Force–Temperature Behavior of Rigid Rod Polymeric Fibers

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Synopsis

The force versus temperature behavior (at constant length) of poly(*p*-phenylene benzobisthiazole) fibers (PBT) and Kevlar fibers has been investigated. Thermal expansion coefficients are evaluated for heat treated PBT (PBT-HT) and Kevlar 49, to be -1.1×10^{-6}/°C and -3.2×10^{-6}/°C, respectively. Kevlar 49, PBT-HT, and steel fibers exhibit a linear thermal elastic behavior whereas Kevlar 29 and as-spun PBT do not. Material changes which occur during heat treatment processing are detected in the force-temperature profile. A correspondence between the thermal and mechanical energy input which induces these material changes has been found.

INTRODUCTION

Force versus temperature (F–T) experiments have been used extensively for the thermodynamic analysis of rubbers.[1,2] More recently, the force–temperature behavior of elastomeric materials has been used to examine structure property relationships.[3,4] In this paper, force–temperature analysis is extended to anisotropic rigid rod polymeric fibers: Kevlar 29, Kevlar 49, (DuPont's heat-treated version of Kevlar 29), as-spun poly(*p*-phenylene benzoisthiazole) (PBT), and heat-treated PBT.

Thermal expansion properties of materials may be readily examined from simple force–temperature experiments. Writing the total differential for force *f*, in terms of length *L*, and temperature *T*, one can readily obtain the relation

$$\left(\frac{\partial f}{\partial T}\right)_L = -\left(\frac{\partial f}{\partial L}\right)_T\left(\frac{\partial L}{\partial T}\right)_f \tag{1}$$

Normalizing the equation by a reference area A_0 and length L_0, the equation becomes

$$\left(\frac{\partial \sigma}{\partial T}\right)_\epsilon = -\left(\frac{\partial \sigma}{\partial \epsilon}\right)_T\left(\frac{\partial \epsilon}{\partial T}\right)_\sigma = -E\alpha \tag{2}$$

where σ = uniaxial stress, ϵ = uniaxial strain, E = Young's modulus, and α = linear thermal expansion coefficient.

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The slope of the axial stress vs. temperature plot is, therefore, the negative of the product of the axial modulus and the axial thermal expansion coefficient. The thermal expansion coefficient α can be obtained from the slope of the (F–T) curve if the modulus is determined independently.

Additionally, this technique provides a unique way to study material changes during the heat treatment processing of these fibers. Recently, a systematic study of the effects of heat treatment parameters on the mechanical properties of PBT has been performed.[5] From that work, it has been shown that both thermal input (temperature) and mechanical input (tension) are important factors for enhancement of the mechanical properties. In this paper, experiments examining the F–T behavior of PBT and Kevlar are undertaken to study any possible correspondence between thermal and mechanical input during heat treatment processing.

EXPERIMENTAL

A schematic of the force–temperature apparatus employed in this work is shown in Figure 1. A 30-cm yarn sample was fed through the oven; one end was clamped to a load cell while the other end was attached to a movable clamp. The sample was stretched to a fixed length by adjustment of the movable clamp, and the temperature of the oven was controlled manually with a variac at a rate of approximately 5°C/min. The temperature was monitored by a platinum resistance (RDT) thermocouple situated in the middle of the oven. The resulting fiber's stress and its change with temperature were monitored on an X-Y recorder. To prevent degradation of the material at the high temperatures achieved, nitrogen was continuously flushed through the oven.

The PBT fibers investigated in this work were dry-jet wet spun at the Celanese Research Co. from anisotropic polymer solutions. These same fibers were heat treated and designated PBT-HT. Kevlar 29 yarn and Kevlar 49 yarn were obtained commercially from DuPont. Steel yarn was obtained from Bekeart Steelwire Corp.

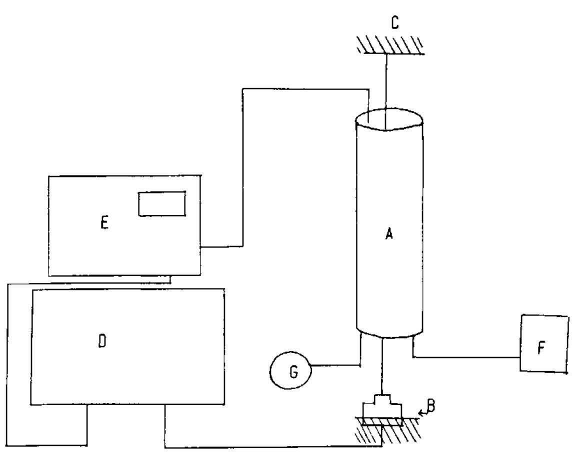


Fig. 1. Schematic of force–temperature apparatus: (A) oven; (B) load cell; (C) adjustable clamp; (D) X-Y recorder; (E) temperature readout-thermocouple; (F) N2 source; (G) variac.

The tensile properties for these materials were determined on single filaments in accordance with ASTM standards for testing high-modulus single filament materials.[6] Reported moduli were corrected for the compliance of the testing machine and were based on the linear densities of the materials. The deniers were furnished for PBT, by the Celanese Research Co., and for Kevlar 29 and Kevlar 49 by DuPont.[6,7] The denier of the steel yarn was calculated by weighing the sample.

Wide-angle x-ray diffraction results were obtained from both diffractometric and flat film techniques. Flat film fiber patterns were obtained in a Warhus (Statton) camera employing pin-hole (0.2 mm) collimation and a sample to film distance of 18 mm Diffractometer (2θ) scans of equatorial reflections were obtained on a Siemens D-500 Diffractometer utilizing line focus collimation. Incident beam diffractometer slits of 0.3° (2θ) with a final slit of 0.15° (2θ) were used for a scan rale of 1° (2θ)/min. CuKα tubes operated at 40 kV and 30 mA were used for both the Warhus camera and Siemens diffractometer.

RESULTS AND DISCUSSION

According to eq. (2), materials possessing a positive thermal expansion coefficient (as most materials do), will experience a stress drop with increasing temperature when maintained at constant length. To test the validity of this equation and the accuracy of the F–T apparatus, a steel yarn was first examined. A stress drop with increasing temperature is observed for the steel yarn (Fig. 2) indicating a positive thermal expansion coefficient, as expected. The F–T behavior is reversible on cooling and the thermal expansion coefficient calculated from the slope of the F–T curve is approximately 7×10^{-6}/°C based on a temperature dependent modulus of 250 g/d. Since steel is known to have a thermal expansion coefficient of 9–11 $\times 10^{-6}$/°C,[7] the calculated value of α is in reasonable agreement considering the experimental errors inherent in the apparatus such as a 30°C temperature distribution within the oven and possible load cell compliance, as well as the neglect of any thermal expansion of the clamps.

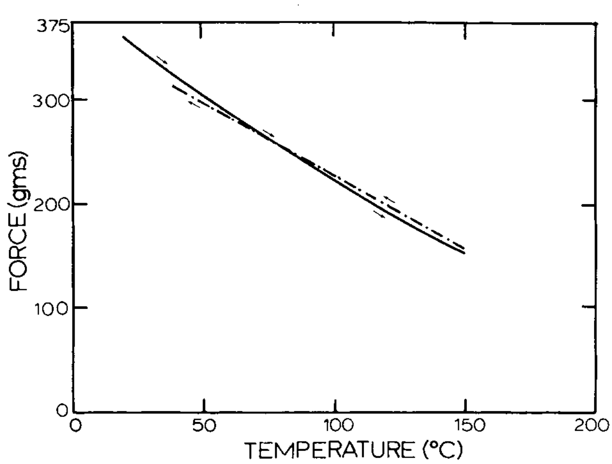


Fig. 2. Force vs. temperature profile for steel yarn: (—) heating; (– • –) cooling.

The F–T behavior of the heat-treated PBT yarn is shown in Figure 3(a). The stress is observed to increase with increasing temperature indicating the existence of a negative thermal expansion coefficient. Similar behavior is displayed by the Kevlar 49 yarn as shown in Figure 3(b). Although the modulus of PBT and Kevlar is known to vary with temperature,[5] the thermal expansion coefficient can be approximated using the room temperature modulus values of 1600 g/d for PBT-HT and 1000 g/d for Kevlar 49. In these calculations, the yarn modulus is approximated by the single filament modulus. The calculated thermal expansion coefficient for PBT-HT and Kevlar 49 are approximately -1.1×10^{-6}/°C and -3.2×10^{-6}/°C, respectively. This value of α for Kevlar 49 is in close agreement with reported values of $-(2–4) \times 10^{-6}$/°C.[8]

From the F–T behavior of Kevlar 49 [Fig. 3(b)], it is observed that the stress does not increase linearly with temperature between 50 and 100°C. On cooling followed by subsequent reheating, the stress is observed to vary linearly over this same temperature range. In order to understand this initial behavior, a sample of Kevlar 49 was heated to 200°C, cooled and allowed to relax at room temperature at atmospheric conditions for 24 h. Upon reheating, the initial nonlinear behavior returns, as shown in Figure 4. A similar sample which is heated to 200°C, cooled, and then placed in a

(a)

(b)

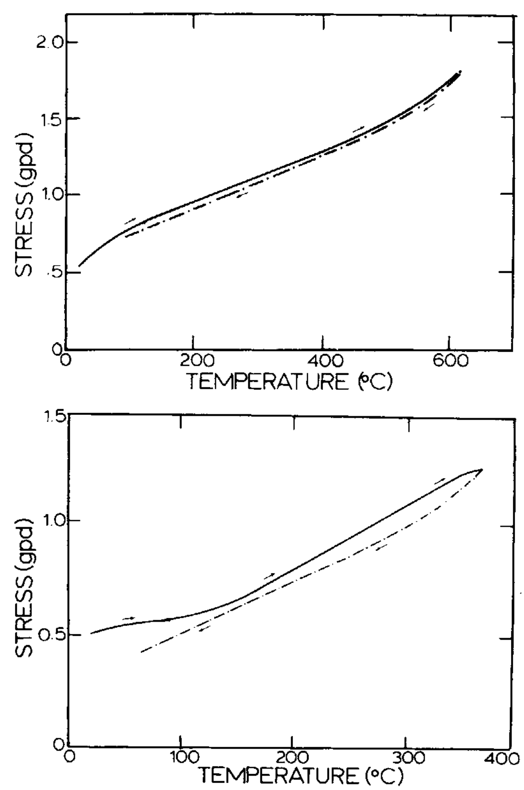


Fig. 3. (a) Stress vs. temperature profile for PBT heat-treated yarn at 650°C for 8 s: (—) heating; (-·-) cooling. (b) Stress vs. temperature profile for Kevlar 49 yarn: (—) heating; (-·-) cooling.

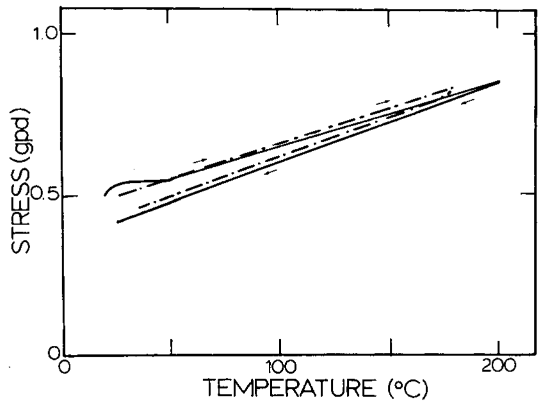


Fig. 4. Stress vs. temperature profile of Kevlar 49 yarn 24 h after the first heating cycle (—) undesiccated; (– • –) desiccated.

desiccated environment for 24 h exhibited a linear increase in stress with temperature upon reheating (see Fig. 4).

It, therefore, appears most likely that moisture absorption by Kevlar 49 causes this initial irreversible nonlinearity of the stress vs. temperature curve. The removal of residual moisture is accomplished by the application of heat as evidenced by the linearity of the cooling curve. After removing the residual moisture, the stress level at room temperature is lower than stress level at room temperature before the application of heat (see Fig. 4). This result is consistant with the possibility that Kevlar has a negative axial swelling coefficient whereby the material gets longer when it dries.

Since the F–T profile for the PBT-HT sample is linear and completely reversible, PBT-HT yarn is less moisture sensitive than Kevlar 49.

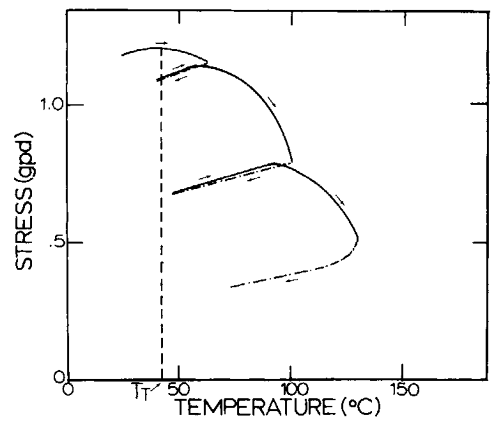
The F–T behavior of the as-spun PBT and Kevlar 29 yarns are most interesting, as shown in Figure 5. For both materials, there is a dramatic stress drop with increasing temperature after the fiber has reached a critical temperature, denoted as T_T. In addition, the behavior of these fibers are seen to depend on their thermal history whereby the material upon cooling and subsequent reheating displays a linearly reversible behavior up to the maximum temperature it has been exposed to previously. At that point, the material again exhibits a drop in stress.

It is suggested that the observed stress drop with increasing temperature is associated with a change in molecular order or more simply, with the onset of effective heat treatment. If this is so, then a fiber would be expected to exhibit enhanced mechanical properties and increased molecular order if it has undergone a force–temperature history were T_T is observed.

A comparison of wide angle x-ray diffraction patterns of Kevlar 29 and Kevlar 29 force–temperature-cycled (FTC)† shows sharpening of the equatorial reflections in the FTC–Kevlar 29 (Fig. 6), indicative of an improvement in the extent and perfection of lateral molecular order. In addition, there is a sharpening of the meridional reflections, which are now quite similar to those observed for Kevlar 49.

† The sample was subjected to a load of 5 g/d, heated to 300°C and cooled to room temperature.

(a)



(b)

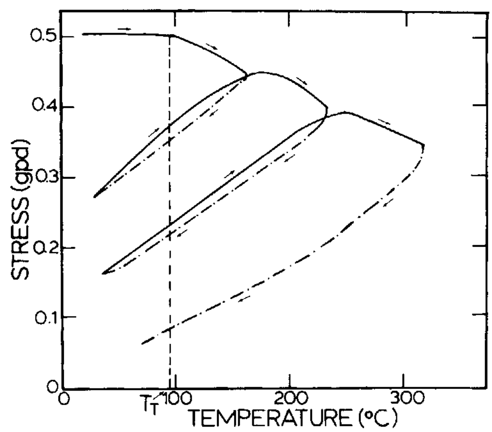
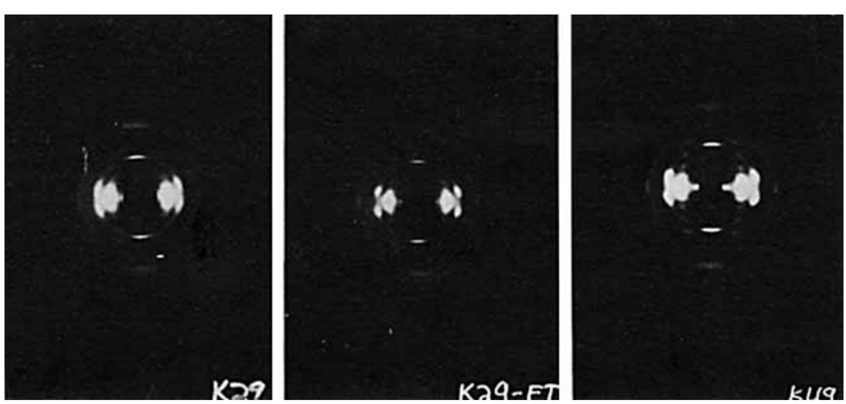


Fig. 5. (a) Stress vs. temperature profile of as-spun PBT yarn: (—) heating: (–••–) cooling. (b) Stress vs. temperature profile of Kevlar 29 yarn: (—) heating; (–••–) cooling.



(a) (b) (c)

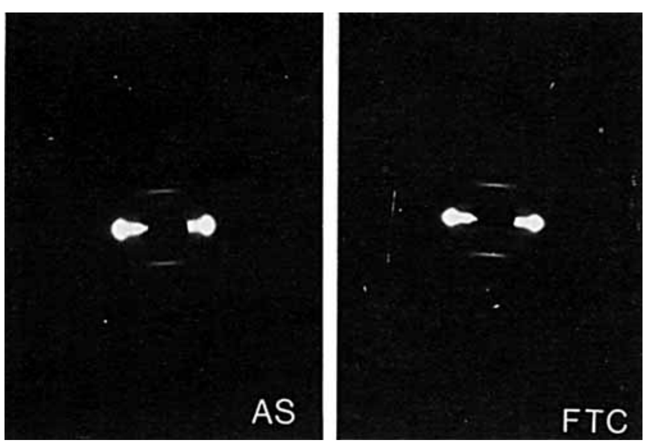
Fig. 6. Wide angle X-ray diffraction patterns of (a) Kevlar 29, (b) FTC-Kevlar 29, and (c) Kevlar 49.

The WAXS diffraction patterns of as-spun PBT yarn before and after the force temperature cycling reveal no readily observable differences (see Fig. 7). However, line profile analysis of the equatorial reflections shows a narrowing [measured as the full width at half-maximum intensity above background (FWHM)] for the FTC-PBT (see Table I). In addition, there is a shift in the equatorial peak position to lower scattering angles. Such narrowing of the peaks and the shifting of the peak positions indicate the existence of a higher degree of perfection of the lateral molecular order.[5]

The tensile properties of Kevlar 29, FTC-Kevlar 29, as-spun PBT, and FTC-PBT are shown in Table II. There is an enhancement of modulus with a reduction in strain at break for the cycled Kevlar 29 and as-spun PBT material. For PBT, the strength also increases when cycled whereas, for Kevlar 29, the strength is the same within experimental error. This data agrees with known changes in mechanical properties due to heat treatment of PBT and Kevlar.[5,9,10]

Both Kevlar 29 and as-spun PBT exhibit enhanced mechanical properties and increased molecular order after they have undergone a force–temperature history in excess of T_T. Thus, it is evident that the dramatic stress drop observed in the force–temperature behavior of these materials depicts the onset of material change or of effective heat treatment.

The temperature of the onset of heat treatment, T_T, is dependent upon the applied stress as shown in Figure 8 for both as-spun PBT and Kevlar 29. With increasing applied stress, T_T decreases. By increasing the mechanical input (applied stress), less thermal input (oven temperature) is required to reach the activation energy required to induce material changes. The experimental data indicates that there is a linear correspondence between these two heat treatment parameters: stress and temperature. In addition, the slope of T_T vs. applied stress for Kevlar 29 is greater than that of as-spun PBT. Thus, the onset of material changes for Kevlar 29 is much more sensitive to the application of tension than as-spun PBT, while



(a) (b)

Fig. 7. Wide angle X-ray diffraction patterns of (a) PBT as-spun and (b) FTC–PBT.

TABLE I
WAXS Diffractiometric Data of As-Spun PBT

Sample	As-spun PBT		Cycled PBT	
Peak number	e_1	e_2	e_1	e_2
Position	16.3°	25.9°	15.4°	25.6°
Peak width	5.0°	4.5°	3.2°	3.8°

the onset of material changes in as-spun PBT are more sensitive to temperature.

SUMMARY

Force–temperature analysis provides a unique way to study the thermal expansion properties of a material. For PBT-HT and Kevlar 49, the thermal expansion coefficients are evaluated to be approximately -1.1×10^{-6}/°C and -3.2×10^{-6}/°C, respectively. The F–T technique provides a unique way to study the heat treatment processing of fibers. F–T results for as-spun PBT and Kevlar 29 display, in the form of a dramatic stress drop, material changes as evidenced by mechanical and stuctural changes which are due to a heat treatment process. A linear correspondence between the temperature at which the stress drop begins, T_T, (thermal input) and the initial stress applied (mechanical input) to induce material changes is found.

From the F–T behavior of Kevlar 29 as as-spun PBT, it is evident that these materials do not exhibit a linear thermal elastic behavior whereas Kevlar 49, PBT-HT, and steel do exhibit such behavior. This complex-history-dependent behavior should be carefully considered in any engineering use of Kevlar 29 and as-spun PBT.

It is proposed that Kevlar 29 and as-spun PBT should exhibit considerably more creep under constant stress with the application of heat than their heat-treated counterparts. It is suggsted that the creep behavior of these materials is not viscous in origin since it is believed to be associated with a change in structure. The strain–temperature behavior of these rigid rod materials warrants further investigation.

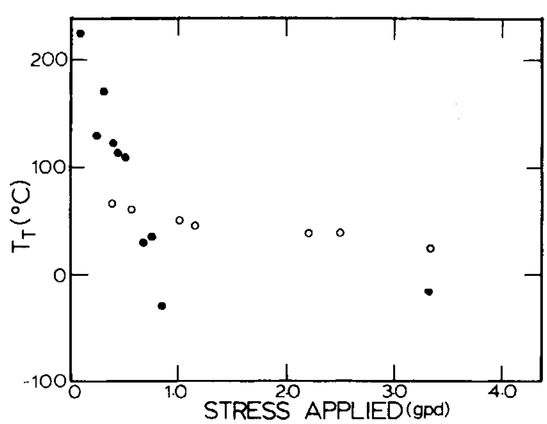


Fig. 8. Plot of T_T, temperature of onset of stress drop, vs. applied stress for (○) PBT (as-spun) and (●) Kevlar 29.

TABLE II
Mechanical Properties

Sample	As-spun PBT	FT-cycled PBT	Kevlar 29	FT-cycled Kevlar 29
Modulus	700 gpd ± 100 gpd	1440 gpd ± 90 gpd	600 gpd ± 100 gpd	1145 gpd ± 180 gpd
Strength	8 gpd ± 0.8 gpd	10.0 gpd ± 1.25 gpd	26 gpd ± 5 gpd	23 gpd ± 3 gpd
Strain	2.1% ± 0.2%	0.7% ± 0.1%	3.9% ± 0.4%	2.5% ± 0.8%

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