

Heat Setting

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Received 8 November 2000; accepted 18 November 2000

ABSTRACT: As-manufactured polymeric fibers are oriented semi-crystalline structures in which the macromolecules are rarely in their equilibrium state. Further instabilities are imparted when the fibers are converted to yarns and the yarns to fabrics. Heat setting is an important industrial process, since it rids them of their instabilities. This review article first considers aspects that are relevant to the broad area of heat setting, viz., the origin of instability, the durability of set, thermal and dynamic mechanical transitions, thermodynamic basis of setting, shrinkage and shrinkage stress, and characterization of the degree of set. The heat setting of major thermoplastic fibers, viz., polyester, polyamide, polyacrylonitrile, polypropylene, and polyethylene has been described in terms of the conditions of heat setting, the structural and morphological changes that occur on heat setting, and the changes in their physical properties. It is shown that heat setting affects such important properties as stress-strain and recovery behavior, dye-uptake, optical properties, and thermal properties. The structural and morphological changes have been described in terms of changes in crystallinity, crystal size and their size distribution, crystal defects, crystal orientation, the nature of the amorphous phase and its orientation, the coupling of the crystalline and amorphous phases, etc. The structural basis of property changes is then discussed. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 586–609, 2002

Key words: heat setting; polyester fibers; polyamide fibers; polyacrylonitrile fibers; polyolefin fibers

INTRODUCTION

Polymers in the form of natural fibers such as cotton and wool have been used as clothing for many centuries and have continued to provide humans with protection and comfort in all seasons. However, it was only around the first quarter of this century that the structural basis of their physical properties began to be appreciated. The two major findings that made this possible were first that the polymers were composed of long chains of covalently bonded molecules and second that the fibers contained small crystallites or micelles in an amorphous matrix. Because the

molecules were much larger than the micelles, it was concluded that individual molecules pass through a number of crystallites, alternating with segments in the amorphous or disordered regions and thus provide integrity to the system. This was the basis of the fringed-micelle model, as a natural corollary of which the roles played by the two phases, viz., the crystalline and amorphous phases, became more clear. It began to be recognized that cohesion, stability, strength, and durability were in a large measure provided by the crystals whereas the molecules in the noncrystalline regions were mainly responsible for extensibility, pliability, toughness, and a path for diffusion. The important and essential property of recovery on unloading of the fiber could then be looked upon as a characteristic in which both the

phases and interaction between them made their contribution. It is thus not surprising that all successful textile fibers that have since been manufactured, are based on intrinsically crystallizable polymeric structures that have the potential to be oriented and that ultimately give semicrystalline fibers.

Fibers based on polymers are extensively used as commodity textile fibers and also as industrial fibers. In the as-manufactured state, the macromolecules in these oriented semicrystalline structures are rarely in their equilibrium state in either the crystalline regions or the amorphous regions of the fiber. As a result, they are susceptible to dimensional instabilities caused by application of load, temperature, or solvent. When the fibers are converted to yarns and the yarns to fabrics, further instabilities are imparted to these structures. Means are therefore needed that will rid the fiber of the instability, because otherwise there may be considerable thermal shrinkage or permanent deformation, which of course, is totally unacceptable. The setting of fibers and fabrics aims to achieve this. Thermoplastic fibers such as poly(ethylene terephthalate) (PET), nylon-6, nylon-66, polypropylene, and polyethylene, and to a limited extent, polyacrylonitrile, can be made dimensionally stable to a significant extent by heat treatment, often aided by moisture and tension. However, natural fibers such as cotton, wool, and silk require chemical treatments, aided by heat, tension, and moisture, for dimensional stability. The present contribution will be limited to a consideration of the heat setting of only thermoplastic fibers. However, some of the less-used fibers, eg., cellulose acetate, cellulose triacetate, polyvinyl alcohol, and polyvinyl chloride will not be considered. It is intended to concentrate on structure-property correlations in textile fibers that have been subjected to a variety of heat setting treatments, and the emphasis will be on fundamentals.

It must be emphasized at the outset that the fibers under consideration are heterogeneous in more than one respect. An important cause of the heterogeneity at the fine structure level in melt-spun fibers is the temperature variation across the cross-section when the fiber is solidified by cooling during fiber production. As a consequence, during heat setting, the rate of change toward equilibrium may be different in different parts of the fiber. Hearle¹ has expressed this in terms of a multiplicity of energy levels existing in the fiber and has stated that heat setting may shift them

toward lower energy levels, thus moving the whole system closer to equilibrium. The other level of heterogeneity is at the macroscopic level with the outer skin of the fiber having a different morphology compared with the interior of the fiber. Solution-spun acrylic fibers may contain voids and other such defects because of two-way mass transfer during coagulation. It would be expected that heat setting would heal some of these causes of instability.

Besides imparting dimensional stability to the yarn and the fabric, heat setting is also useful in some other respects. For example, twisted or doubled filaments have a strong tendency to curl or snarl and this has a deleterious effect on further processing. Also, planar structures such as fabrics produced from unset, continuous filaments, or fibers display unfavorable creasing behavior when in use. In all of these operations, heat setting, sometimes in the presence of swelling agents and tension, achieves the common objective, viz., to take the product toward equilibrium to attain resistance against thermal shrinkage, dimensional changes, curling, and creasing. Sometimes improvements in physical properties, particularly mechanical properties, may also be achieved.

The conditions of heat treatment depend on the nature of the polymer and the type of fiber.² Heating systems applied in industry include dry air contact heating elements, water vapor, liquid baths, etc. When swelling media are used, stabilization results from both temperature- and solvent-induced molecular motions. Depending on the desired mechanical characteristics, stabilization can be performed in the free state (to minimize residual shrinkage) or under tension (to reduce breaking elongation). The stabilization temperature, which is predominantly determined by the nature of the polymer, should be higher than the maximum temperature of application to ensure stability under application conditions, where the kinetic equilibrium can be reached in a reasonably short time. This requirement is met by heat treatment between the two principal thermal transition temperatures, viz., glass transition temperature (T_g) and melting point (T_m). Finally, the upper temperature to which a textile fiber can be heated is limited by the thermal stability of the material, e.g., PET fibers undergo depolymerization when heated at higher temperatures in the presence of water whereas polyethylene and polypropylene are sensitive to oxidation, etc.

THE ORIGIN OF INSTABILITY IN FIBERS

To trace the possible origin of instability in fibers and to understand the processing-structure-property relationships, reference may be made to a very interesting contribution made by Barham and Keller,³ who invoked thermal shrinkage as a criterion to distinguish between a variety of samples, all made from polyethylene through fundamentally different processing routes and then establish a criterion for stability.

It was noted that solution-grown Shish Kebab fibers and capillary melt extrudates showed little shrinkage; the authors called them category I fibrous structures. However, drawn individual single crystals, drawn single crystal mats, and drawn spherulitic sheets showed significant shrinkage. These were termed category II fibrous structures. They defined fibers belonging to these two categories as follows. category I: comprising substances whose molecules had been actually synthesized in the chain extended form such as biological polymers and crystals formed by *in situ* polymerization and all forms of stress- and flow-induced crystallization; and category II: comprising the products of solid state drawing or rolling, in which crystalline textures already present are disrupted and the chains are aligned in the direction of orienting influence.

Based on these studies, the authors invoked the following test to distinguish between these two categories: if heated close to the melting range without, however, converting the full sample into the molten state, the dimensions of category I remain essentially unaltered whereas category II shrinks drastically. They attributed this behavior of the latter to "locked-in stresses, usually attributed to stretched tie molecules spanning different crystallites, which are not present in Category I, at least not to the same extent."

To this wide range of samples, we may add one more polyethylene sample, which is of more recent origin, viz., ultrahigh molecular weight high-density polyethylene (UHMWHDPE) fiber made by the gel-spinning and drawing route. This fiber is made by drawing the gel-spun fiber in the presence of a significant amount of solvent. It is a highly crystalline fibre and is stated to show little shrinkage over a wide temperature range. Because it is like a "continuous crystal," it hardly needs any setting treatment.⁴ However, close to but below its melting temperature, it shows significant shrinkage.

That locked-in stresses are indeed responsible for dimensional instability can be illustrated with the help of a study on amine etching of a drawn PET fiber before and after heat setting.⁵ The stress cracking has been shown to occur in such cases only when a specimen supports an internal or externally applied stress, above a critical level. It was found that the drawn fiber showed high crack density whereas in heat-set fibers, the crack density was very low.

The setting of twist and the removal of snarling tendency in a doubled yarn on heat setting can also be explained on the same basis, viz., the relaxation of residual stresses and thereby "fixing" the shape.

At the fine structure level, the residual stresses will be expected to principally reside either in the amorphous phase or in the defective crystallites or at the crystal amorphous interphase.

Strictly speaking, the term "residual stress" is used to describe a self-stressed state induced, for example, during the cooling stage of processing.⁶ The local state and the energy elastic stress vary from point to point within the product. Internal stresses of this type should not be confused with molecular orientation, and frozen-in orientation should not be classified as a type of stress. At best, orientation could be termed a "passive stress," because a shrinkage stress would develop if the sample were to be heated above T_g while held in a fixed position—the relaxation of orientation being an entropic effect. However, the term residual stress will be used herein to include both internal stress and passive stress. The various terms used in the literature for such stresses and their origins have been considered by White.⁷

THE DURABILITY OF SET

One of my earliest recollections of the complex nature of setting in yarns was the rather surprising observation that a false-twist-textured PET yarn taken off from the package looked no different from the flat PET yarn. However, when it was gripped between the hands and subjected to a jerk, the yarn showed a whole spectrum of crimps, loops, and curls. This phenomenon has been described in very apt terms by Hearle¹ as follows: when a false-twist yarn is pulled carefully off the package, it does not appear bulked. Bulk develops as a result of slight mechanical action or wetting which destroys the final temporary set achieved on the wind-up and demonstrates the permanent

set imposed by heating and cooling. To understand the mechanism of latent crimp in textured PET yarn, we conducted some studies, and because they shed interesting light on the mechanism of temporary set, the key results will be summarized herein.

Temporary Set and Its Structural Basis

The effect of tension in the winding zone of the false-twist texturing process on the crimp properties of textured PET yarn was studied using only the primary heater⁸ and overfeeds from 2 to 8% in the winding zone. It was observed that crimp gets progressively suppressed as the winding tension increases, i.e., as the percentage overfeed decreases. As shown in Figure 1, mechanical conditioning decreases the role of wind-up tension in rendering the crimp latent. The temporary set in this case has been attributed to the applied tension in the winding zone which straightens the filaments in the yarn and suppresses the torsional and bending stresses that would normally cause the yarn to develop crimp and contract.¹ However, the actual mechanism by which this happens required a comprehensive theoretical and experimental analysis and it was found⁹ that the tangential contact forces between the filaments, which decrease with increase in bulk, pro-

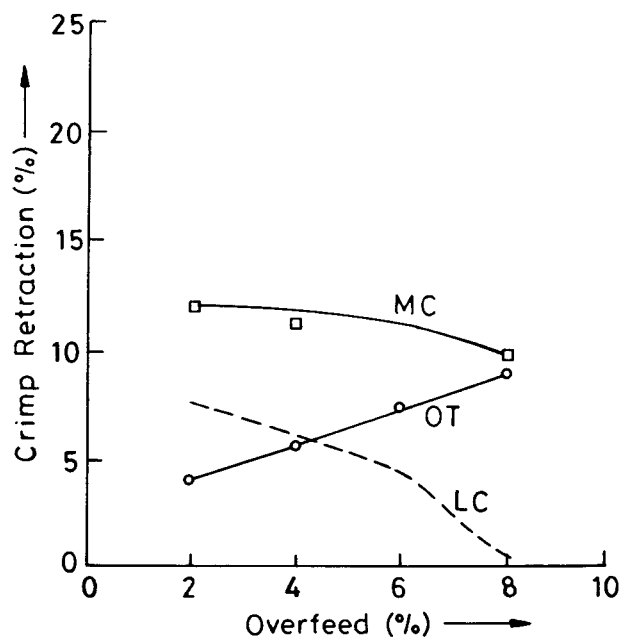


Figure 1 Illustration of the suggested origin of latent crimp (LC) for mechanically conditioned (MC) yarn (OT, original textured).

vide the possible sites for location of residual stresses. The other factor was amorphous orientation which was found to be higher in the as-textured yarn as compared with that in the mechanically conditioned yarn.

Two further examples of temporary set are¹: 1. wrinkling of "set" synthetics, which is an unintended and undesirable temporary set. This can be removed by domestic ironing which gives the fabric the intended and desirable set; and 2. differentially shrinkage fibers which are combined in the yarn to give high-bulk yarns.

The possible mechanisms for temporary set have been discussed by Hearle¹⁰ in terms of the various intermolecular forces in fibers. The weakest forces are the van der Waals forces between the molecules and are the dominant forces in polypropylene and polyethylene. They hinder free rotation of chains and to that extent can contribute to temporary set. The interactions are much stronger if strong dipolar groups are present like the $-\text{C}\equiv\text{N}$ group in polyacrylonitrile fiber. They have the ability to induce temporary set, but above 80°, they are not effective. In nylon-6 and nylon-66, temporary set may arise from the formation of hydrogen bonds in a particular position in the deformed fiber. If the fiber is heated to 50°C, for example, the hydrogen bonds will break and relieve the stress. On cooling, the hydrogen bonds will reform and stabilize the structure.

McIntyre¹¹ considers intermolecular forces from the point of view of oriented chains that are prevented from sliding over each other in the fiber by these forces. Besides the interchain forces considered above, he also includes entanglements and crystallites. Undoubtedly, these will act as physical and chemical crosslinks respectively and will also play a role in temporary set.

Permanent Set and Its Structural Basis

Most industrial setting is based on permanent set, which results from structural changes that cannot be reversed unless a more severe treatment is given.

A useful concept in considering the setting of fibers and fabrics is that of the reference state.¹ This is the state to which the system (fiber) returns when it is allowed to settle down free of any restraints after being given a small degree of mobility; for example, by slight heating or wetting. If the changes do not alter the reference state, there is no new permanent set. Temporary or semipermanent set may be achieved in other forms but

the reference state can always be reached again. In permanent set, however, a new reference state is found. Such a transformation is obtained through a change in crystalline morphology through a number of routes, some of which are considered below.

Partial Melting and Recrystallization

The most common route for permanent set is partial melting or at least partial mobilization of small, imperfect, or irregular crystallites at a temperature much below the real melting point, and a growth of larger, more perfect crystals. The first evidence for partial melting and crystallization was given for PET by Zachmann and Stuart.¹² Partial melting relaxes any internal stresses and the recrystallization stabilizes the new form, thus providing an irreversible mechanism of set.

Crystallization of Oriented Amorphous Phase

Another route leading to crystallization during heat setting involves the molecules in the amorphous regions that are well parallelized but not in register. With the aid of thermal energy, they can gain enough mobility to reduce their free energy by forming small crystallites.

Perfection of Crystals

A third possibility during heat setting is that the larger existing crystallites can become more perfect by expelling the defects out of the crystal.

Thickening of Crystals

Another interesting route has been suggested from studies on the thickening of polyethylene crystals in which refolding is stated to occur by localized axial movement of fold stems without involving chain portions outside the body of the crystal.¹³ More recently, it has been demonstrated that during annealing of regularly stacked lamellar crystals of UHMWHDPE at temperatures above the α -relaxation (110°C), the lamellar thickness increases to twice the initial value via a mutual chain rearrangement between the adjacent lamellae involving a sliding motion along the chain axes resulting in welding and fusion of the structure.¹⁴ However, further thickening beyond twice the initial value occurs via a melting and recrystallization process.

Entanglement Slippage

Buckley and Salem¹⁵ have proposed entanglement slippage as a mechanism of permanent set in PET. At high heat setting temperatures, situated between the glass transition and melting regions, entanglements, which tie crystalline blocks, can slip out and the ensuing viscous flow process can lead to a change in crystal morphology.

Chemical Healing

There is still another way in which crystalline morphology changes on high temperature annealing. For the specific case of PET fiber, this involves chemically induced morphological changes in the solid state. For example, ester-inchange reactions can turn chain folds into intercrystalline tie molecules or other similar transformations^{16,17} and thereby render the ductile fiber brittle.¹⁸

THERMAL TRANSITIONS

The two important thermal transitions in a semicrystalline fiber are the glass transition and melting, the respective temperatures of these transitions being denoted by T_g , which is characteristic of the amorphous phase and T_m , which relates to the crystalline phase. Whereas T_m is a primary transition involving a change of phase from a solid to a liquid, T_g is a secondary transition.

T_g

When a semicrystalline fiber is heated up to and just beyond T_g , it acquires enough thermal energy to overcome the resistance to large-scale motion of the molecules in the amorphous regions, which arises from factors like cohesive forces holding these molecules together, intrinsic attributes of the chain such as its rigidity, the constraints imposed by the crystallites which act as chemical crosslinks, etc. As a result, the amorphous portions in the fiber "soften" or "melt" whereas the crystalline portions remain solid.¹⁹ In terms of the free volume theory, above T_g , enough free volume becomes available for rotation of molecular segments, leading to a more rapid increase of specific volume.

Next considered is the transition from the rubber-like state to the glassy state as the sample is cooled. As the temperature is lowered, the relax-

ation time increases and, under normal cooling rates used in industry, the equilibrium state of the polymer and the corresponding structure are rarely achieved. The amorphous regions in semicrystalline fibers are generally in a metastable state below T_g . The theories of T_g invariably treat the observed value of T_g as a kinetic (rate-dependent) manifestation of an underlying thermodynamic phenomenon.¹⁹

Melting Temperature

In polymers, melting occurs over a wide temperature range; however, frequently a precise temperature is quoted as the melting temperature.

At the melting point, equilibrium exists between the liquid and the crystal. The equilibrium melting point, T_m° , is the temperature at which a perfect polymer crystal of infinite size would melt, and is given by $T_m^\circ = \Delta H_m / \Delta S_m$ (enthalpy of melting)/ ΔS_m (entropy of melting), as determined from a consideration of the thermodynamic basis of setting (see below).

Heat Setting Close to the Melting Point

In a very interesting study, Kitano et al.²⁰ annealed PET continuously under vacuum for a period of up to 2 years, the temperature being raised gradually to 280°C at a rate of 0.5°C per day. Increments of only 0.2°C per 4 days were used above 280°C to a final value of 290°C for about 6 months. After the annealing process, the sample tube was cooled from the bath temperature to 230°C at a rate of 2°C per day and from 230°C to room temperature at 10°C per hour. The PET thus obtained had a high melting point of 302.1°C, an observed density of 1.468 g/cm³, and a differential scanning calorimetry (DSC) crystallinity of 95%. The highly crystalline material, according to the authors, consists of molecules that are either fully extended or contain only a few folds.

It has been pointed out by Keller²¹ that the possibility that a finite crystal size could correspond to a state of lowest free energy was first suggested by Frank²² on the principle that the rise in energy caused by an interruption of the lattice continuity could, under appropriate circumstances, be more than compensated by the associated increase in entropy. It is now accepted that the folding behavior of crystals is of kinetic origin and, according to the kinetic theories, the observed chain folded crystals correspond to the structure with maximum crystallization rate,

rather than maximum thermodynamic stability; the latter corresponds to chains fully extended or folded with substantially greater fold length.

It would thus appear that the PET samples prepared by Kitano et al.²⁰ are indeed closer to their equilibrium state as a result of prolonged high temperature annealing.

Multiple Melting Endotherms

Investigations of a number of annealed semicrystalline fibers by DSC have often revealed two or even three melting endotherms in which temperatures and relative areas depend on the temperature and the duration of the thermal treatment. Those showing doublets include PET, some polyolefins, polyamides, and various polyesters [for example see Reference 17 and references given therein]. Though the structural origin of the two endotherms is still controversial, the partial melting and recrystallization of the sample in the DSC cell with the recrystallized fraction melting at the high temperature endotherm, has been invoked by a number of authors as the likely cause for the melting doublet. Triple melting of heat set PET, nylons, and poly(ethylene naphthalate) has been reported [for example see Reference 23 and references given therein]. Whereas the second and third endotherms are stated to have similar origin as for the doublet in the case of PET, the first small melting endotherm is stated to probably originate from the last steps of secondary crystallization during heat setting.

DYNAMIC MECHANICAL TRANSITIONS

In the dynamic mechanical spectrum of a fiber, when $\tan \delta$ is plotted as a function of temperature, a number of transitions generally occur. Each of these relaxations involves dissipation of energy and a decrease in dynamic modulus. Thus, as the fiber transverses these transitions, the residual stresses will tend to relax out and the fiber will become more stable. The actual efficiency of these transitions in terms of stress relaxation would depend on the molecular origin of the transition and its intensity. The dynamic mechanical spectra of various polymers have been described in McCrum et al.²⁴

PET fiber shows three loss peaks below room temperature, viz., at -165°C, -105°C, and -53°C and one above room temperature at between 87 to 127°C. The three low temperature

relaxations are important in determining the room-temperature properties of the polymer, in particular its flexibility. Sub- T_g aging of PET, which densifies the structure through free-volume collapse, is also dependent on the molecular mobility provided by these relaxations. Heat setting the fiber at T_g is believed to result in temporary or semipermanent set mainly through the redistribution of free volume or its collapse but, as shown later, it is likely that structural reorganization might be occurring in the fiber at a more subtle level. Buckley and Salem^{15,25} have studied the recovery of as-drawn and heat set PET monofilament for small torsional and bending modes of deformation. When fractional recovery was plotted as a function of heat setting temperature, a gradient of the plot was visible at around T_g (α relaxation) for the as-drawn samples whereas in the preset specimen a gradient was also visible at the heat setting temperature of around 200°C, which they labelled as the α' relaxation. The origin of the latter process is postulated to be slipping of stressed entanglements by molecular diffusion in a polymer network that is incompletely crosslinked by crystals. As stated earlier, this viscous flow process has been suggested as a mechanism of permanent set.

Nylon-6 and Nylon-66 fibers show a dynamic mechanical spectrum which in some respects is broadly similar to that shown by PET in that the loss peak caused by T_g is above room temperature (80–100°C) and the β peak is below room temperature (–80 to –30°C).

The dynamic mechanical spectra of polypropylene and polyethylene fibers also have some common features but they are different from those for PET and polyamide fibers in two respects. First, the T_g of high density polyethylene (–80°C) and polypropylene (–10°C) fibers are below room temperature, and second, both of these fibers show loss peaks around 100°C, which are believed to be related to motion in their crystallites. Thus, heat-setting processes leading to permanent set would be performed at temperatures above these high temperature loss peaks.

Acrylic fibers are very different compared with other thermoplastic fibers, so much so that they have to be spun through the solution spinning route. The main reason for this is the strong dipolar intermolecular bonding. The two distinct loss peaks at 110°C and 160°C (at a frequency of 110 Hz) may both be glass transitions arising from less ordered and more ordered amorphous phases, respectively in the fiber.²⁶ There is a per-

ceptible drop in modulus of about one order of magnitude at 100°C. The modulus rises beyond 200°C, apparently because of crosslinking. There does not appear to be any possibility of inducing permanent set through heat setting of this fiber. A typical heat setting of acrylics through relaxation in saturated steam at 130°C would at best be a semipermanent set.

THERMODYNAMIC BASIS OF SETTING

Dimensional stability of fibers requires that the application of mechanical stress to the fiber or exposure to a thermal or thermomechanical environment does not lead to irreversible changes in the system. Thermodynamics provides a basis for considering the equilibrium state of a system undergoing a variety of changes, particularly thermomechanical, thermal, or mechanical.

Because of the limited mobility of the long polymer chains in textile fibers, they do not reach their equilibrium conformation within the time available. The equilibrium state is characterized by a minimum in Gibbs free energy, G , which is given by:

$$G = H - TS$$

Such a state can be reached by two paths: by minimizing the internal energy (or the enthalpy, H) or by maximizing the entropy (because TS , the product of absolute temperature (T) and entropy (S), has the units of energy, it is convenient to use this term in the consideration of equilibrium).

In the solid state of a crystallizable material, at sufficiently low temperatures, TS is small for all values of S and the predominant term in the free energy formula is H (or internal energy); thus, ordered states of low internal energy are preferred. At high temperatures, TS is very large for disordered states and dominates the free energy; disordered states thus become stable as the temperature is raised. As shown in Figure 2, in a plot of G as a function of temperature, the slope for the melt, starting from a higher temperature, is greater than that of the crystal. The equilibrium condition may be stated as:

$$\Delta G = \Delta H - T\Delta S = 0$$

It follows that, below the point of intersection (Fig. 2), only the crystal state is stable; at tem-

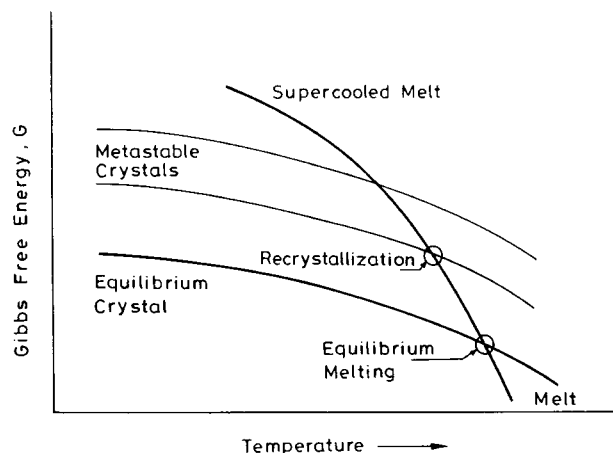


Figure 2 Variation of free energy with temperature for a crystallizing polymer.

temperatures higher than the point of intersection, only the melt is stable. The two forms may coexist for about 10 to 25 K before the liquid form takes over.

The equilibrium state of the fiber in the solid state may be regarded as one in which the internal stress arising from the inherent retraction tendency of the potentially rubber-like chains is balanced by the forces between the chains by which any such movement is restrained. Any change of temperature alters the point of equilibrium for, whereas the intermolecular forces are substantially independent of temperature, the retractive force increases with increasing temperature.²⁷

SHRINKAGE AND SHRINKAGE STRESS

As stated above, during fiber manufacture, orientation results in compact packing of molecules. If the consequent decrease in energy compensates for the drop in entropy, the molecular orientation will be stable. Such a situation exists only if cohesive forces between polymer chains are sufficiently strong; for example, in the regions of high crystallinity in semicrystalline fibers.²⁸ In amorphous regions, the state of molecular orientation is not stable and may be maintained only after cooling the system below T_g , where molecular motions are short range and so slow that the orientation is practically "frozen-in." The stability of orientation in various structural elements constituting the fibers is different; from the high stability of crystals of higher perfection through the

lower stability of less perfect crystalline regions and crystal amorphous interphases to rather unstable oriented amorphous phase.²⁸

In the case of as-drawn PET fiber, it has been suggested²⁹ that, depending on temperature and time, the overall shrinkage process involves a rapid initial stage of rubber-like contraction of the molecular network, associated with disorientation in the amorphous phase and is essentially responsible for the fiber length change. Chain folding is associated with the later crystallization stage. In drawn PET fiber with highly defective crystals, crystallization can be extremely rapid, particularly at high temperatures, and can impede shrinkage.³⁰ If the fiber is held at constant length and not allowed to shrink, the entropic forces of contracting segment are balanced by the reaction of external constraints. Then the whole molecular network is under tension which hinders further shrinkage and increases the possibility of relaxation processes becoming operative, like breaking of the physical links of the stressed network leading to intermolecular slipping.²⁸

The amount of fiber shrinkage and the development of the shrinkage force caused by boiling water or dry heat, for example, will affect the processing behavior of these yarns and will bring about dimensional changes in the fabrics made from these yarns. Differences in shrinkage behavior of either warp or weft threads may lead to a cockled appearance in the fabric after the hot-wet treatments in the course of finishing.

Sometimes advantage is taken of the shrinkage to generate high bulk in yarns.

Having considered some important aspects relevant to heat setting, the heat setting of individual fiber types will now be described.

HEAT SETTING OF PET FIBER

Introduction

PET fiber is perhaps the most-studied fiber as far as heat setting is concerned. Though these extensive studies have enhanced our understanding of process-structure-property relationships, a number of issues still need to be resolved; only two examples will be given here. The first example relates to the morphology of PET. A recent detailed study of molecular deformation processes in PET fibers³¹ gives strong support for a series model for the fiber, whereas it is widely accepted

Table I Some Physical Characteristics of PET

Characteristic	Crystal	Amorphous	As-Drawn Fibre
Density (g/cm ³)	1.455 ⁴⁰ 1.477 ⁴¹ 1.515 ⁴²	1.33	1.38 (1.468 ²⁰) ^a
Melting point (°C)	280 ⁴³ 284 ⁴⁴ 290 ⁴⁵	Not applicable	264 (302.1 ²⁰) ^a
T_g (°C)	Not applicable	68 (Dry) 58 (Wet)	125 (Dry) 110 (Wet)
Moisture absorption (%)	~0	1.0	0.4
Elastic modulus (10 ¹⁰ dynes/cm ²)			
Longitudinal	137	12	18
Transverse	3.68	1.82	2
Hermans orientation factor	0.94	0.58	0.88

^a Measured value for a very highly oriented fiber.

that a parallel-series model is more appropriate.^{32–35} The second example relates to structure–property relationships. An important parameter such as the elastic modulus of PET fiber is stated in the literature to be primarily related to the fraction of taut tie molecules in the interlamellar region,³⁶ average orientation,³⁷ amorphous orientation and crystal size,³⁸ and trans content in the crystalline and amorphous regions.³⁹ A clear understanding of the structure and structure–property relationships will contribute much to making heat setting a more effective tool to bring the fiber close to its equilibrium state.

Some Physical Characteristics of the Fiber and of the Crystalline and Amorphous Phases

Some physical characteristics of a typical as-drawn PET fiber and its two phases are shown in Table I. The higher density, melting point, modulus, and orientation of the crystalline regions are noteworthy. Thus, if a semicrystalline polymer is considered as a two-phase system as has been recently recommended,⁴⁶ it may be assumed that permeability in the crystalline phase is negligible compared with that in the amorphous phase because the crystalline phase, with a relatively higher density, is much more compact compared with the amorphous phase.

Processing-Structure-Property Correlations in Heat-Set PET Fibers

The as-drawn yarn (control) was isothermally heat set in silicone oil in the temperature range

100–255°C under constant length (taut-annealed or TA) and free to shrink (free annealed or FA) conditions. Some processing-structure-property correlations in these yarns will now be presented.

Thermal Shrinkage

The data on free shrinkage in boiling water for the control and both sets of heat-set yarns are shown as a function of heat setting temperature in Figure 3. The higher boiling water shrinkage of taut-annealed samples is apparently because of

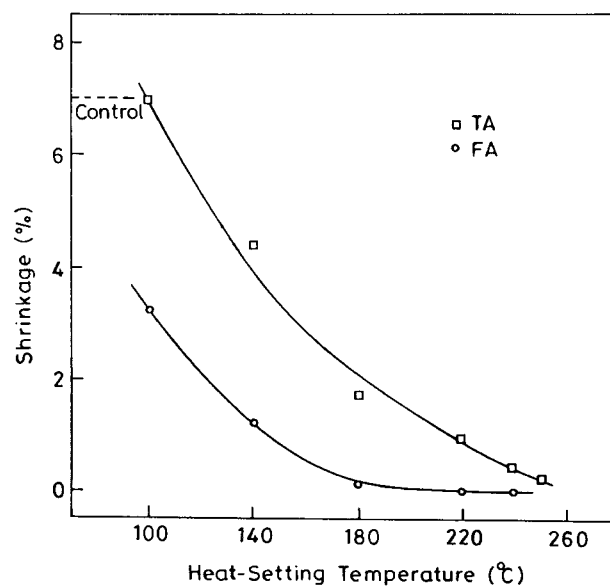


Figure 3 Shrinkage in boiling water as a function of heat-setting temperature.

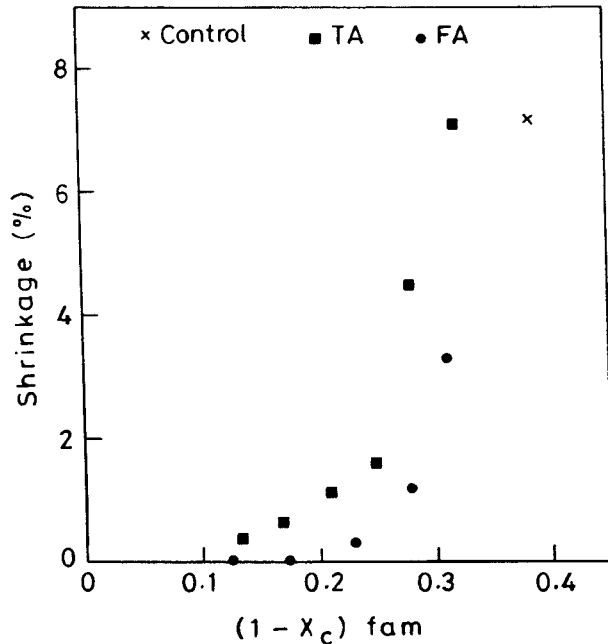


Figure 4 Dependence of boiling water shrinkage on $(1 - X_c) f_{am}$.

the presence of a greater degree of residual stress in these fibers.

It is generally believed that in PET yarns shrinkage is a unique function of the product of amorphous volume fraction and amorphous orientation factor.³⁷ When the thermal shrinkage is plotted as a function of $(1 - X_c) f_{am}$, where X_c is the crystalline fraction and f_{am} the amorphous orientation factor, the two sets of samples appear to form two distinct populations (Fig. 4) showing that for the same value of $(1 - X_c) f_{am}$, the taut-annealed samples show a higher shrinkage than the free-annealed samples.

To see whether the situation can be improved, it may be argued that only that part of the amorphous phase that is oriented, will contribute to shrinkage. Because, in the present sets of samples, the control sample and those heat set at low temperatures have a more prominent interfibrillar phase³⁵ and also show high shrinkage, a modified Takayanagi model (Fig. 5) with the interfibrillar amorphous phase (AF) having much higher orientation than that of the interlamellar amorphous phase (AL) may be more appropriate. It is interesting to note that Fu et al.⁴⁷ found this to be the case for the PET fibers they examined. λ and ϕ in the figure are measures of series and parallel coupling, respectively. With this assumption, only the right-hand branch of the modified Takayanagi model will be mechanically active

during shrinkage and, in that case, shrinkage should correlate with $(1 - \lambda) f_{am}$. The plot in Figure 6 shows that the correlation has now indeed improved compared with that shown in Figure 4, thus suggesting that the nature of coupling may have a role in thermal shrinkage.

The Scheme of Crystallization

Through wide- and low-angle X-ray scattering, the structural and morphological changes in the free- and taut-annealed fibers on heat setting were closely monitored.⁴⁸ Based on the results of these studies, the scheme of crystallization on heat setting of the fiber may be described as follows: 1. in the 100 to 180°C range, small crystallites of approximately the same dimensions as in the control sample are formed, apparently at the expense of the oriented amorphous phase. As a result, the average long period decreases (Fig. 7). The large number of small crystallites that are formed increase the constraints on the amor-

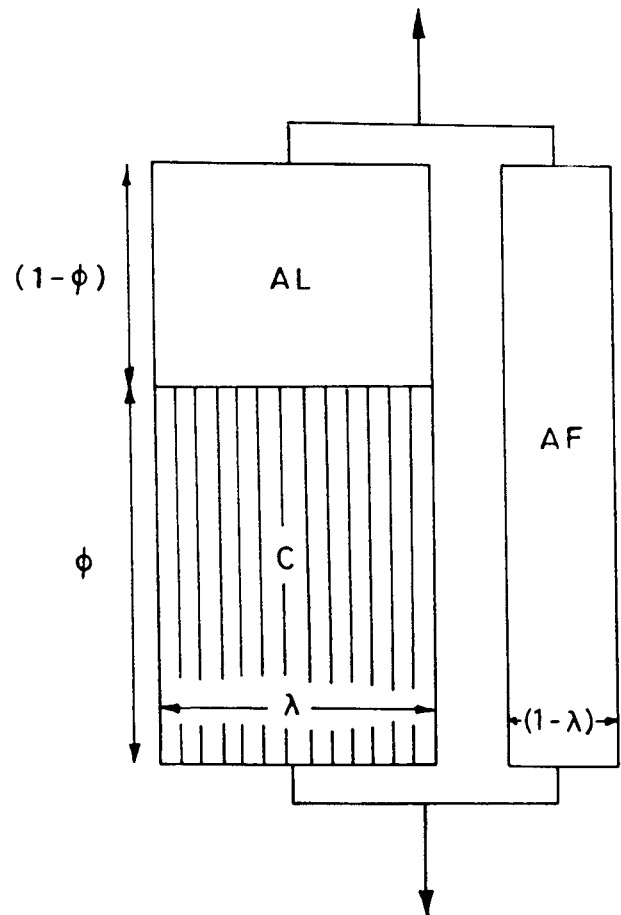


Figure 5 Modified Takayanagi model.

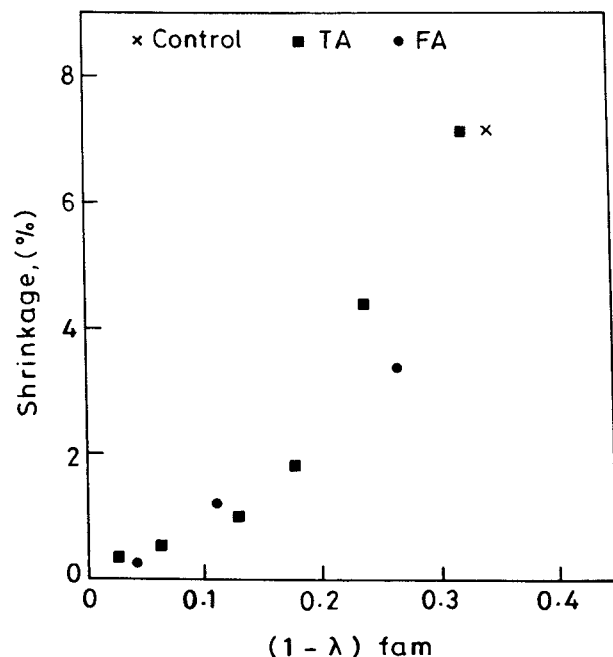


Figure 6 Dependence of boiling water shrinkage on $(1-\lambda) f_{am}$.

phous regions of the fibers and, as a result, T_g increases; 2. in the 180 to 250°C range, the long period increases and so does the crystal width.

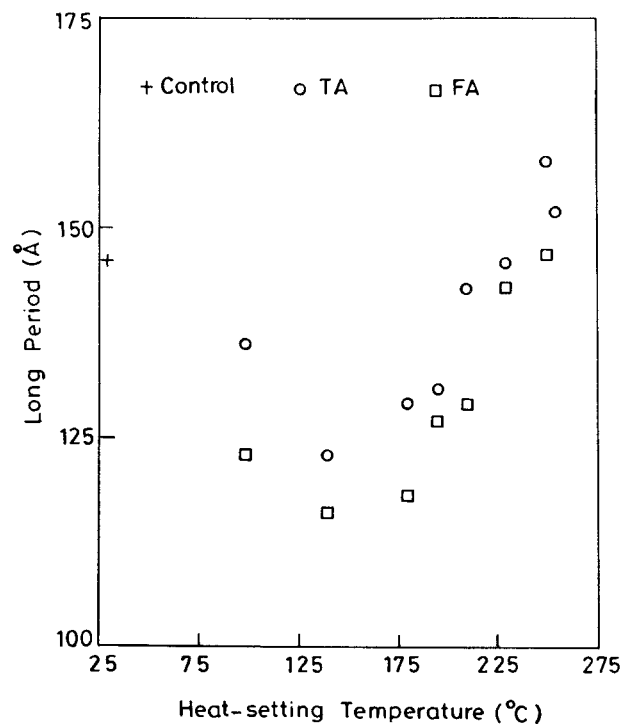


Figure 7 Dependence of axial long period on heat-setting temperature.

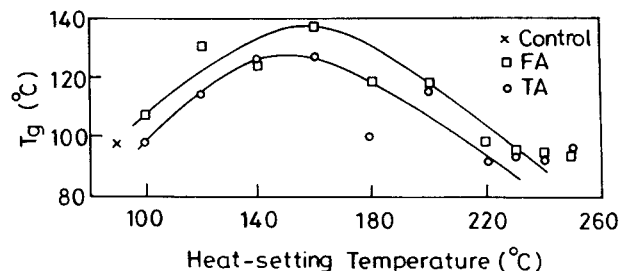


Figure 8 Variation of T_g with heat-setting temperature.

The data are consistent with the formation of a small number of large crystallites, which results in large amorphous volume per crystal and consequently a drop is observed in T_g . Thus, above 180°C, the crystallization occurs through transverse growth of existing crystallites.

The above structural model is consistent with the currently accepted ideas on crystallization, according to which nucleation dominates over crystal growth up to 180°C. Under these conditions, the material crystallizing from the amorphous regions between existing crystallites can only form small crystallites. In the intermediate range of temperature, the nucleation and crystal growth processes are comparable and larger crystals can grow. At temperatures near the melting point, reorganization of the structure that formed at low temperatures will be the controlling factor. It is interesting to note that when isotropic, amorphous PET was isothermally annealed at various temperatures up to 170°C, the diffusion of amorphous chain segments appeared to be the controlling step for increase in density whereas partial melting controlled the kinetics above 180°C.⁴⁹

Integration of Structure with Properties

The scheme of crystallization described above helps in integrating structure with physical properties of the fiber. The data on T_g and dye uptake as a function of heat setting temperature for the two sets of samples are shown in Figures 8 and 9, respectively. The highly constrained nature of the amorphous phase with a large number of small crystallites acting as crosslink points at a heat setting temperature of 160°C leads to the highest T_g and also a minimum in dye uptake. That the amorphous phase is highly constrained at a heat setting temperature of 160°C also becomes apparent when shrinkage stress is measured in a running yarn in a dynamic thermal stress tester,⁵⁰ as

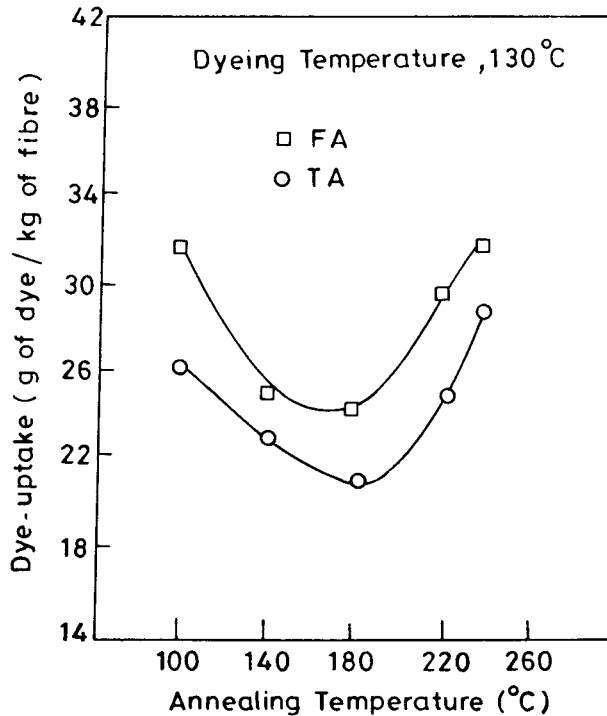


Figure 9 Dye uptake data for heat-set samples.

shown in Figure 10. However, as expected, the peak shrinkage stress in the heat set samples (Fig. 11) progressively decreases with the sample heat set at 220°C for 4 h, showing almost complete relaxation of residual stress.⁵¹ It is of his-

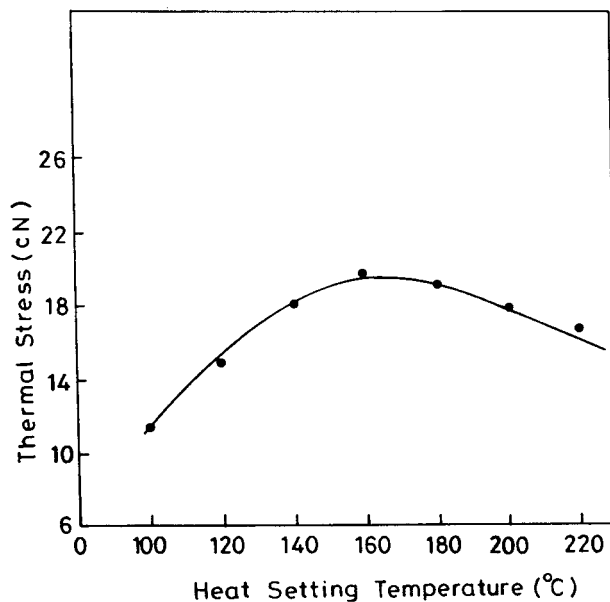


Figure 10 Peak thermal stress developed in PET yarn at various temperatures (adapted from Pal et al.⁵⁰).

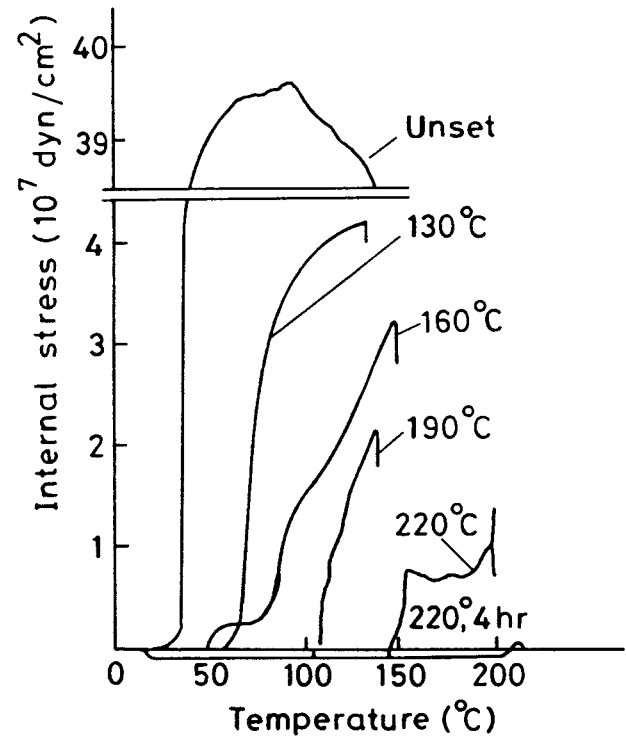


Figure 11 Thermal shrinkage stress measured on a thermo-mechanical analyzer for slack-annealed PET yarns (from Zhang et al.⁵¹).

toric relevance to recall that Dumbleton and co-workers^{52,53} developed the basic concept of amorphous volume per crystal in PET, which is the total amorphous volume divided by the number of crystals, i.e., $(1-\beta)/(\beta/V_c)$, where β is the volume crystalline fraction and V_c the volume per crystal. They showed that for PET samples heat set in the slack condition, the amorphous volume per crystal shows a minimum at approximately 180°C. The results presented herein vindicate this idea and integrate it with such important parameters as T_g and shrinkage stress. That the constraints are higher in the taut-annealed samples becomes clear when the low-angle integrated intensity of the meridional reflection for the two sets of heat set fibers is plotted as a function of heat-setting temperature (Fig. 12). Slack annealing facilitates phase separation, which results in enhanced low-angle intensity.

Multiplicity of Structures and Morphologies

In an effort to understand how the crystalline and amorphous phases are arranged within the PET fibers annealed in the slack and taut states, the crystalline volume fraction in the microfibrils

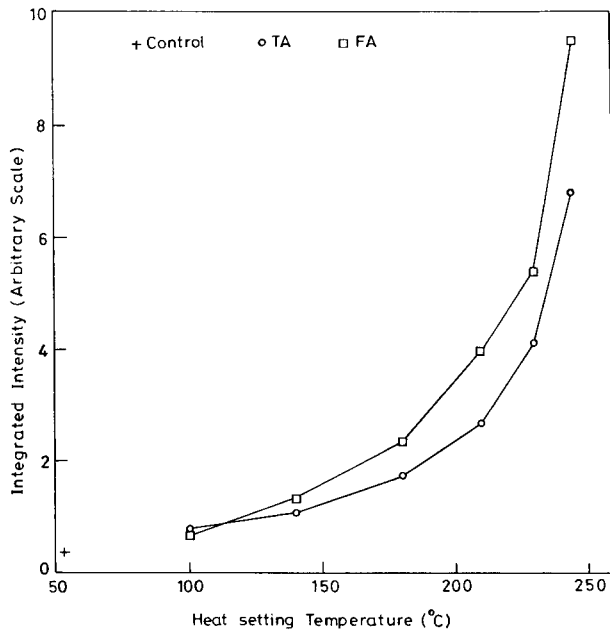


Figure 12 Integrated intensity of the low-angle meridional reflection of PET fibers as a function of heat-setting temperature.

was estimated assuming a series coupling of the two phases. The volume fraction of the crystallites in the fibers was estimated using the X-ray and the density methods; in the latter case, the actual measured crystal and amorphous densities were used.⁴⁸

The volume fraction crystallinities of the fibers, as estimated from X-ray diffraction and density, are plotted as a function of the volume fraction crystallinity of the fibrils in Figures 13 and 14, respectively. The basic trends shown by the two measures of fiber crystallinity are similar in that, in both cases, fiber crystallinity is lower than fibril crystallinity, thus suggesting that amorphous material is present in these samples at locations other than the fibril. Because the crystals in the heat-set samples are relatively defect free,⁵⁴ the most likely location for the amorphous phase outside the fibril would be the interfibrillar region. A consequence of this morphology is that the coupling of the two phases is more appropriately described in terms of a series-parallel model rather than a series model. Previous estimates of the coupling between crystalline and amorphous phases in heat-set PET fibers through indirect methods had shown⁵⁵ that in the samples that had been annealed in the slack state at the higher temperatures, series coupling predominated, whereas the corresponding taut-annealed sam-

ples had a significant degree of parallel coupling superposed on the series coupling. The present results also show that the samples slack annealed at the higher temperatures are closer to the series model. In addition, it is quite clear that there is a variable amount of interfibrillar material in different heat-set samples, and therefore a single model is inadequate to represent the morphology of PET heat-set yarns. The multiplicity of structures and morphologies of PET fibers means that any models claiming to represent their fine structure would differ significantly as a function of heat-setting temperature and applied tension.

Stress-Strain Behavior

The stress-strain behavior of PET yarns is considerably affected by the heat-setting conditions. This may be illustrated by examining the average stress-strain curves for the control and the free- and taut-annealed samples heat set at various temperatures for 1 min (Fig. 15). It is noteworthy that the stress-strain curves for samples annealed at constant length are quite close to one another and to the control. The curves for the free-annealed samples, however, show considerable variation; in particular, they show a more

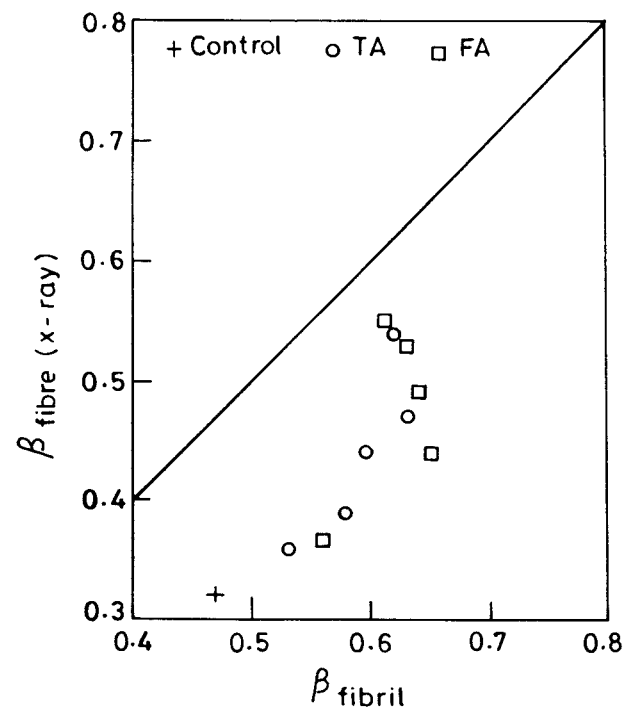


Figure 13 Volume fraction X-ray crystallinity of PET fibers as a function of volume fraction crystallinity of fibrils.

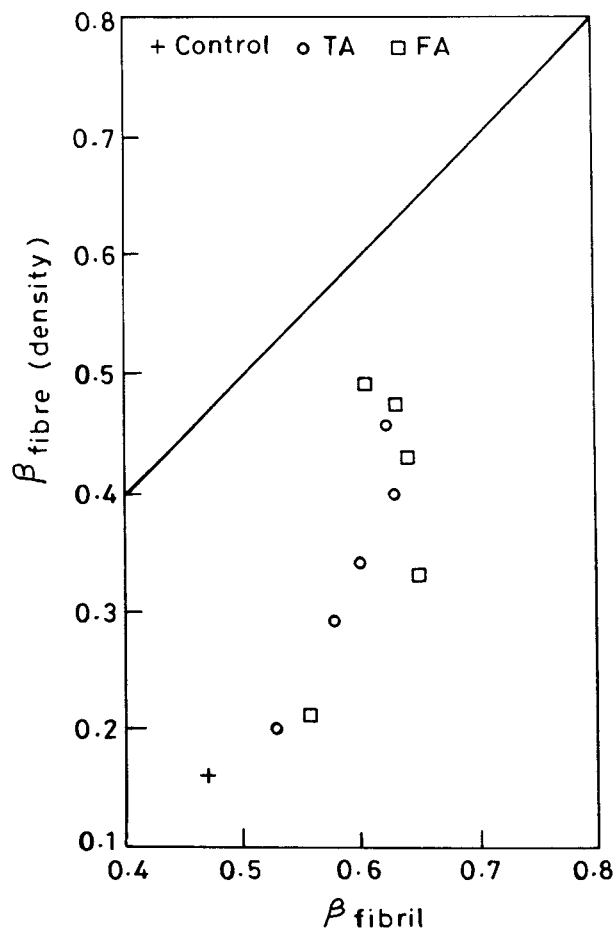


Figure 14 Volume fraction density crystallinity of PET fibers as a function of volume fraction crystallinity of fibrils.

distinct yield behavior and their ductility increases with increase in heat-setting temperature. These differences in tensile properties arise from structural and morphological differences between these two fiber types which have essentially similar crystallinity. The main structural difference is that the orientation of the molecules in the amorphous regions is much lower in the free-annealed sample. The main morphological difference is that the two phases are more distinctly separated in the free-annealed sample and they are predominantly connected in series. Both of these factors lead to lower modulus, lower strength, and higher extensibility of the free-annealed samples.

It is noteworthy that most of the industrial heat setting is done under tension; this ensures that the stress-strain characteristics of taut-annealed samples are closer to the regular PET filaments. A further interesting observation is that

the stress-strain characteristics of the FA-160 yarn are close to those shown by a regular PET staple fiber.

Two further investigations, one involving estimation of crystal width by X-ray diffraction as the heat-set samples were stretched⁵⁶ and the other involving simultaneous recording of stress-strain curves and the structural changes on stretching by rapid scan mode on the Fourier transform infrared spectrometer⁵⁷ allowed the structural basis of the stress-strain curves to be obtained. In the free-annealed samples, the orientation of the molecules in the amorphous phase showed a gradual improvement throughout the test, whereas chain unfolding occurred in the sample above 20% strain. In the taut-annealed sample, however, chain unfolding occurred at low strains, thus indicating that longitudinal slip is the main mechanism of the deformation in this sample.

Recovery Behavior

There have been only a limited number of studies to gain an understanding of the structural features that influence recovery. The recovery behavior of PET (2 GT) has been shown to be relatively poor compared with 3-GT and 4-GT fibers.⁵⁸ This was attributed to the dominance of the amorphous phase in controlling recovery in 2-GT fibers, whereas in 3-GT and 4-GT fibers, the crystallites also play an important role. Brody⁵⁹ analyzed the recovery data for a number of fibers including PET and concluded that recovery could be attributed to the elastomeric nature of the amorphous phase.

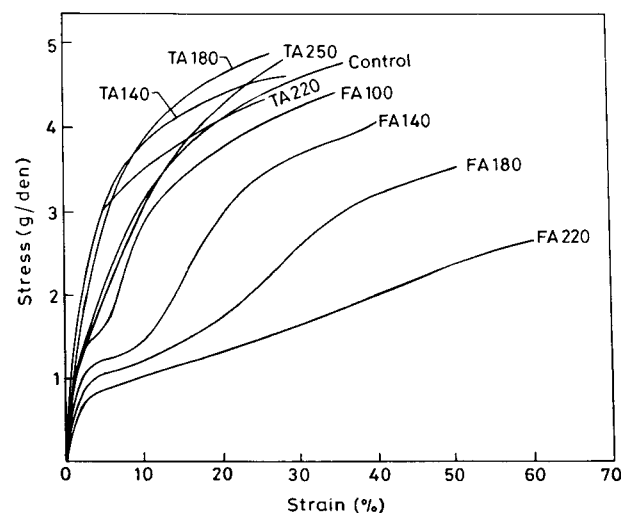


Figure 15 Stress-strain curves for control and heat-set PET fibers.

Some studies on PET yarns heat set in the relaxed state and at constant length have shown that the samples heat set at constant length have superior recovery behavior.⁶⁰ It has been suggested that at low strains, the recovery behavior is dominated by the amorphous phase in both of the samples; because the taut-annealed samples have higher amorphous orientation, they show better recovery. At higher strains, in taut-annealed samples, both the crystalline and amorphous phases influence the recovery behavior and this is mainly because of the parallel coupling between them. In the free-annealed samples, the amorphous phase dominates the recovery behavior.

It is noteworthy that thermal shrinkage of fibers and their recovery behavior, which are both indices of their dimensional stability, are governed by different structural considerations.

Optical Properties

In an earlier publication,⁶¹ it was noted that the intrinsic birefringence of the PET crystal, Δn_c , has been reported to be between 0.212 and 0.31 and that whereas the lower values arose from studies on cold-drawn fibers, the higher values were based on studies on heat-set fibers. Because it could be expected that improving crystal perfection by heat treatment⁵⁴ would result in higher Δn_c , it was suggested that a crystal with perfection index P_c will have birefringence of $P_c \Delta n_c$, assuming that an ideal perfect crystal will have P_c equal to unity.⁶² The measured birefringence Δn of a fiber of crystallinity β and crystallite orientation f_c can be written as $\Delta n = P_c \Delta n_c \beta f_c + P_{am} \Delta n_{amo} (1-\beta) f_{am}$, where P_{am} is the perfection index of the amorphous phase, Δn_{amo} , its intrinsic birefringence, and f_{am} , its orientation. Thus, because fibers have different degrees of defect density, the reported dependence of intrinsic birefringence on morphology is not surprising. This observation has received support from the studies of a number of research workers.⁶³⁻⁶⁵ PET fibers with birefringence of 0.26 or higher⁶⁵⁻⁶⁸ have been produced, thus confirming that Δn_c for these fibers would be much higher than its usually accepted value.

Effect of Setting Conditions and Fiber Structure

As stated above, industrial setting of PET fabrics is usually done in the presence of some tension, the setting temperature being at best 30 to 40°C

higher than any temperature to which the material will be exposed afterward.⁶⁹ The range of setting temperatures used is quite wide, reportedly being 140°C in steam and 190 to 220°C in dry air. The time of heat setting may vary from less than a second to over 60 min.

Heat treatment may be considered under three temperature regimes, first sub- T_g aging; second, heat setting at and around T_g , and third, heat setting at higher temperatures.

In sub- T_g aging of PET, densification of the structure occurs as a result of free-volume collapse; the fractional free volume being that portion of the thermally expanded volume that may be redistributed with no energy change. A model based on the assumption that density fluctuation in a glassy polymer can be considered as quasi-point defects, interprets sub- T_g aging in terms of diffusion-aided annihilation of such defects until a new thermodynamic (metastable) equilibrium is reached at that temperature.⁷⁰

Setting PET fiber at and around T_g is believed to result in temporary or semipermanent set,¹⁰ again mainly through free-volume collapse. However, some recent findings on isotropic, amorphous PET have shown⁷¹ that when PET is annealed from the glassy state at 80°C (5°C above T_g), the frozen gauche conformations in the amorphous glassy state begin to transform to the *trans* conformations. The parallel-ordered dense domains lead to a more efficient packing of parallel-oriented chains to form crystal nuclei. Thus, much below the cold crystallization temperature (135°C), stable nuclei are formed.

In oriented cold-drawn PET samples, crystallization was found to occur on annealing at 60°C, which is just below T_g .⁷² It must be remembered that in cold-drawn structures, the crystallites are small and highly defective. Because defects in the lattice reduce the energy for molecular motion,⁷³ the presence of defects can result in faster crystallization (or at lower temperatures), which would stabilize the structure.

In this context, it is interesting to recall that Peterlin⁷⁴ had concluded that a highly oriented system can be obtained only by starting from a highly crystalline polymer, at least in the case of polyethylene. In PET, however, Evstatiev et al.⁶⁷ have shown that the most favorable structure for the achievement of high orientation is the crystalline structure but an imperfect one. There are important differences in the development of orientation in polyethylene and PET, as pointed out by Ward.⁷⁵ The development of orientation in

PET is not pseudo affine but rather that of a stretched network and the crystalline and amorphous regions in PET are all-*trans* and *trans/gauche*, respectively. Orientation induces conformational changes in the overall *trans-gauche* content and crystallization is promoted at high draw ratios.

The heat setting of PET fibers at higher temperatures and the various routes to their structural transformation have already been considered in detail above.

HEAT SETTING OF POLYAMIDE FIBERS

Introduction

The broad similarity in the main features of the dynamic mechanical spectra of PET and polyamide fibers has already been referred to above. However, there are some important differences between these two classes of thermoplastic fibers. The first difference is that, in contrast to the polyester fibers, the polyamide fibers are very sensitive to moisture. The second difference is that the polyamide fibers (in particular nylon-6 fiber) exhibit polymorphism.

Warwicker^{76,77} studied the structural changes in nylon-6, nylon-66 and PET yarns when subjected to dry and wet heat. His results showed that the effectiveness of setting is considerably enhanced with wet heat for the two nylons, as observed from the density changes. In the presence of moisture, there is considerable depression in the melting point of the nylons which will result in a higher degree of set because of greater mobility of the molecular chains. With PET, no appreciable difference in the densities between dry and wet heat-set samples was seen. This means that water or other solvents can be used to enhance the power of heat-setting treatment for polyamide fibers. Heuvel and Huisman⁷⁸ have shown that in the case of nylon-6 yarns, working with saturated steam is directly comparable with heating *in vacuo* but at extremely high temperatures. In other words, the moisture favors the mobility of the molecules, by loosening the hydrogen bonds, to such a large extent that a given temperature in saturated steam corresponds to a much higher temperature in the dry state.

Heat-Setting During Texturing

Setting is perhaps the most crucial stage of the texturing process. During setting, the yarn has to

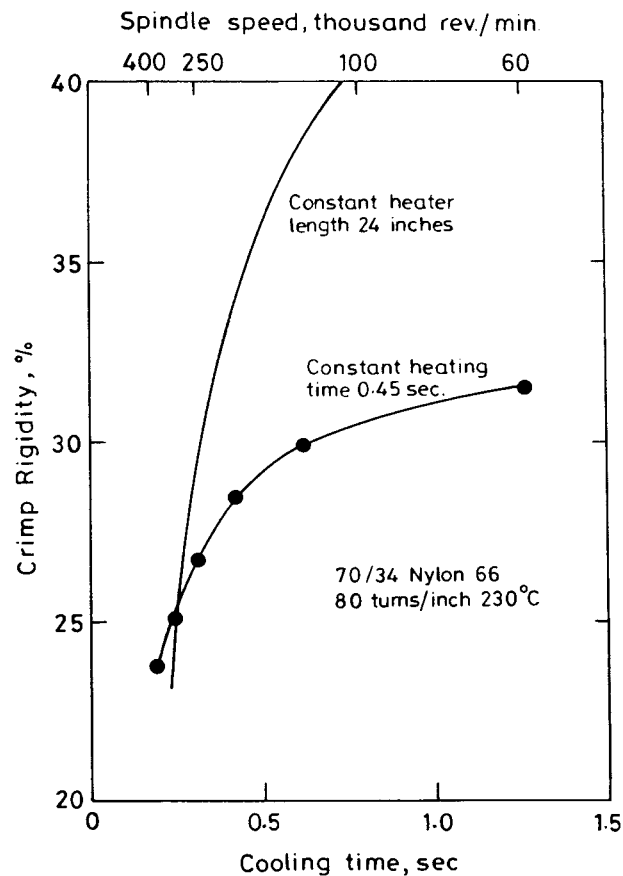


Figure 16 Effect of cooling time on crimp rigidity (crimp retraction) (from Denton and Morris⁷⁹).

be heated to the softening point, the stresses in the filaments must be allowed to decay, and the yarn permitted to cool before being untwisted at relatively high tension.

Denton and Morris⁷⁹ have pointed out that setting of textured yarns does not occur in heating but in cooling. The crimp retraction, which is a measure of bulk, increases with increase in cooling time (Fig. 16) for nylon-66, the effect being most pronounced at short times. The combined effects of changes in heat setting and cooling time are shown in the upper curve. The effect of reduced heating time is greater but the effect of reduced cooling time becomes more important as processing speeds increase.

Heat Setting of Carpet Yarn

Heat-set nylon-66 and nylon-6 yarns are extensively used for manufacturing cut pile carpets. Heat setting greatly improves the newness retention of the carpets by inhibiting the untwisting of

the cut ends of the tufts which occurs when the carpets are subjected to foot traffic.⁸⁰ The heat-setting procedures and conditions for nylon-66⁸⁰ and nylon-6⁸¹ include either batch or continuous processes and heat treatment in the presence of steam or in the dry state. It has been pointed out that nylon-66 yarns produced by the various methods show satisfactory floor performance (twist retention) but in dyeing rates there may be major differences between the yarns set under different conditions used in the various processes.

Structural Changes on Heat Setting

Heat setting of nylon-66 [see for example References 82–85] and nylon-6 [see for example References 86–89] fibers introduces structural and morphological changes that are broadly of a similar nature as described above for heat-set PET fibers. For example, a recent study on heat setting of nylon-6 fibers⁸⁸ concluded that slack annealing results in an increase in crystallinity, crystal size, crystal perfection and density, and a decrease in anisotropic amorphous fraction. It is interesting to recall that long ago, Dismore and Statton⁸² had made similar observations for nylon-66 fiber when it was slack annealed. Thus, although the structural changes in polyester and polyamide fibers show broad similarity in this respect, it needs to be emphasized that polyamide fibers show additional degrees of complexity, which was briefly referred to above. First, during heat setting, they may undergo polymorphic transitions, and second, the presence of moisture during heat treatment has a much greater effect on the structural changes in these fibers compared with those in polyester fibers, apparently as the polyamides absorb a greater amount of moisture and as a result show a much higher enhancement of molecular mobility. It may be added that the polymorphic transitions in the nylons are not clearly understood, particularly their role in heat setting and therefore will not be discussed further. The other aspect relating to heat setting in the presence of moisture will be considered briefly.

Dye Uptake Behavior

The dye uptake behavior of heat-set polyamide fibers is more complex than that of PET fibers because, besides the temperature of heat setting and the tension, moisture makes a considerable difference. Application of tension during heat setting does not allow the two phases to separate

substantially and thus reduces dye-uptake compared with that of a slack-annealed sample; this was also the case for PET fibers. However, in nylon-66 and nylon-6 fibers, the rate of dyeing is very sensitive to the presence of moisture—being high for steam-set material and low for dry-set material.

In nylon-6 fiber, with increasing heat-setting temperature, dye uptake has been shown to decrease^{90,91} for samples that have been dry heat set; the decrease could arise from the increase in crystallinity. In the case of samples that have been steam set, dye uptake first decreases and then increases at higher temperatures of heat setting. The increase at high temperatures shown by steam-set samples may arise from the much greater openness of structure at high temperatures of heat setting.

In nylon-66 fibers, the diffusion coefficient of CI acid blue dye 40 at 25°C was measured⁸⁵ in samples of bulk continuous filament (BCF) carpet yarn that had been heat set at 100% relative humidity at temperatures varying from 30 to 170°C. The diffusion coefficient first dropped modestly as the heat-setting temperature increased, went through a shallow minimum, and then increased very steeply at higher temperatures of heat setting. Detailed structural studies of such carpet yarns have been made for nylon-6,⁹² and both the long period and the crystal size were seen to increase only after 170°C treatment in dry atmosphere and after 100°C in saturated steam or hot water. The authors stated that the increase in density is probably attributable to an increase in crystal perfection and hence crystal density rather than axial growth of the interfibrillar amorphous chains onto the existing lamellae. In a later publication, however, it was suggested⁸⁸ that the increase of crystallinity on heat setting can also be attributed to the crystallization of the oriented amorphous fraction.

A possible reason for the complexity in dye uptake behavior of nylon-6 can be understood by examining the dependence of the long period of nylon-6 filaments subjected to various heat-setting treatments (Fig. 17). It is important to note that although both tension and steam have a considerable effect on the long period, the major role played by steam during heat setting is very apparent. Steaming opens the structure and enhances both the dye diffusion rate and total dye uptake. The structure is predominantly chain-folded and despite its high crystallinity, is more open. The differences in dye uptake characteris-

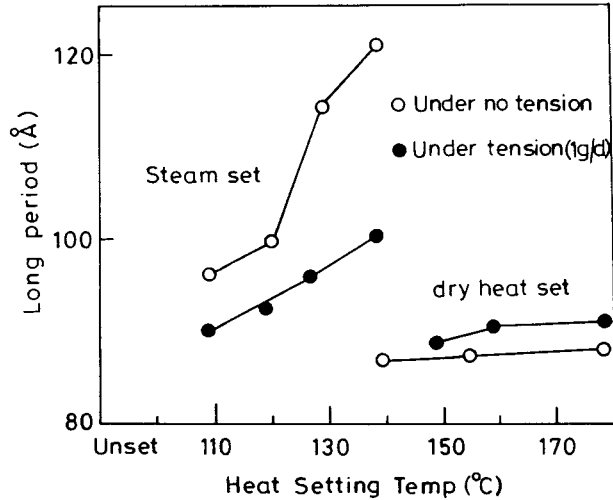


Figure 17 Changes in the long period of nylon-6 filaments on heat setting (Tsurata and Koshimo⁸⁶).

tics of polyamide fibers may relate to the differences in processing of the sample and the consequent differences in structure.

Stress-Strain Behavior

The stress-strain curves for free- and taut-annealed nylon-6 multifilament yarns heat set at 122 and 162°C in the unconstrained and constrained states are shown in Fig. 18.⁹¹ Again the similarity to the corresponding data for PET is noteworthy. The taut-annealed nylon-6 fibers have characteristics identical to those of the control sample whereas the free-annealed samples become relatively more compliant.

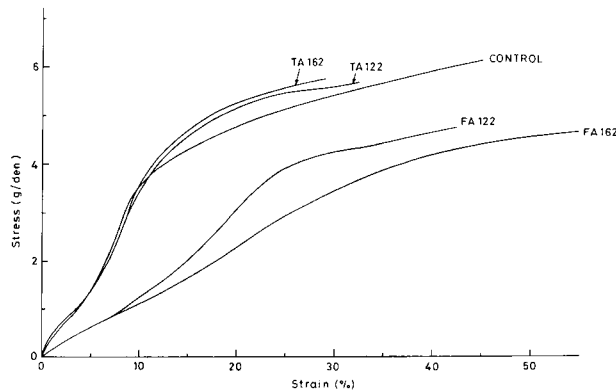


Figure 18 The stress-strain curves for the control and heat-set nylon-6 yarns.

HEAT SETTING OF POLYPROPYLENE FIBERS

Introduction

Polypropylene crystallizes in different geometries giving rise to the three well-known polymorphs of isotactic polypropylene. In addition to these polymorphs, quenching of the isotactic polypropylene melt gives rise to the smectic phase, which is discussed below.

The dynamic mechanical spectra of polypropylene show two prominent loss peaks. The high-temperature peak (α relaxation) appears at around 100°C and is believed to be either a crystal relaxation or a lamellar slip process. The β relaxation (T_g) occurs around 0°C.

A highly oriented polypropylene fiber does not show any change of crystallinity up to 100°C. Between 100 to 150°C, the fiber shows significant enhancement of crystallinity.⁹³ Any meaningful heat setting would therefore have to be done between 120 and 150°C.

Nonequilibrium Nature of Polypropylene Fibers

It has been reported⁹⁴ that drawn polypropylene fibers, when quench cooled to room temperature from temperature below the melting region undergo a remarkable spontaneous stiffening during storage at room temperature. Because yarn texturing and fabric heat setting may involve sudden cooling to room temperature, this phenome-

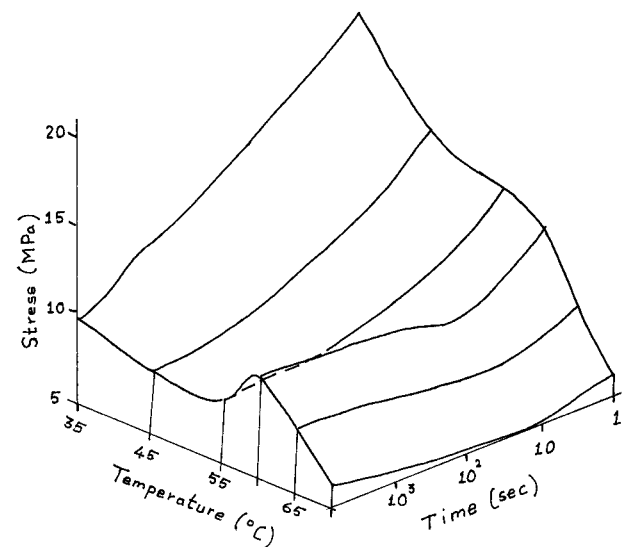


Figure 19 Stress relaxation data for polypropylene yarn.

non is of practical relevance. In the reported study,⁹⁴ after quenching, the fiber was annealed at 140°C in the free and taut states. The annealed fiber was again quenched in a silicone oil both maintained at 20°C. It was found that this sample continued to show changes in properties like modulus and density with time. For example, its modulus increased from 50 to 100% in less than 2 months. The increase in modulus was shown to arise from a densification of the structure through free-volume collapse in the noncrystalline regions of the fiber. The authors state that such effects are a general property of polypropylene and the fact that this “physical ageing” extends to temperatures above T_g has been attributed to the expected local decrease of segmental mobility of the noncrystalline fraction, thereby broadening the glass transition region.

Another illustration of the nonequilibrium effects in polypropylene fiber relates to an unusual observation made during stress relaxation experiments on as-drawn polypropylene multifilament yarn that had not been subjected to any conditioning treatment.⁹³ It was observed that at 0.5% pre-strain and at temperatures of 60°C and above, the stress after an initial decrease registered an increase. The stress relaxation data in Figure 19 show the unusual stress relaxation behavior. A more detailed study showed that the inverse relaxation was caused by the generation of shrinkage stress and that the unusual behavior coincides with the onset of the α relaxation.

The relaxation of stress with time is a composite response arising from both viscoelastic and structural relaxation. The most likely reason for the observation of the structural relaxation would be the nonequilibrium nature of the as-drawn sample. Repeated stress relaxation tests moved the sample toward equilibrium. Also, when the samples were heat set at 140°C, the unusual effect was no longer visible.

Some Characteristics of Annealed Fibers

A well-oriented polypropylene multifilament yarn was annealed in a silicon oil bath at 140°C for 5 min in the taut and free states. The structural data for the as-drawn and the two annealed fibers are presented in Table II. The as-drawn sample is seen to be a well-oriented, semicrystalline fiber with a significant amount of residual stress, which gives rise to high shrinkage. On heat setting, crystallinity increases whereas amorphous orientation decreases, the decrease being partic-

Table II Some Structural Data on As-Drawn and Heat-Set Polypropylene Fibers

	As-Drawn Fiber	Heat-Set Fibers	
		TA140	FA140
Density (g cm ⁻³)	0.907	0.912	0.913
Birefringence	0.039	0.043	0.038
Crystallinity (%)			
Density	60.1	65.4	66.5
X-ray	52.5	59.8	61.4
Crystallite orientation, f_c	0.942	0.974	0.87
Amorphous orientation, f_{am}	0.82	0.65	0.38
Boiling water shrinkage (%)	8.5	3.4	0.4

ularly significant in the free-annealed sample. The shrinkage of the annealed samples is much lower than that of the as-drawn sample, indicating that on annealing, residual stresses may have relaxed to a significant degree.⁹³

In another study,⁹⁵ the effect of annealing a uniaxially drawn polypropylene film at 120, 145, and 158°C was studied; the shrinkage at 158°C was 50%. It was found that annealing allows relaxation of the intercrystalline material together with recrystallization leading to a clear two-point low-angle pattern. The number of interlamellar tie molecules is reduced.

Fibers with Improved Mechanical Properties

Heat setting plays a very important role in producing fibers with improved mechanical properties, as was seen to be the case for PET. Rapidly quenched polypropylene fibers attain much higher total orientation on cold drawing than the slowly cooled fibers.⁹⁶ Quench cooling is known to retard crystallization and a phase possessing order intermediate between the amorphous (atactic) and crystalline states is obtained. It is referred to as the smectic phase, which is the metastable pseudohexagonal form of polypropylene. When drawn and/or annealed, they move toward the more stable α monoclinic form. The zone-drawing and zone-annealing method, which involves the use of temperatures close to the melting point, has also been used to produce fibers and films of polypropylene with improved mechanical properties.⁹⁷

Table III Structural and Mechanical Data for the Drawn and Annealed HDPE Filaments

Filament Type	Crystallite Orientation Factor (f_c)	Birefringence (Δn)	Degree of Crystallinity	Modulus (g/den)
As-drawn	0.989	0.054	0.60	94
TA 125	0.970	0.046	0.74	107
FA 125	0.986	0.048	0.84	52

HEAT SETTING OF POLYETHYLENE FIBERS

Polyethylene fibers are not classed among the major synthetic fibers but, in view of their simple structure, they have received much attention from researchers. Branched or low-density polyethylene gives a fiber of low tenacity and low melting point (115°C) whereas linear or high-density polyethylene (HDPE), though still low melting (135°C), gives a fiber of reasonable tenacity (5 g/den). HDPE fibers will be considered very briefly here. As stated above, this fiber shows a crystalline relaxation at around 100°C and any meaningful heat setting would be done around 120°C.

Although there is a wealth of data on polyethylene and on the structural changes that occur on heat setting, the studies made on fibers are very limited. Some results of a study made on HDPE fibers (density 0.965 g/cm³, melting point 136.3°C) made by stretching as-spun HDPE filaments (with X-ray crystalline fraction of 0.56) at 80°C to a draw ratio of 8 and then heat setting the fiber in the taut and free states in a silicon oil bath maintained at 125°C^{98,99} are summarized in Table III. Further analysis in terms of a simple one-phase model showed that the modulus was related primarily to the average orientation of the molecules in the amorphous regions.

HEAT SETTING OF POLYACRYLONITRILE FIBERS

Polyacrylonitrile fibers show lateral order but give no indication of any regular arrangement along the length of the chains. One of the important characteristics of acrylic fibers, viz., their ability to give bulk through differential shrinkage, has been related to the ill-defined molecular arrangement.¹⁰⁰ The high-shrinkage component of a high-bulk yarn is formed by applying tension

in the fiber while it is at a temperature above its T_g , i.e., above 80°C. The fiber extends and, if cooled in this state, does not relax when the tension is removed. The elongated structure is stable until the temperature is raised again to T_g or above. The fact that no change in crystallinity occurs on stretching is largely responsible for this. Thus, acrylic fibers are easily deformed under hot conditions, particularly in water, and this ease of stretching can cause a problem during dyeing. It is therefore sometimes suggested that the fiber should be prepared from an isotactic polymer. If this was done, then the bulking properties would probably be lost.

The stretching of acrylic fibers is generally performed in water at 100°C, 25°C above its T_g . The effect of heat treatment on T_g and dyeability have been reported¹⁰¹ for Orlon 42 tow, which was subjected to a series of heat treatments—dry heating at 110 and 150°C and saturated steam heating at 110°C for a period of 5 min under tension or in the slack state. Steam-treated taut- and slack-annealed samples gave the highest T_g (108–109°C) whereas the steam-treated slack-annealed samples gave the highest dye uptake.

The effect of annealing temperature and pretension on shrinkage stress and thermal shrinkage of acrylic fibers by thermo-mechanical analysis has been reported.¹⁰² The shrinkage stress [Fig. 20(a)] in the samples annealed at 110°C shows two peaks. On annealing at higher temperatures, the low-temperature peak disappears thus indicating that the shrinkage stress largely originates from the stress frozen during fiber formation, in particular during stretching and drying. The thermal shrinkage data under different pretensions [Fig. 20(b)] clearly show that the amount of shrinkage at the same temperature decreases as the pretension increases, as expected. At large pretension, the fiber elongates instead of shrinking.

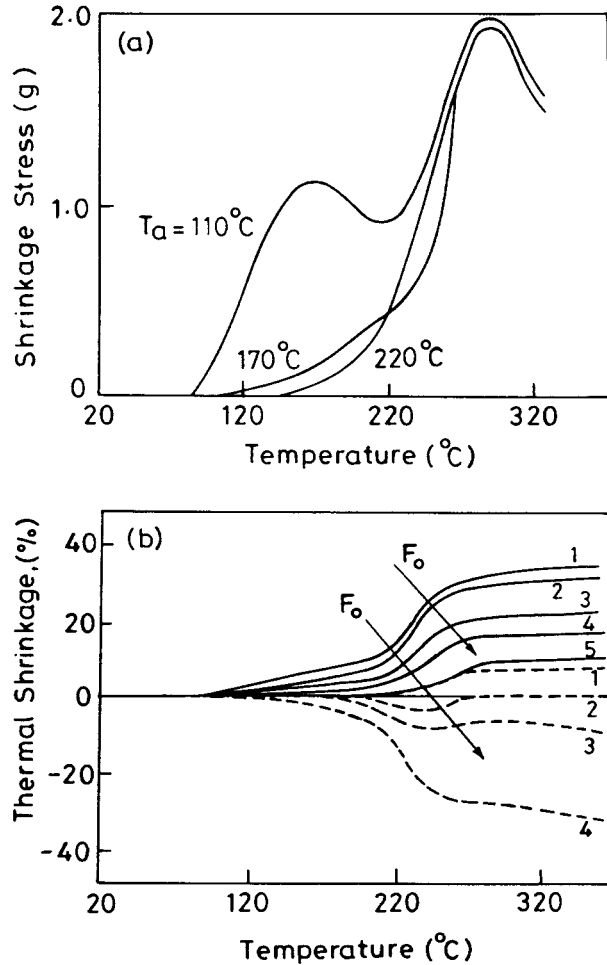


Figure 20 (a) Shrinkage stress and (b) shrinkage data for polyacrylonitrile fibers. (b) solid lines, $F_0 =$ (1) 5 mgf, (2) 50 mgf, (3) 300 mgf, (4) 500 mgf, (5) 800 mgf; dashed lines, $F_0 =$ (1) 1010 mgf, (2) 1200 mgf, (3) 1450 mgf, (4) 1950 mgf (adapted from Qian et al.¹⁰²).

Relaxation of the dry fiber by heat alone is generally not recommended because the high temperatures that are required cause discoloration. The water plasticizes the molecules and fuses the cracks, voids, fissures, and fibril-to-fibril contacts, thus healing the defects within the fiber. The major structural response during relaxation is amorphous disorientation without any significant effect on crystallite orientation or crystallinity.

THE DEGREE OF SET

The success of the setting operation lies in the degree and permanence of set which need to be

measured. A number of methods may be used for this; some of them are briefly described below.

Permanent Deformation as a Measure of Degree of Set

The degree of set for fibers and fabrics has been considered in detail by Lindberg,¹⁰³ who suggests the following definition of setting. Setting is a change in the stress-free form of a fiber or a fabric resulting from a deformation and subsequent treatments before the release of the sample.

If a fiber of length l_0 is subjected to a tensile strain ϵ_0 to its new length l_1 , held there for some time (the stress relaxes to a new value) and then unloaded, it will recover a part of its deformation and come back to strain ϵ_1 at which its length is, say l_2 . The degree of set, S , is described as:

$$S = \frac{l_2 - l_0}{l_1 - l_0} = 1 - \left(\frac{\epsilon_r}{\epsilon_t} \right)$$

where ϵ_r is the recovered strain and ϵ_t the total strain.

Recovery from Bending Strains as a Measure of Set

Prevorsek et al.¹⁰⁴ measured settability and permanence of set against bending deformation for nylon and polyester fibers. For measurement of degree of set, they wound fibers under constant tension onto a rod of suitable diameter (the diameter of the rod was changed to vary the strain) for a predetermined number of turns. After heat setting for 10 min, the rod was allowed to cool. The fiber was then released so that it was free to recover. Measurements were then made of L_2 and N_2 (described below) after 10 min or at various stages during recovery of the helix.

The set, S , was estimated using the following formula:

$$S = (N_2/N_1)[1 - (L_2/L)^2]^{1/2} \times 100$$

where L is the initial extended axial length of the helix, L_2 is the length of the recovered helix, N_1 is the initial number of helical turns, and N_2 is the number of turns after recovery.

Thermal Shrinkage

Thermal shrinkage is also often used as a measure of dimensional stability. The experiment is

simple and the fiber rapidly comes to equilibrium. Shrinkage in an oven at higher temperatures is also used by industry to evaluate dimensional stability.

Critical Dissolution Time (CDT)

The time needed to dissolve a filament in a solvent of known concentration at a given temperature is called CDT and correlates with density or crystallinity. Because during heat setting, the mechanism of permanent set is stabilization through crystallization, CDT can be used to compare the effectiveness of the heat-setting operation.

Crimp Stability

Crimp stability is a measure of the retention of crimp by a yarn when subjected to a mechanical or thermal treatment. Crimp stability is defined as the ratio of crimp retraction after the treatment to crimp retraction before the treatment.

LOOKING TO THE FUTURE

This review of the broad area of heat setting of thermoplastic fibers has first attempted to consider the various components of this important subject and then highlighted some of the advances that have taken place in our understanding of these aspects, particularly in the past two decades or so. We can take comfort from this review in that the causes of instability in fibers are better understood today and the molecular basis for such important phenomena as thermal shrinkage and shrinkage stress and of mechanical, optical, thermal, and transport properties of heat-set fibers along with their structural origins have evolved to a satisfactory level.

However, our comprehension of the way in which molecules organize themselves under uniaxial stress fields, first in the spinline and then under solid-state drawing needs to be enhanced. Some issues that need to be resolved have been referred to in the text. Progress in this area will allow the mechanism of heat setting to be better understood and an analysis of structural-dependence of properties to be made. Some specific issues that must be addressed include the phenomenon of partial melting and recrystallization and other mechanisms of permanent set. The various production processes are all moving toward

higher and higher speeds with superior controls, for example, of time, temperature, twist, and tension in texturing of multifilament yarns. Texturing machines capable of achieving speeds of 1500 m/min with short heaters of length 0.6 m capable of operating at temperatures up to 600°C are already being produced by machine manufacturers. This makes it necessary to study/develop the following: heat transfer at such high heating rates, development of thermo-mechanical techniques capable of simulating industrial conditions, collection of structural information on crystallinity, crystallize orientation, crystallite size, birefringence, etc. under the same conditions, crystallization kinetics at such high rates of heating and cooling, etc. Such studies will allow optimum heat setting of fibers to be achieved under industrial processing conditions.

Another important area that needs attention is development of improved models using molecular dynamics and computer simulation for fiber shrinkage, shrinkage stress, recovery, and settability. The crystal size distribution, orientation distribution, and other similar structural parameters could then be routinely fed into such models to predict fiber behavior. Hearle¹⁰⁵ has recently made an interesting proposal following the ideas presented by Roger Penrose, to apply the quantum mechanics approach, for example to the transitory liquidization of crystallites which would allow annealing and stabilization of the deformed fiber.

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