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DIFFERENTIAL SCANNING CALORIMETRY OF SPIN-ORIENTED POLYESTER YARN

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Polyester yarn spun over a range of wind-up speeds has been characterized using differential scanning calorimetry. Samples prohibited from shrinking during the thermal analysis show slightly smaller heats of fusion and crystallization and reduced cold crystallization temperatures than samples that are free-to-shrink, particularly in the intermediate wind-up speed region. One critical observation made is that the cold crystallization temperature reaches a minimum at some relatively low overall molecular orientation ($\Delta n \sim 0.020$) and fails to decrease further. A likely explanation is that crystallization continuously removes polymer from the melt in the spinline in regions where the local orientation reaches some critically high value.

Partially oriented yarn (POY) of poly(ethylene terephthalate) (PET) has been a textile feedstock for a number of years. The properties of the spun yarns have not remained unchanged during this transition; most notably, orientation, measured by birefringence, has steadily increased as wind-up speed has increased. It is likely that this trend will continue in years to come as winder technology improves. Properties of POY yarn spun at high wind-up speeds have been the subject of a number of recent publications (e.g., [1–6]). One set of properties and that are examined in this article is the thermal properties; specifically, results based on differential scanning calorimetry (DSC) are presented.

Conventional preparation of samples for DSC entails encapsulation of aluminum pans. During the heating process, the fibers are relatively free to shrink within the pan. PET POY samples are characterized by high free shrinkage which occurs above the glass temperature and is driven by entropy maximization forces. Consequently, thermal curves derived from this sort of test characterize not the fiber sample per se, but rather the fiber sample undergoing dynamic shrinkage. In order to obtain information on spun yarn (crystallization) behavior which might correlate with threadline (crystallization) behavior, a technique by which filaments could be tensioned throughout the thermal scan was sought.

A technique which was successfully developed is outlined in this article and the results on PET POY which ensue demonstrate not only the utility of the technique, but also show the effect of orientation on crystallization dynamics in PET POY.

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Experimental

Sample preparation — Fiber spinning

Polymer employed was standard, textile-grade PET which contains delusterant (0.2–0.4% titania) and is characterized by an intrinsic viscosity of 0.64 dl/gm in a 0.1% solution of *o*-chlorophenol. Spinning was conducted by Dr. W. E. Bessey (Fiber Industries, Charlotte, NC) on full-scale equipment under commercial conditions. Wind-up speed was varied from 25 to 80 m/s. Spun yarn and filament denier decreased with wind-up speed as shown in Table 1.

Table 1 Select thermal data of PET yarns

Wind-up speed (m/s)	Birefringence	Prep.	Yarn, denier/fils	ΔH_c, kJ/kg	ΔH_f, kJ/kg	T_g, K	T_c, K	T_m, K
25.6	0.011	pan	510/133	28	41	355	408	525
		spool (0.1 g)		26	40	355	406	525
46.2	0.031	pan	310/33	20	42	354	390	525
		spool (0.1 g)		17	45	353	377	525
		spool (4 g)		18	42	353	375	525
66.7	0.064	pan	220/33	11	45	348	377	527
		spool (0.1 g)		12	44	–	372	529
		spool (4 g)		9	42	–	374	529
76.9	0.085	pan	190/33	5	49	355	374	531
		spoon (0.1 g)		5	40	–	–	533
		spoon (4 g)		3	49	–	–	532

Thermal analysis

A Perkin–Elmer DSC 2 and a DuPont 1090 coupled to a 910 Cell Base were employed for all the work. Free-to-shrink samples were prepared by lightly crimping the lid on the standard aluminum pans containing chopped fibers. To facilitate analysis of restrained fibers, small aluminum spools were fabricated and single filaments under load were wrapped about the spool and the fiber end fixed in place with epoxy. The weight of the sample filament was determined by taking the product of length and denier. The spool was about the same weight as a sample pan plus three lids; a reference of suitable weight was constructed. After curing, the spool (plus fiber and epoxy) was placed in the thermal analyzer and the temperature scanned at 10 K/min. Sufficient experimentation was conducted to insure that the epoxy did not interfere with the thermal traces of the PET. Incidentally, H. Tadokoro independently developed a similar technique and has used it successfully on annealed poly(butylene terephthalate) [7]. Other researches have also utilized the technique more than a decade ago [8–13].

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.

Results and conclusions

Typical DSC traces from a portion of the samples are shown in Fig. 1 and the results of the thermal analyses conducted on a series of POY's are shown in Table 1. ΔH_c is the heat of crystallization; ΔH_f is the heat of fusion; T_g is the glass transition temperature; T_c denotes the peak of the cold crystallization exotherm; and T_m denotes the peak of the melting endotherm. "Prep." indicates how the yarn was prepared for thermal analysis; "pan" signifies the conventional technique was used and "spool" signifies that samples were restrained to constant length. The number that follows "spool" is the weight in grams that was suspensed from the yarn while wrapping and glueing.

Close examination of the data shows that the absolute experimental scatter is small for transition temperatures and larger when heats of transition are assessed. On a percent basis the error in measurement of heat of cold crystallization is large when the size of the transition is small. This stems from the difficulty in assigning a baseline to the heat flow curves, particularly to those characteristic of oriented samples. Qualitatively, the data shows certain undeniable trends. One important observation is that the effects of preload on the measured thermal properties are invariant with preload—so long as the sample was constrained during the test. This seems reasonable in light of the magnitude of the entropic shrinkage *force* developed during the thermal scan (i.e., 0.05–0.1 g/d) as well as the time allowed for relaxation [5, 14]. Cold crystallization temperature and heat of both crystallization and fusion are the properties which show the greatest discrepancy between free-to-shrink and constrained samples as shown in Figs 2 and 3. The data suggest that once the orientation reaches a certain value ($\Delta n \sim 0.20$), then cold crystallization begins (and reaches its maximum rate) at a temperature which is significantly lower than that characteristic of unoriented polymer (ca. about 370 K compared with 400 K).

When the sample is constrained, less crystallinity develops during scanning than in the free-to-shrink case. At low wind-up speeds, the orientation is low and, consequently, so also is the shrinkage. At high wind-up speeds, the orientation is very high and substantial crystallinity develops in the spin line. Consequently, shrinkage is once again very low. In these two limiting cases, the cold crystallization behavior is not affected by whether the sample is restrained or not.

Direct application of this knowledge to the dynamics of melt spinning is difficult. The results suggest that the *orientation* is enhanced sufficiently at even low speeds ($\Delta n \sim 0.20$) to induce oriented crystallization which, of course, depends on tem-

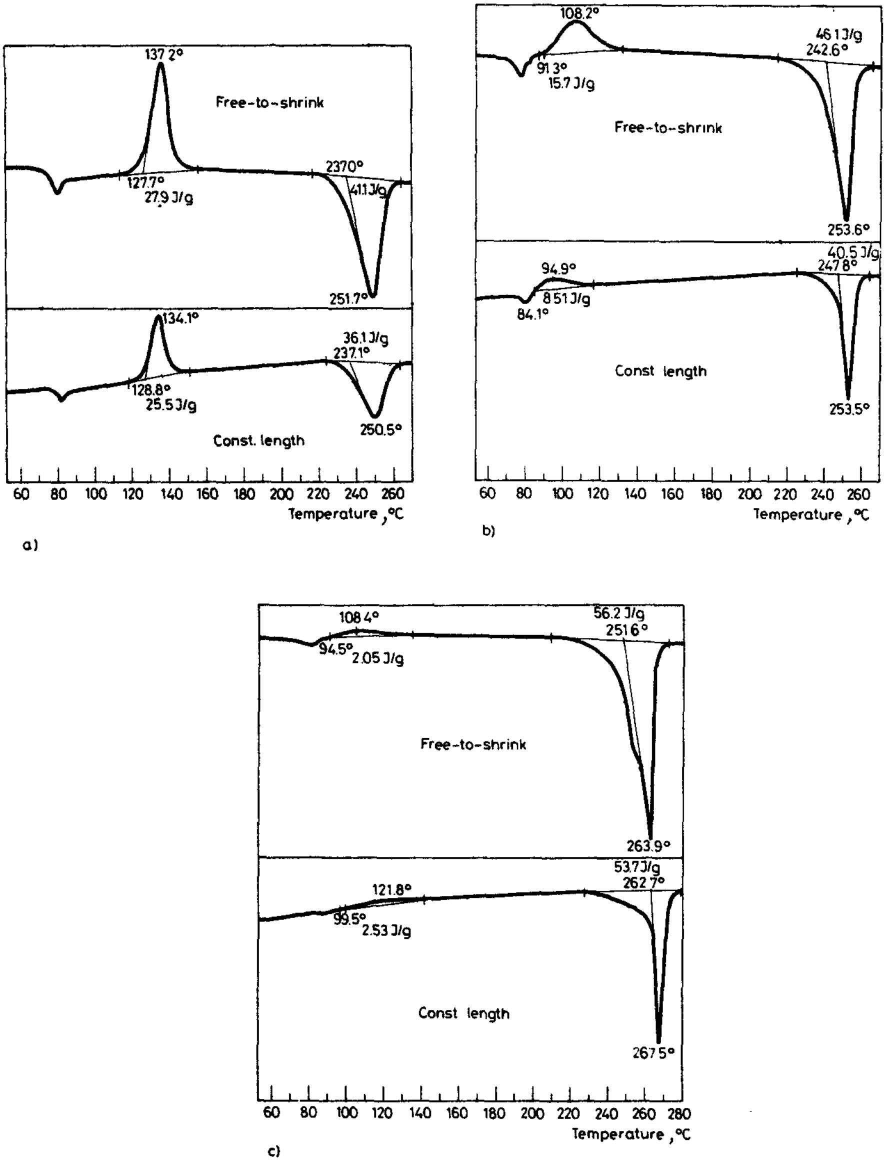

Fig. 1 Typical DSC curves of PET fibers. Wind-up speed a: 25.6 m/s; b: 56.4 m/s; c: 97.4 m/s

perature, cooling rate, and many other process conditions. The temperature of cold crystallization may show the leveling behavior with increasing wind-up speed because the more highly oriented polymer is constantly being "removed" by crystallization *during* spinning.

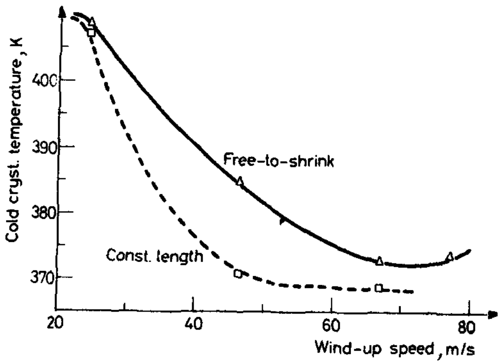

Fig. 2 Effect of tension on cold crystallization temperature of PET fibers

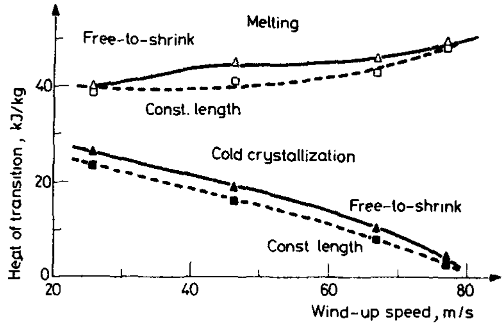

Fig. 3 Effect of shrinkage on the heats of transition of PET fibers

Summary

Polyester yarns, in which the orientation is imparted by varying wind-up speeds in the range of 25–80 m/s, have been analyzed by differential scanning calorimetry. Samples were prepared for DSC both in the conventional fashion and by wrapping on small aluminum spools. In the former case, samples are free-to-shrink during thermal testing; in the latter case, they are constrained from shrinking. The results show that the heats of fusion and cold crystallization are smaller when samples are constrained, indicating less crystallization occurs during the thermal testing. In addition, the temperature of cold crystallization, T_c, in the intermediate wind-up speed range occurs at lower temperatures under conditions of fiber constraint. Once the average birefringence (orientation) of the yarn reaches a value of about 0.020, T_c has decreased from 400 to 370 K. T_c is insensitive to further increases in orientation.

It is suggested that this behavior is a result of crystallization in the spin line; as polymer attains some critically high orientation in the spin line, it crystallizes, thereby continually removing the highly oriented molecules from the melt.

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Zusammenfassung — Mit verschiedenen Aufspulgeschwindigkeiten gesponnenes Polyestergarn wurde durch DSC charackterisiert. Die während der tyermischen Analyse am Schrumpfen gehinderten Proben zeigen, besonders bei mittleren Aufspulgeschwindigkeiten, eine etwas geringere Schmelz- und Kristallisationswärme und niedrigere kalte Kristallisationstemperaturen als Proben, die ungehindert schrumpfen konnten. Die kalte Kristallisationstemperatur erreicht bei enier relativ niedrigen Gesamtmolekularorientierung ($\Delta n \sim 0.020$) ein Minimum und nimmt nicht weiter ab. Wahrscheinlich ist, dass durch die Kristallisation das Polymer in den Bereichen, in denen die lokale Orientierung einen kritischen Wert erreicht, kontinuierlich aus der Schmelze entfernt wird.

Резюме — Полиэфирная пряжа, вытянутая с различными скоростями наматывания, была охарактеризована методом дифференциальной сканирующей калориметрии. Образцы, забракованные из-за усадки, во время термических исследований показали слегка меньшие температуры плавления и кристаллизации, а также пониженные температуры холодной кристаллизации по сравнению с образцами, свободными от усадки, и, особенно, в области промежуточной скорости наматывания. Наблюдалось, что температура холодной кристаллизации достигает минимума при некоторой относительно низкой молекулярной ориентации ($\Delta n \sim 0.020$) и дальше не падает. Это может быть обьяснено тем, что кристаллизация непрерывно удаляет полимер из расплава в нити вытягивания в областях, где локальная ориентация достигает некоторого критически высокого значения.