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High-modulus–high-strength poly-(*p*-phenylene benzobisthiazole) fibres

Part 1 *Heat treatment processing*

S. R. ALLEN,* R. J. FARRIS, E. L. THOMAS
Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003, USA

Heat-treatment processing of dry-jet wet-spun poly-(*p*-phenylene benzobisthiazole) fibres was undertaken to enhance fibre tensile mechanical properties. The effects of fibre tension and temperature and time of heat treatment in a nitrogen atmosphere on fibre mechanical properties were systematically investigated. Fibres possessing a tensile modulus as high as 300 GPa along with a tensile strength of 3 GPa have been produced. To attain this level of tensile properties, heat-treatment temperatures of 630 to 680° C for residence times of under one minute were required while applying tensions approaching fibre breaking stress at the elevated temperatures; conditions bordered on fibre degradation. Fibre structural changes associated with heat treatment and enchancement of mechanical properties are discussed in Part 2 of this work.

1. Introduction

Polymeric fibres possessing a tensile modulus of 300 GPa along with a tensile strength of 3 GPa have been produced via the heat-treatment processing of dry-jet wet-spun fibres of the extended-chain polymer poly-(*p*-phenylene benzobisthiazole) (PBT). This level of tensile mechanical properties is comparable to that of commercial carbon fibres (100 to 700 GPa modulus, 1 to 4 GPa strength) and to that of steel (200 GPa modulus, 2 to 3 GPa strength) which far exceed the tensile mechanical properties of common polymeric fibres. On a weight basis, PBT fibres can exhibit a tensile modulus of 2500 g/denier and strength of 25 g/denier and as such have potential applications as a lightweight, high-performance reinforcing fibre.

High-modulus–high-strength fibres derived from synthetic organic polymers have received a considerable amount of attention during the last two decades [1–4]. Due to the further development of conventional wet-spinning techniques, lyotropic liquid-crystalline solutions of extended-chain polymers have been spun to yield high-performance polymeric fibres. This success in obtaining high values of tensile mechanical properties in extended-chain polymeric materials has spurred further investigations of other rod-like macromolecules. The US Air Force Materials Laboratory has been involved in this area in attempting to improve the thermal and oxidative stability of polymeric materials as well as exploring the physical and mechanical properties of such new materials [5]. The goals of the Air Force Ordered Polymers Research Program have been addressed by focusing on extended-chain, aromatic heterocyclic molecular structures, poly-(*p*-phenylene benzobisthiazole) [6, 7] being produced as part of this programme [5].

The physical nature of PBT polymer excludes its being processed from a melt so that solution-processing methods are employed for fibre spinning. As is commonplace for other solution-spun polymeric fibres, a post-spinning heat treatment is found beneficial for the improvement of structural order and uniformity and for the enhancement of mechanical properties.

*Present address: Pioneering Research Laboratory, Textile Fibers Department, E. I. DuPont de Nemours Company, Inc., Wilmington, Delaware 19898, USA.

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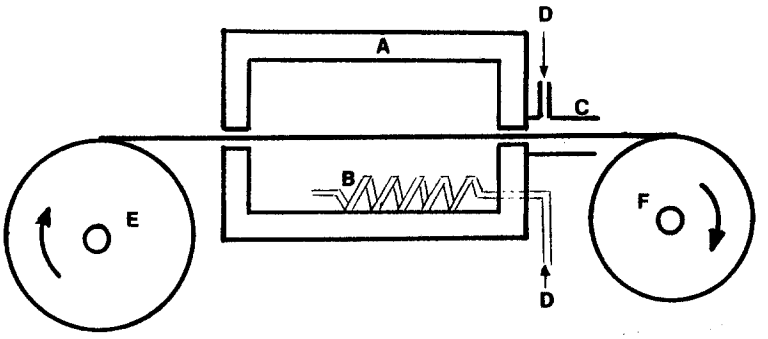

Figure 1 Schematic of heat-treatment apparatus. A. Laboratory furnace. B. Atmosphere preheat coil. C. Aftercooler. D. Atmosphere supply. E. Fibre supply spool/dynamometer (torque control). F. Fibre take-up spool.

In previous works [8–10] we have reported the high-modulus–high-strength potential of PBT fibres. This present work is concerned with the further development of high-performance PBT fibres through a systematic examination of the heat-treatment processing of fibres spun from lyotropic solutions of PBT polymer in polyphosphoric acid. The primary focus in Part 1 of this work is on the mechanical-property enhancements attainable for this material. Part 2 of this work is concerned with PBT fibre morphological changes resulting from heat treatment and the relationship between fibre structural characteristics and mechanical properties.

2. Experimental details

A twenty-filament PBT yarn (produced from a 0.2 wt% solids solution of PBT polymer (inherent viscosity in methane sulphonic acid of 14 dl g^{-1}) in polyphosphoric acid), dry-jet wet-spun at the Celanese Research Company, was used for the fibre heat-treatment studies. Mechanical properties at each condition were obtained from the average of eighteen single-filament tensile tests of six filaments randomly selected from the yarn with tensile moduli being corrected for machine softness in accordance with ASTM Standard D3379-75e for high-modulus, single-filament materials. Fibre diameters were measured by light scattering and fibre deniers were measured by weighing and/or vibroscopic determination.

Fig. 1 illustrates schematically the apparatus constructed for the PBT fibre heat treatment. The process parameters of heat treatment were temperature, atmosphere, yarn velocity, and tension. Thirty-five possible residence times were available by means of the take-up spool which is attached to a multiratio gear motor (APCOR 2202) and a ten-speed transmission (APCOR 2415). Residence times of 2 sec to 27 min were possible based on measurement of the interior oven length and calculated speed of the take-up spool. A dynamometer (MAGTROL HD-500-1) connected to the fibre supply spool allowed for the careful measurement and control of the applied tension. The tension applied to the fibre is calculated from the torque reading of the dynamometer, the radius of the supply spool and the size and number of filaments in the yarn. Torque readings on the scale of the dynamometer were checked by dead-weight calibration for the fibre supply spool used.

The heat-treatment chamber consisted of a modified laboratory-size furnace (GRIEVE AC-493) with automatic temperature control up to 1000° C. The furnace door and back were drilled with 0.25 in (6.4 mm) holes into which brass tubes, slightly longer than the oven insulation thickness, were inserted and cemented into place. The brass tubes provide entrance and exit ports for the yarn and are arranged to coincide with the centreline of the furnace. The door and other extraneous openings were cemented to prevent possible draughts. Nitrogen is admitted into the furnace at flow rates of from 4 to 10 litre min^{-1} through a coiled tube (see Fig. 1) to allow some nitrogen preheating before bulk mixing within the approximately 2.5 litre chamber. Heat-treatment temperature is monitored both by the furnace thermocouple and by a platinum resistance (RDT) element placed within the chamber. Before the RDT element was cemented into a fixed position it was moved about the chamber to measure temperature gradients. For typical gas flow rates, temperature variations of only 10 to 15° C were observed within the chamber when it was maintained at temperatures of 500 to 600° C. A nitrogen-atmosphere cooling chamber was attached to the fibre exit port to provide an inert cooling atmosphere for the hot yarn exiting the furnace. Based on fibre and process heat-transfer characteristics, a heat-transfer analysis [11] suggests

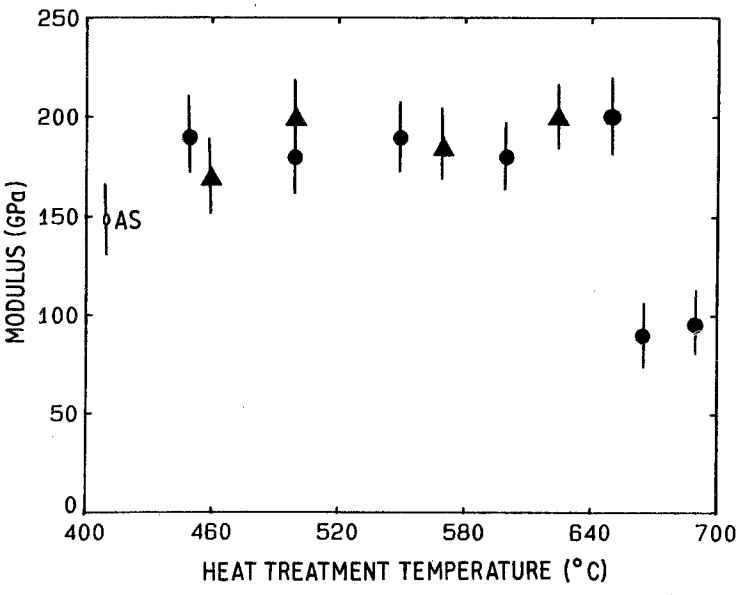

Figure 2 Modulus of annealed PBT fibres (●8, ▲81 sec).

that the fibre thermal history may be conservatively approximated as one of constant temperature over the furnace length.

A typical heat-treatment run consisted of first selecting a heat-treatment temperature and allowing the oven to stabilize at this temperature while being flushed with nitrogen. The as-spun fibre to be heat-treated was wound on the dynamometer spool, the amount being determined by the length of the run desired. The fibre was then threaded through the oven by tying it to a piece of piano wire (which is passed through the oven from the exit side) and then taped onto the take-up spool connected to the transmission and motor which are preset to achieve a desired fibre velocity and hence residence time. The take-up motor is then turned on, drawing the fibre through the oven with the dynamometer control turned down to give minimal tension on the yarn. When the fibre is running smoothly through the apparatus, the tension is increased to a desired value and after running for two to three residence times a marker is placed on the fibre take-up spool and heat-treated fibre is collected. Generally, after two to three residence times of sample collection, another marker is placed on the fibre, the tension increased to a higher value and an additional sample collected. For a given residence time and temperature, four to five tension values were employed for a single run. To generate heat-treated fibre for zero applied tension a length of the fibre was simply drawn through the oven without the use of the supply spool or the dynamometer.

3. Results and discussion

Preliminary investigations of PBT fibre heat treatment have indicated that temperatures in excess of 500° C for relatively short residence times, both with and without applied tension, can significantly enhance the tensile modulus and tensile strength of as-spun PBT fibres [11]. (It should be noted that the stress–strain behaviour of heat-treated PBT fibres is linear-elastic.) To define a workable range of heat-treatment temperatures, zero-tension heat treatments (annealing) were carried out for residence times of 8 and 81 sec for temperatures in the range of 450 to 690° C. Figs. 2 and 3 summarize modulus and strength, respectively, for this range of annealing temperatures. Slight modulus improvements are observed for temperatures up to 650° C, while fibre strength remained the same or decreased slightly for this same temperature range. For the two highest temperatures examined (660 and 690° C), a significant degradation of both modulus and strength was observed (when compared with as-spun properties, 150 GPa modulus, 1.5 GPa strength). Thus, a workable temperature-range having been defined, a series of tensioned heat-treatments of this fibre were performed for the range of 450 to 715° C with most of the work focused on temperatures around 650° C, for residence times of 8 to 10 sec. The effect of longer residence times is discussed later.

Significant enhancement of fibre modulus resulted from the heat treatments investigated, with heat-treated fibre moduli of up to 330 GPa (~ 2500 g/denier) being achieved. Fig. 4 illustrates

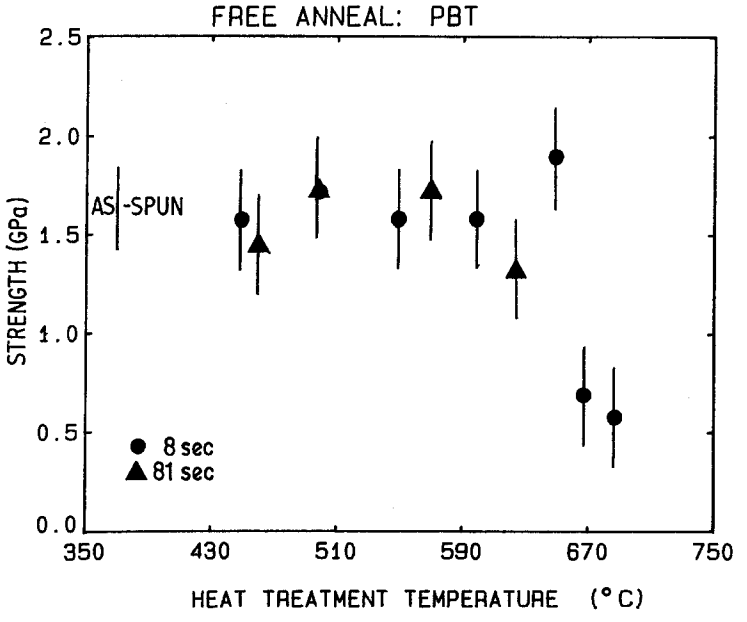

Figure 3 Strength of annealed PBT fibres (●8, ▲81 sec).

the trend observed for all temperatures: increasing modulus of the heat-treated fibre for higher values of tension applied during heat treatment so that additional plots would be redundant. The importance of heat-treatment temperature on the resulting heat-treated fibre modulus is illustrated in Fig. 5, where the values plotted are for an applied tension of approximately 130 MPa (approximately 1 g/denier). Generally, tensions approaching 200 MPa resulted in yarn breakage, so that 130 MPa provided an easily obtainable reference tension. It should be pointed out, however, that these values of modulus do not correspond to the maximum values obtained at the given temperatures. Higher values of modulus than those shown in Fig. 5 were obtained at each temperature by using tensions greater than 130 MPa (Table I).

A level or slightly increasing trend of tensile modulus with increasing heat-treatment temperature is observed (Fig. 5). Modulus values in the range of 300 to 330 GPa were obtained for this fibre for heat treatments in the range of 450 to 660° C for an applied tension of approximately 130 MPa. Above approximately 680° C, the

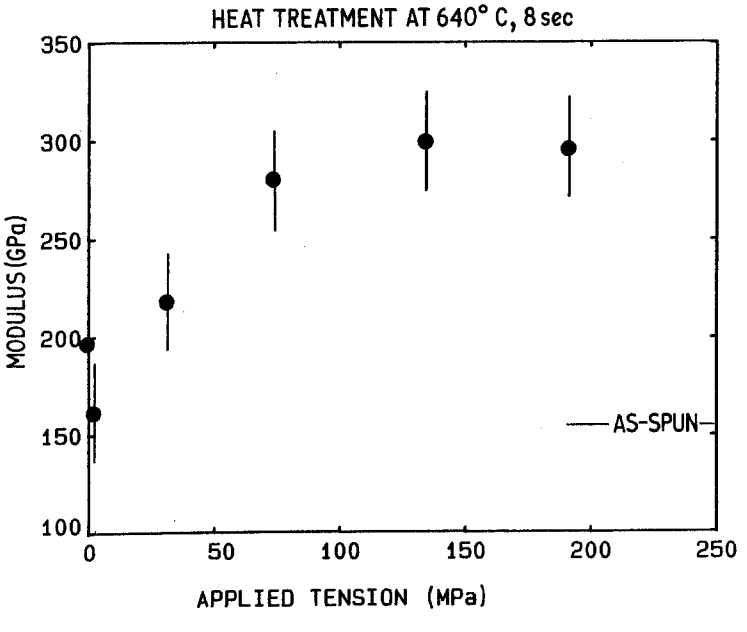

Figure 4 Modulus of 640° C, 8 sec tensioned heat-treated fibres.

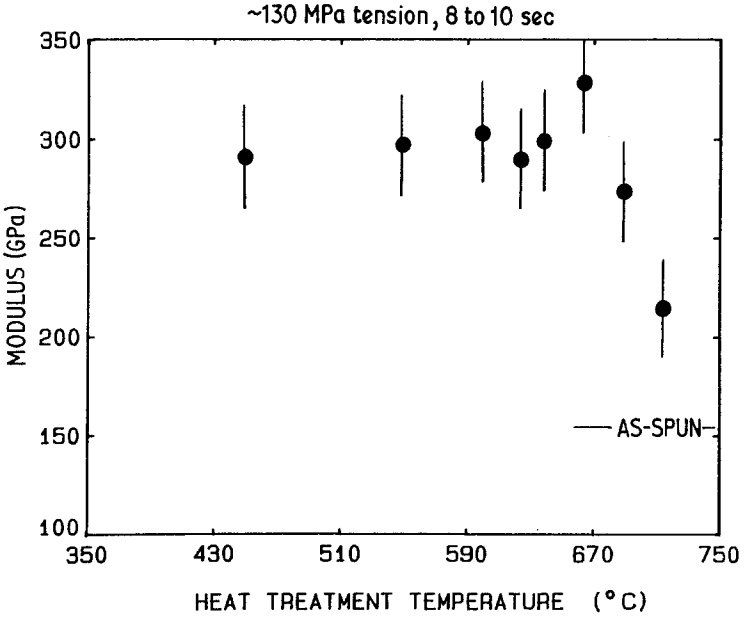

Figure 5 Heat-treated fibre modulus for various heat treatment temperatures (8 to 10 sec residence time, ~ 130 MPa tension).

modulus of the heat-treated fibres is observed to be lower than 300 GPa and further decreases with increasing temperature (690 and 715° C). This "upper temperature limit" of about 680° C for maximum enhancement of modulus corresponds fairly well with that seen in the zero-tension heat-treatment study.

Previous studies [11] have shown that while significant modulus enhancement is easily obtained for heat-treatment temperatures of 450 to 600° C, strength enhancement has been only minimal in this range. The zero-applied-stress heat treatments discussed earlier (Fig. 3) did not yield strength improvements for this fibre. Strength improvement was however found to be strongly affected by the tension applied during heat treatment. Fig. 6 shows this marked improvement in fibre strength for higher values of applied tension during heat treatment observed for a 640° C heat treatment. Similar trends were observed at the other temperatures investigated, as can be seen from an examination of Table I.

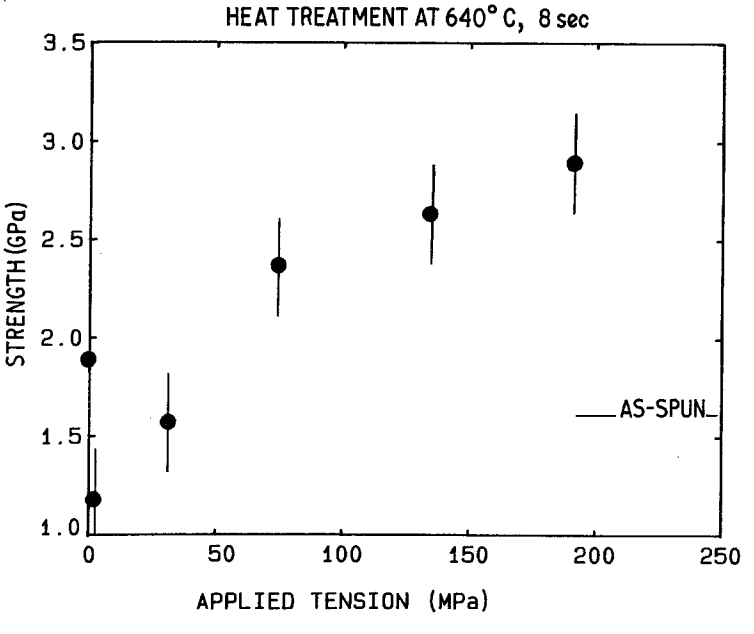

Figure 6 Strength of tensioned heat-treated fibres (640° C, 8 sec).

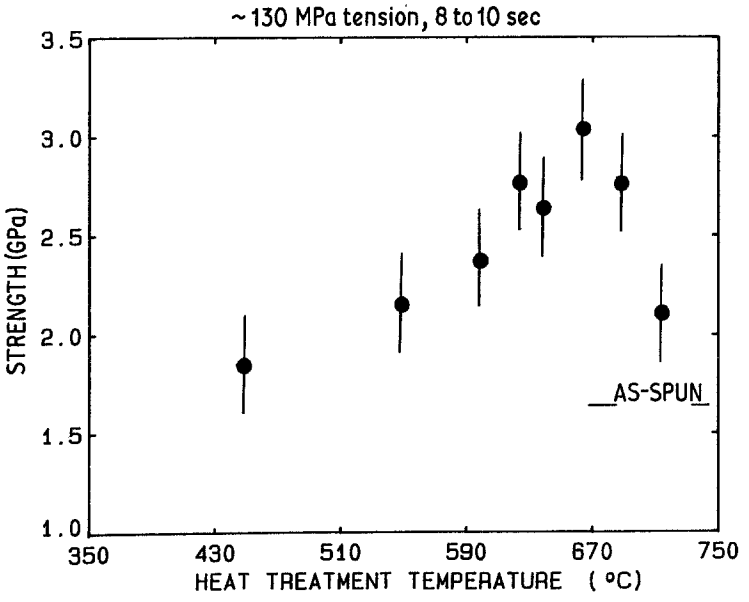

Figure 7 Strength of heat-treated PBT fibres (8 to 10 sec, ~ 130 MPa tension).

A comparison of heat-treated fibre strength obtained for an applied stress of ~ 130 MPa (1 g/denier) is given in Fig. 7 for the various temperatures used. As was the case for fibre modulus, these strengths are not the highest strengths obtained for each of the temperatures, but the strength resulting from an applied tension of approximately 130 MPa. In contrast to what was observed for fibre modulus (Fig. 5), there is a substantial effect of the heat-treatment temperature on the resulting fibre strength. Higher strength is obtained for higher temperatures in the range of 450 to 670° C, while heat treatment above this temperature range causes a degradation in strength for increasing temperature.

Tensioned heat-treatment for temperatures in the range of 630 to 670° C resulted in a fibre strength of 3 to 3.2 GPa. This represents a significant improvement over the as-spun fibre strength of 1.6 GPa. In order to achieve these high values of strength, tensions of 120 to 200 MPa (1 to 1.5 g/denier) during heat treatment were necessary. The tension control is perhaps the major disadvantage of the experimental design, in that the dynamometer maintains a constant force on the yarn, so that if one filament breaks then the resulting increase in stress on the remaining filaments generally causes total yarn breakage. Heat treatment with stretch control would be a more stable design (for yarns possessing few filaments), allowing for stresses approaching 200 MPa in the yarn without total yarn breakage should a single filament break occur.

The heat treatment results discussed above were for either an 8 or a 10 sec residence time. Longer residence times have also been examined for both tensioned and nontensioned heat treatment [11]. Figs. 2 and 3 contain data for both 8 and 81 sec residence times for the zero-tension heat treatments (see figures for explanation). For these two residence times, similar results were obtained for the temperature range examined. Tensioned heat treatments for 8, 40 and 81 sec at 625° C and for 8 and 326 sec at 600° C were also examined, and their results are included in Table I. Given the range of variability from sample to sample found in the measurements of strength and modulus, it appears that the 8, 40 and 81 sec heat treatments at 625° C yielded similar results. The long-time heat treatment (~ 5 min) at 600° C, however, indicated a slight deterioration of fibre modulus over that obtained for the 8 sec treatment, while the strengths obtained were higher (3 GPa against 2.4 GPa). Additional work is needed to examine longer residence periods for temperatures of 650° C or higher, where it might be expected that modestly higher strength and comparable modulus (relative to the 10 sec runs) would be produced.

It had originally been hoped to find a correspondence between the effects of thermal energy and mechanical energy input during heat treatment such that a single energy parameter might be defined to correlate the results. For example, isomodulus or isostrength contours were looked for as a function of the heat treatment parameters (on a three-dimensional plot or triangular diagram of

TABLE I Heat treatment summary of PPA spun PBT fibre*

Heat treatment parameters			Tensile modulus (GPa)	Tensile strength (GPa)
Temperature (°C)	Time (sec)	Tension (MPa)		
	as-spun		150 ± 25	1.6 ± 0.3
450	8	0	190 ± 35	1.6 ± 0.3
	10	55	210 ± 15	1.4 ± 0.2
	10	175	330 ± 40	2.0 ± 0.4
500	8	0	180 ± 30	1.8 ± 0.4
	81	0	200 ± 20	1.7 ± 0.3
550	8	0	190 ± 45	1.6 ± 0.4
	10	50	265 ± 15	2.0 ± 0.2
	10	160	315 ± 30	2.3 ± 0.3
600	8	0	180 ± 30	1.6 ± 0.2
	8	45	250 ± 20	2.2 ± 0.3
	8	165	270 ± 50	2.2 ± 0.4
600	326	115	260 ± 25	2.8 ± 0.3
	326	210	280 ± 30	3.2 ± 0.3
625	8	135	295 ± 35	2.8 ± 0.3
	8	185	310 ± 30	2.8 ± 0.3
625	40	135	305 ± 30	3.2 ± 0.3
	40	185	305 ± 30	3.1 ± 0.3
625	81	0	200 ± 30	1.4 ± 0.3
	81	140	285 ± 30	3.1 ± 0.3
640	8	3	165 ± 20	1.2 ± 0.3
	8	30	225 ± 25	1.6 ± 0.3
	8	75	285 ± 30	2.4 ± 0.3
	8	140	305 ± 75	2.7 ± 0.5
	8	195	300 ± 30	3.0 ± 0.4
650	8	0	200 ± 20	1.9 ± 0.3
665	10	0	90 ± 35	0.7 ± 0.3
	10	85	305 ± 30	2.5 ± 0.5
	10	135	335 ± 35	3.1 ± 0.2
690	10	0	95 ± 25	0.6 ± 0.2
	10	90	245 ± 30	2.4 ± 0.3
	10	140	280 ± 25	2.8 ± 0.3
	10	175	320 ± 20	3.1 ± 0.5
715	10	80	200 ± 40	1.8 ± 0.2
	10	135	220 ± 30	2.2 ± 0.3
	10	180	225 ± 35	2.3 ± 0.4

*A more extensive listing can be found in [11].

temperature, time and stress) to find equivalent conditions for the production of a particular modulus or strength value. While the number of experimental conditions actually investigated is quite large (Table I and [11]), the large amount of variability of modulus and strength combined with the number of possible conditions yet to be explored prohibited such a correlation of results with heat treatment parameters. In order to pursue this area further, fibres of better uniformity would be needed, as well as examination of lower temperature, higher stresses and longer times.

4. Summary

Specific processing conditions enabling significant improvements in fibre modulus and fibre strength for heat-treated PBT fibres relative to as-spun PBT fibre have been identified. Heat-treated PBT fibres possessing 300 GPa modulus (2500 g/denier) and 3 GPa (25 g/denier) strength were produced from a dry-jet wet-spun PBT fibre characterized by as-spun properties of 150 GPa modulus and 1.6 GPa strength. This engineering level of tensile mechanical properties is comparable to certain commercial carbon fibres and to steel and, because of the low density of PBT fibres, indicates the material's potential use as a lightweight, high-performance reinforcing fibre. For the production of heat-treated fibre possessing a modulus of 300 GPa and a strength of 3 GPa, temperatures of 630 to 680° C with residence times of under one minute were required. The application of tension or stretch to the fibre during heat treatment is also essential for attaining these properties. Tensions of 150 to 200 MPa (which approach the fibre strength at these high temperatures) are required, or, it would seem equivalent, a stretch ratio approaching that at which filament breakage begins to occur. Heat treatment for lower temperatures and/or lower tensions results in lower modulus and strength. Temperatures above 680° C in a nitrogen atmosphere lead to an onset of degradation of mechanical properties and the fibre becomes brittle (shattering into many pieces after a tensile test). Tensions above 200 MPa lead to yarn breakage at temperatures above 600° C. The best conditions for heat treatment appear, then, to border on conditions where the onset of degradation begins. Structural changes associated with this enhancement of fibre properties resulting from post-spinning heat treatment will be considered in Part 2 of this paper [12].

Acknowledgements

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