly in the 0.020–0.080 birefringence range. From this one may infer that the *level* of molecular orientation rather than the source, be it drawing or spinning, determines the behavior of the yarn in DSC. When the orientation attains or exceeds a value of only about 0.020 birefringence units, the onset of cold crystallization is below 373 K and this may interfere with the drawing behavior at 373 K in some instances.

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References

1 S. B. Warner, J. Thermal Anal., 28 (1983). 2 S. B. Warner and J. N. Brown, The Microscope, 23 (1982) 35.

Zusammenfassung — Bei verschiedenen Aufspulgeschwindigkeiten gesponnenes and anschliessend bei 373 K gestrecktes Polyestergarn wurde durch DSC charakterisiert. Die während der thermischen Analyse am Schrumpfen gehinderten Proben verhalten sich anders als die Proben, die ungehindert schrumpfen konnten. Im Bereich mittlerer Orientierung weisen die am Schrumpfen gehinderten Proben eine typisch niedrigere kalte Kristallisationstemperatur auf, im Bereich hoher Orientierung ist die Schmelztemperatur der am Schrumpfen gehinderten Proben typisch erhöht. Die Ergebnisse sind in quantitativer Hinsicht denen ähnlich, die bei der Untersuchung von Fasern erhalten wurden, in denen die Orientierung direkt durch Spinnen mit hoher Geschwindigkeit erzielt wurde.

Резюме — Полиэфирная пряжа, полученная при различных скоростях наматывания, а затем вытянутая при 373 К, была охарактеризована методом ДСК. Образцы с усадкой показали различное поведение по сравнению с образцами без усадки. В области промежуточной ориентации усадочные образцы показали типично более низкую температуру холодной кристаллизации, тогда как в области высокой ориентации — типично более высокую температуру плавления. Эти результаты количественно подобны тому, что наблюдалось на волокнах, в которых ориентация наделялась высокой скоростью наматывания.