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THERMAL SHRINKAGE STRESS RELAXATION IN PET HIGH SPEED SPUN YARNS.

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ABSTRACT

An apparatus for the characterization of thermal shrinkage stress relaxation of PET partially oriented yarns at temperatures above Tg is described. The apparatus is used to characterize the glass transition of the yarns. Two modes of relaxation are observed and related to network orientation and frozen stresses. The extent of the relaxation modes reflects the spinning conditions. The method reveals a novel shrinkage stress peak evolution at longer times, which is related to a special crystallization process in the taut annealed yarn.

INTRODUCTION

An apparatus for measuring the shrinkage stress at different temperatures in continuous yarns was especially designed to overcome the drawbacks of the commercially available thermomechanical analyzers. While the standard equipment uses short samples of 10 cm, the apparatus analyzes 35 meters long skeins. This fits the apparatus especially for POY (partially oriented yarn) analysis, since during high speed spinning of POY the short samples correspond to very short spinning times (at 3300 m/min spinning speed, 10 cm correspond to $1.8 \cdot 10^{-3}$ seconds), which are shorter than the threadline tension fluctuations. Therefore, longer samples are needed to average out the short-range threadline variations. The shrinkage stress vs. time patterns of the taut Poly (ethylene terephthalate) POY yarns at temperatures above the glass transition, obtained in the apparatus, are used to characterize the fibers, to evaluate their spinning history, and to detect processes that take place during the taut annealing of POY yarns.

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EXPERIMENTAL

Material: Commercial Poly (Ethylene terephthalate) POY (partially oriented yarn) 116/34 denier yarns, spun at 3300 m/min from polymer of 0.649 intrinsic viscosity, containing no delustrant.

The shrinkage stress relaxation measurement apparatus is described in Fig. 1. The sample skein is suspended from a hook with the lower end connected to a force transducer, connected through an amplifier to a strip chart recorder. The pretension is controlled through a vertical adjustment of the sample hook position. The heater is a slotted tube, wrapped by a thermoelectric heating tape, which can swing around and locate the pretensioned skein through the opened slot along the center of the heating tube. The temperature is measured with a thermocouple, mounted 3 mm from the center of the skein. In order to have a uniform temperature and to prevent chimney effects, a mild nitrogen flow is maintained along the heating tube. Measurements of shrinkage stress vs. time were performed at temperatures between 80°C to 185°C.

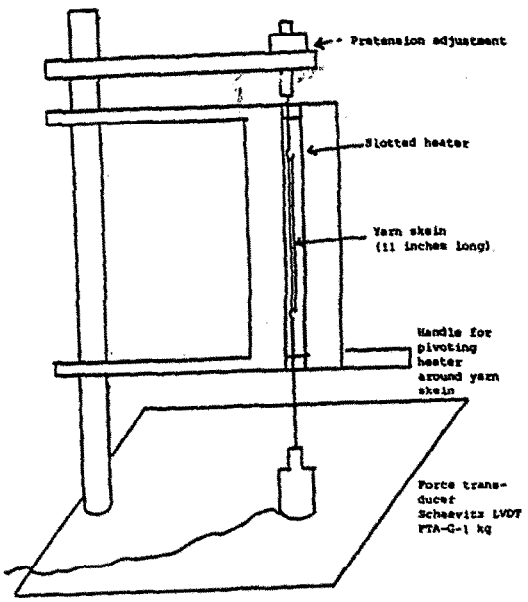

Fig. 1 Shrinkage force analyzer. The skein shrinkage force is recorded as a function of time for different temperatures.

Raman spectra in the low frequency region were obtained as described by Deblase et al using conventional [1] and rapid [2] Raman spectroscopy techniques.

RESULTS AND DISCUSSION

The shrinkage force can be defined as the tensile force that must be applied to a fiber to prevent shrinkage. It originates in the fiber from the entropic retraction force exerted on the extended long chain molecules in the amorphous phase above its glass transition, following the statistical theory of rubber elasticity [3].

Fig. 2 depicts the molecular conformational changes accompanying the spinning process: the molten filaments diameter attenuation involves stretching of the random coils along the threadline by virtue of their physical entanglements which cross-link the molecules and prevent their viscous flow past each other. Quenching the fibers below the glass transition "freezes-in" the strained network, which develops shrinkage forces upon "unfreezing".

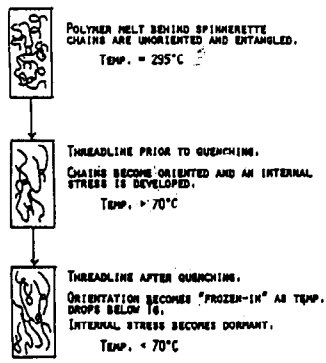

Fig. 2 DEVELOPMENT OF ORIENTATION DURING SPINNING.

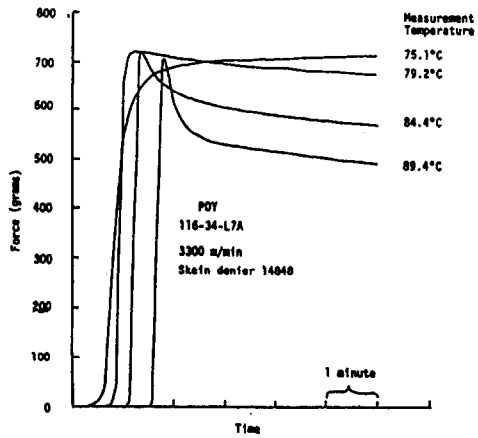

Fig. 3 Shrinkage force curves measured at different temperatures for POY spun at 3300 m/min. The curves are offset on the time axis for clarity.

As seen in Fig. 3, shrinkage forces develop in the taut yarns as the temperature rises above the glass transition.

The rate at which the force develops and subsequently decays increases, the larger the difference between the measuring temperature and the glass transition temperature of the yarn.

Fig. 4 gives a typical shrinkage stress relaxation pattern, defining three parameters that describe the process: the maximum shrinkage force value, referred to as the "initial shrinkage force" (Fin). Once the maximum force is reached, it decays rapidly at first, and then much more slowly. An extrapolation of the slower rate process back to the intersection of the leading edge of the curve represents the initial value of the slowly relaxing force, called the "network shrinkage force" (Fnw). The value of the force measured after 5 minutes is called the "5-minute shrinkage force (F5min).

We believe that Fnw measures the orientation of the entangled chains network set during the hot-drawing stage of the spinning. The value of the difference: Fin - Fnw represents the fast shrinkage force relaxation part and is related to low activation frozen stresses introduced to the yarn at the later stages of spinning, when it cools below the glass transition.

As seen in Fig. 3, the frozen stress relaxation Fin - Fnw values increase as the measurement temperature rises above the glass transition temperature. One can define the glass transition as the temperature at which the frozen stress relaxation diminishes, since long range segmental mobility is needed to facilitate stress relaxation.

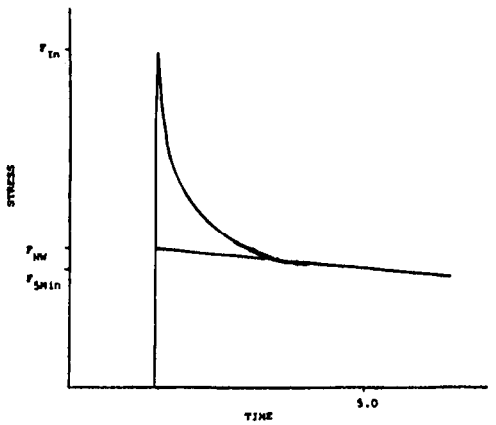

Fig. 4 Thermal stress relaxation pattern obtained at the low-temperature range.

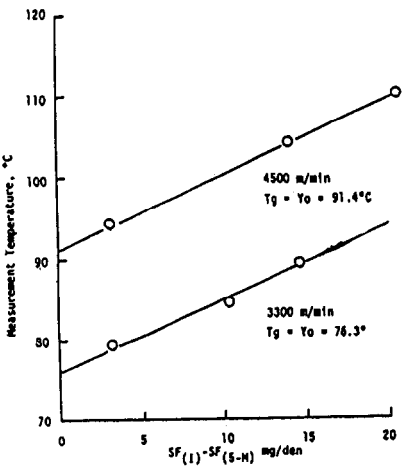

Fig. 5 Graphical Method for extracting Tg from shrinkage force curves.

Fig. 5 gives a simple graphical method to extract the glass transition from the frozen stress Fin - Fnw values - obtained at different temperatures: extrapolation to zero frozen stress relaxation value yields the glass transitions of 76.3°C and 91.4°C for POY yarns spun at 3300 m/min and 4500 m/min respectively. This is in agreement with the literature data on the effect of spinning speed on the glass transition [4].

Pinock and Ward analyzed the shrinkage stress relaxation of low speed spun amorphous yarns [5]. They got a constant stress-optical coefficient, suggesting that the shrinkage stress relaxation proceeds via disentanglements that break down the cross-links and allow individual chains to revert back to their randomly coiled confirmations. The situation in POY yarns is complicated because of the effects introduced by the high spinning speed: cold-drawing and stress-induced crystallization [6], which are superimposed on the disentanglement driven network stress relaxation.

Following the observed two mechanisms of shrinkage stress relaxation, we distinguish between two types of orientation processes in POY spinning: hot-drawing and cold-drawing, above and below the glass transition respectively. Spinning speed, capillary size, melt viscosity and cooling rate affect the hot-drawing, while air-drag and yarn-to-guide friction affect the cold-drawing. In Fig. 6, a decrease in melt temperature, which increases the melt viscosity, causes an overall increase in the shrinkage force, but the frozen stress relaxation values Fin - Fnw are not affected.

Friction induced cold-drawing, on the other hand, causes a large increase of Fin, but no change in F5min and Fnw, giving a large increase in the frozen stress relaxation Fin - Fnw value.

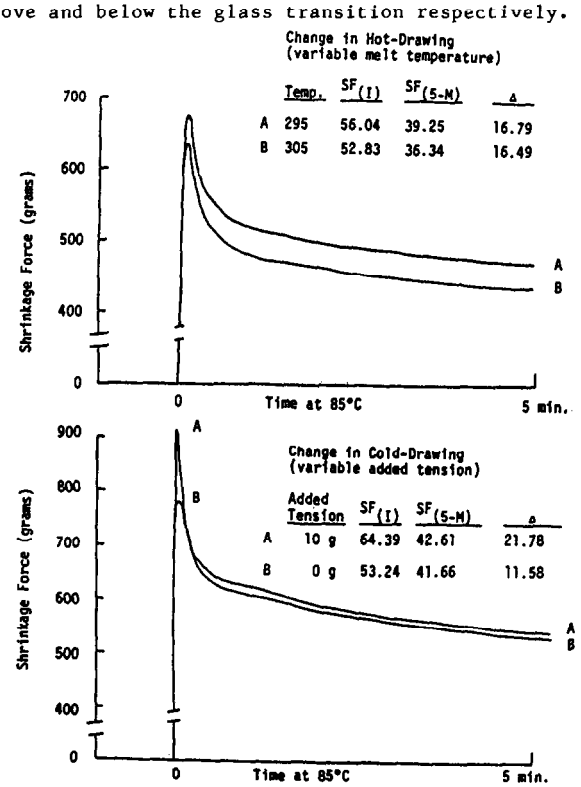

Fig. 6 Comparative responses of shrinkage force curve to hot and cold-drawing.

Fig. 7 shows the response of shrinkage force to cold-draw, induced by the use of slower speed feed roll in the spinning line. The response of the initial force Fin to the cold-draw demonstrates the capability of the technique to distinguish between the drawing mechanisms and to relate yarn properties back to the spinning process.

In Fig. 8, extensive shrinkage stress relaxations at temperatures higher than 100°C occur very rapidly, followed by development of a distinct shrinkage stress peak, which is more pronounced the higher the temperature. The development of shrinkage stress peak during stress relaxation is unique and was reported only once in TMA analysis of PET fibers [7]. The fact that it happens at higher temperatures and associated with the initial extensive relaxation, suggests that both the rapid stress relaxation and stress peak formation are associated with crystallization. Characterization of the degree of crystallinity and birefringence confirmed the assumption. Raman spectroscopy of the yarns, after being subjected to

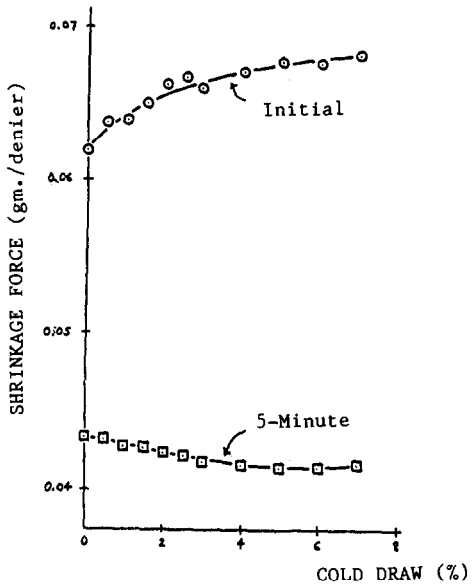

Fig. 7. Response of shrinkage force to cold-draw induced by use of feed wheel. The spinning speed at the winder was 3300 m/min.

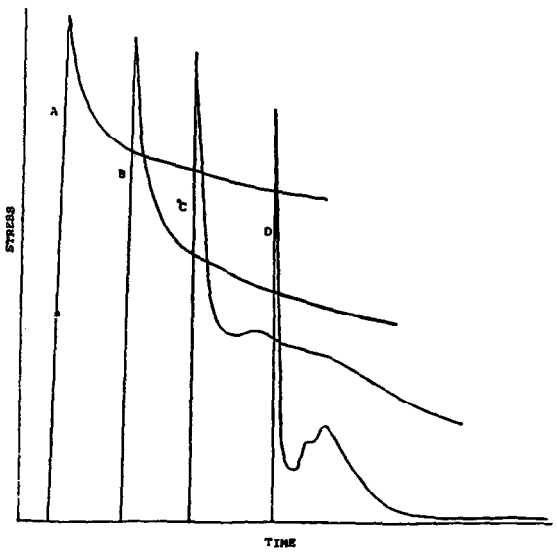

Fig. 8 Thermal stress relaxation patterns at: A - 86°C, B - 100°C, C - 108°C, D - 152°C

the shrinkage stress relaxation test, reveals in Fig. 9 a crystalline intermolecular absorption mode at 63.cm^{-1} [2], corresponding with the shrinkage stress peak development. Accordingly, the shrinkage stress peak is associated with a special mode of crystallization [1].

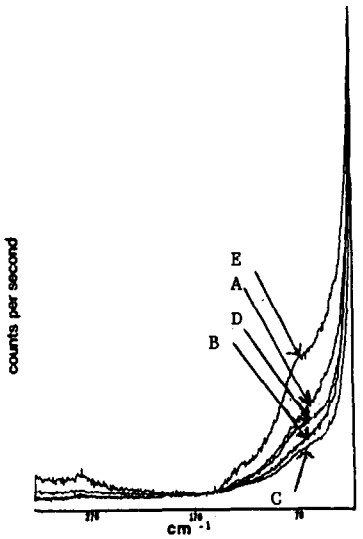

Fig. 9. Raman spectra of single filaments of PET POY fibers. (a) Original fiber, take-up speed of 3290 m/min. (b) Fiber annealed at 70°C for 60 min with ends free. (c) Fiber annealed at 86°C for 2.5 min with ends fixed. (d) Fiber annealed at 122°C for 5 min with ends fixed. (e) Fiber annealed at 152°C for 5 min with ends fixed. All spectra taken at room temperature and normalized to 20-cm^{-1} scattering.

CONCLUSIONS

The apparatus for fiber characterization via shrinkage stress relaxation which is described produces information on large size samples, useful for POY spinning process and quality control. The technique evaluates yarn properties, including the glass transition and crystallization tendency. Two modes of relaxation, related to frozen stresses and network orientation, enable detection of the extents of cold and hot drawing that take place during the spinning process of the yarns.

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