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PROCESSING AND PROPERTIES OF POLY (P-PHENYLENE BENZOBISTHIAZOLE)/NYLON FIBERS

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Polymeric composite fibers of Poly(p-phenylene benzobisthiazole) (PBT) and Nylon 6 and Nylon 6,6 were prepared and investigated. The objective was to achieve a composite in which the PBT was dispersed on a molecular level, to enhance reinforcement and mechanical properties. The effects of wet-stretching, heat-treatment time (0.5,1,2 minutes), heat-treatment tension (10-100 MPa) and heat-treatment temperature (215°C - 295°C) on tensile properties were studied. Also, the influence of the nylon molecular weight (13700 and 17500 g/mole for Nylon 6,6 and 14500 and 20000 g/mole for Nylon 6) on composite fiber properties was studied. Moduli of 40 GPa and tensile strengths of 375 MPa were achieved for 30/70 PBT/nylon composites.

Extended heat treatment of the nylon/PBT fibers at 160°C to 225°C for periods of 12 to 19 hours increased the tensilve modulus values by 20% to 50% and the tensile strengths by 1% to 14%. The inherent viscosity of the nylons increased for 12% to 108% as a result of extended heat treatment, indicating an increase in molecular weight.

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FOREWORD

This report describes the thesis work of the author, for the M.S.Ch.E at the University of Massachusetts at Amherst, during the period September, 1984 through September, 1985. The work was performed under contract No. F33615-83-K-5001, between the Air Force Aeronautical Laboratories, Materials Laboratory, Wright-Patterson Air Force Base, Ohio, and the University of Massachusetts at Amherst. Dr. Charles Lee is the Project Monitor. The thesis work was directed by Professor Michael F. Malone at the University of Massachusetts. Professors Richard J. Farris and Edwin L. Thomas were members of the thesis committee.

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I. INTRODUCTION

1. OVERVIEW

Polymer composites have recently had a large number of applications in the automotive and aerospace industries. Structural materials once manufactured from steel and other metals are in many cases now being constructed from fiber reinforced plastics. The high strength to weight ratio of these composites is particularly desirable, and there is reason to expect that polymeric composites should become predominant engineering and structural materials in the near future[1-3].

Commercial composites consist of a filler in the form of spheres, whiskers, ribbons or fibers imbedded in a matrix polymer. Depending on the form, fillers can be used to stiffen the matrix, reduce creep, increase the polymer strength, improve electrical properties, modify the rheological properties, lower materials cost, etc.[4] Fiber reinforcements are of particular interest because they have the potential to substantially increase the mechanical properties of the composite.[5-7] Typically, silicon dioxide, metal, carbon or aromatic fibers are chopped and mixed into the molten polymer matrix.[8] A significant increase in modulus, strength and rigidity occurs as a result of fiber reinforcement. An example of this is shown by the tensile data in Table 1.[9,10] With 30% glass fiber added to Nylon 6, the modulus increases by a factor of three and similarly with the 33% glass fiber reinforced Nylon 6,6. The tensile strengths are also improved.

TABLE 1

TENSILE DATA FOR GLASS FIBER REINFORCED NYLONS

	E (GPa)	TS (MPa)	ε (%)
NYLON 6	2.7	81.4	200
+ 30 wt% Glass Fiber	6.6	151.7	5
+ 40 wt% Glass Fiber	8.3	206.9	5
Nylon 6,6	2.8	83	60
+ 33 wt% Glass Fiber	9.0	185	2

From References 9,10.

The mechanical properties improve as a result of the added fibers. It is also possible to improve mechanical properties by varying the shape of the reinforcing fibers. A factor governing the composite strength and modulus is the length to diameter ratio of the reinforcing fiber.[6,11-13] By increasing this aspect ratio, the composite mechanical properties increase. Secondly, the influence reinforcing fibers have on the matrix will depend on the strength of the interfacial bond between the fiber and the matrix. At a critical fiber aspect ratio, the load on the composite will be shared equally between the fiber and the polymer matrix, and the force required to pull the fiber out of the matrix will be greater than the strength of the reinforcing fiber. Below this critical aspect ratio, the reinforcing fiber contributes little to the composite strength and failure occurs when the fiber is pulled from the matrix.[12] Lastly, long fibers reduce the points of stress concentration, and the probability of deflecting crack growth in the flexible matrix is higher.[14] The ultimate reinforcing fiber, therefore, would naturally be a single, extended, rigid-rod polymer molecule.[16] Such is the basis of the molecular composite concept.

Rodlike, extended-chain polymer molecules that could be used for these molecular composites have been synthesized and studied.[17-19] Poly (p-phenylene benzobisthiazole) (PBT), a wholly aromatic, heterocyclic polymer currently synthesized by SRI under contract to the Materials Laboratory, has been investigated as a reinforcing material in coil-like polymers (Table 2). PBT degrades before exhibiting a melting point, has high thermal and oxidative stability (weight retention of 50% after 200 hours at 371° C in circulating air[16]), and is soluble only in strong acid solvents.[21-23] The lack of a melting point and limited solubility results in some processing problems. One would ideally like to blend PBT into a coil-like polymer for the purpose of melt spinning. Instead, solution spinning techniques must be employed.

The mechanical properties of molecular composites have been analyzed theoretically. A theory by Halpin and Tsai relates the composite modulus to the individual moduli of the components.[25,26] In the limiting case where the reinforcing fiber aspect ratio approaches infinity, the composite modulus and tensile strength are predicted to follow a linear "rule of mixture." That is, the composite properties are a linear function of the fiber and the matrix properties and volume fraction. This ultimate "rule of mixture" reinforcement has been achieved for composites of PBT in aromatic, heterocyclic matrix polymers,[27,55,56] and the effort has recently been to achieve this with thermoplastic matrix materials.[14,28]

The "rule of mixture" reinforcement is a necessary but not sufficient test for the existence of a composite on the molecular level. In addition, a thermoplastic molecular composite must melt and flow when raised above the melting point of the matrix. The final proof, however, lies in a study of the composite microstructure.

2. BACKGROUND

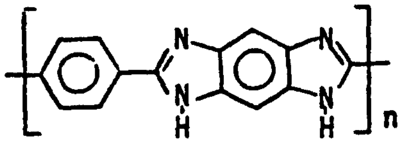
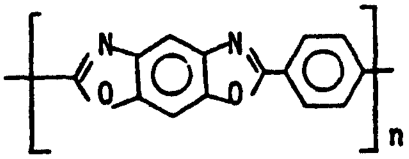
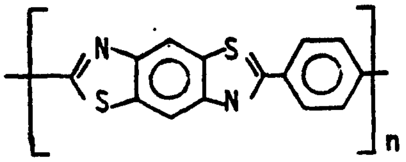
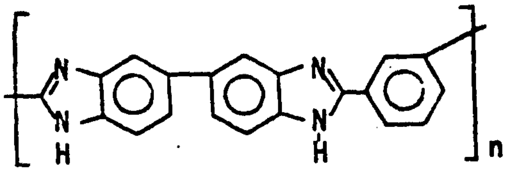
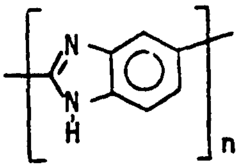
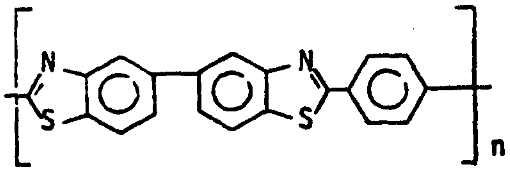
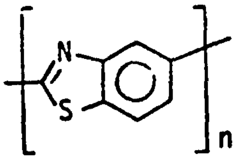
Early work on rodlike polymers involved the ladder polymer, BBL (Figure 1). This polymer formed strong films comprised of individual microscopic sheets of polymer when precipitated from a nonsolvent slurry.[16,57] The high strength of these films was found to be due to the high degree of molecular order of the BBL molecules. This led to a search for other polymers which possessed this same high degree of molecular order.

Three such polymers were synthesized; PDIAB, PBO and PBT (Table 2). PBO was found to be more thermally stable than PDIAB, while PBT has the highest thermal and oxidative stability of the three.[16,57] These highly ordered polymers, especially PBT, have been studied in the neat form as fibers and films.[21-23,37,38,42,44] Through refinement of processing techniques, films and fibers with greatly enhanced thermal and mechanical properties have been attained.

Investigations of these polymers as reinforcement in flexible, aromatic heterocyclic polymers has been made.[15,27,28,33-35,39,55] The key concept in these studies was to prepare composites at the molecular level, with one goal of processing the composites into useful forms for structural applications. Among the flexible aromatic heterocyclic polymer matrices studied were ABPBI, m-PBI, ABPBT and PPBT (Table 2). Various combinations of the rodlike polymers with the flexible coil polymers have been studied.[53,54] ABPBI/PBT composites proved to be particularly interesting[55] and have been the subject of much further study. Composite fibers were wet-spun from dilute methane sulfonic acid

TABLE 2

POLYMERS STUDIED UNDER THE AIR FORCE ORDERED POLYMERS PROGRAM

RODLIKE POLYMERS	CHEMICAL STRUCTURE	ACRONYM
Poly(p-phenylene benzobisimidazole)		PDIAB
Poly(p-phenylene benzobisoxazole)		PBO
Poly(p-phenylene benzobisthiazole)		PBT
COIL LIKE POLYMERS		
Poly(m-phenylene bibenzoimidazole)		m-PBI
Poly(2,5(6')benzimidazole)		ABPBI
Poly(p-phenylene bibenzothiazole)		PPBT
Poly(2,5(6')benzothiazole)		ABPBT

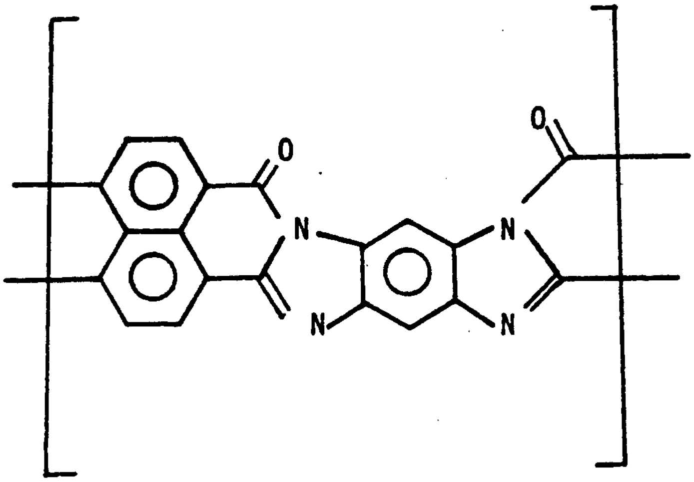


Figure 1 Repeat unit of BBL, Poly[(7-oxo-7,10H-benz[de]imidazo[4',5':5,6]benzimidazo[2,1a]isoquinoline-3,4:10,11-10-carbonyl]

(MSA) solutions and subsequently heat treated under tension. The final fibers were classified as "molecular composites" based on results from SEM and WAXS of the morphology and the uniaxial mechanical properties. This success with aromatic heterocyclic matrix polymers led to the study of thermoplastics as matrix materials. A thermoplastic molecular composite could potentially be melt processed into useful forms.

Two methods of dispersing the rodlike polymer in the thermoplastic have been investigated. One method involves synthesizing block copolymers of rigid rod and thermoplastic polymers.[58,59] The blending method, used for the ABPBI/PBT systems, involves blending the two polymers and rapidly coprecipitating them from solution.

The synthesis of block copolymers, building rodlike sequences into the matrix, has not been as thoroughly studied as the other method. In principle, however, the block copolymer could be processed in the same manner as the matrix. Takayanagi[58,59] created block copolymers of poly (p-phenylene terephthalate), PPTA, and Nylon 6 and Nylon 6,6 and compared them to the physical blends. The physical blends, with the addition of 5 % PPTA, had a yield stress three times that of the matrix. The copolymers, however, showed a greater degree of dispersion of the rigid segment, and the elongation at break was significantly higher than that of the physical blend.

The physical blends of rodlike molecules and flexible coil matrix polymers have been more heavily studied. Takayanagi studied blends of PPTA in Nylon 6, Nylon 6,6, PVC and nitrile butadiene rubber and found outstanding reinforcement with as little as 5 % PPTA. A major emphasis in this work has been on thermoplastics as matrix polymers, specifically nylons. In principle, the molecular composites of nylons and PBT, once formed, could be processed in the same manner as the nylon.

3. THESIS

A composite reinforced with PBT molecules combined with the melt processability of thermoplastics would potentially have a wide range of applications. With this motivation, a study of thermoplastic molecular composite processing, with the primary goal of enhancing mechanical properties, was made. Major variables influencing these mechanical properties include orientation during the spinning process as well as post-spinning heat treatment tension, temperature and time. In addition, the molecular weight of the matrix material can be expected to influence the composite mechanical properties. The influences of these variables are discussed in Chapter II.

Nylon 6,6 is known to undergo solid-state polymerization, and this idea has been applied to the composite systems. A higher molecular weight matrix should result in a composite with enhanced mechanical properties. Thus, it is important to study the influence of the matrix molecular weight, and to find methods of increasing this molecular weight. It may also be advantageous to polymerize the matrix within the composite as opposed to working with an initially high molecular weight matrix polymer. In this way, one achieves the mechanical properties of a high molecular weight matrix while maintaining the ease of processability of the low molecular weight matrix. This process is discussed in Chapter III.

A molecular composite will have mechanical properties which follow the linear "rule of mixture." Although this reinforcement was achieved for the ABPBI/PBT system, it was not achieved for the nylon/PBT systems. We believe that above a certain PBT weight ratio in the nylon composites, a network of PBT fibrils is formed. Thus a molecular composite of PBT in nylon, at 30 weight percent PBT, has not been formed. A method of testing for network formation, that of extracting the matrix from the composite fiber, is discussed in Chapter IV.

Finally, in Chapter V, the research accomplished in this thesis is summarized along with further work.

II. NYLON/PBT COMPOSITES

1. INTRODUCTION

The concept of a molecular composite of rigid rod/flexible coil polymer blends has been investigated with the PBT/ABPBI system. The composites were found to possess good tensile properties that could be improved by heat treatment under tension. The success in forming PBT molecular composites with aromatic heterocyclic flexible coil polymers has led to the study of thermoplastic polymers as the flexible coil matrix. Thermoplastic molecular composites could be melt processed, something not possible with the aromatic heterocyclic matrix composites. Composite films of PBT and nylon have been compression molded into large two-dimensional structural components by Hwang et al.[14] As with the heterocyclic matrices, the thermoplastic properties could be improved with heat treatment.

The main research on thermoplastic matrices has been centered on nylons.[14,29] Hwang et al. studied an amorphous nylon supplied by DuPont.[14] Nylon 6 and Nylon 6,6 were the thermoplastic matrices used in this study. Nylons are a common thermoplastic, widely used and readily available. They can be processed from MSA, and seem to provide a reasonable choice for a thermoplastic matrix material.

Due to the nature of PBT, the composites of PBT and nylon require solution processing techniques although nylons do show a melting point and can be melt-processed. Solution spinning is generally performed when the polymers do not form thermally stable, viscous melts, yet will dissolve in sufficient concentrations in low molecular weight fluids.[30] When the solvent is nonvolatile, as is the case with PBT systems, a wet-spinning process is employed. Wet spinning involves extrusion of the polymer solution directly into a coagulation fluid, a fluid which is miscible with the solvent but not with the polymers. This fluid is water for the systems studied here. Within this water coagulation bath, the PBT/nylon structure is "frozen" by rapid coprecipitation of the blend. Orientation of the fibers is achieved by subsequent wet-stretching between corotating rollers. The fibers, after washing to remove residual solvent, are wet stretched, dried, and heat treated. With the removal of the coagulant fluid, the fiber structure collapses upon itself as evidenced by a change in fiber diameter from the wet to dry state.

In general, dilute solutions are used for the wet spinning processes,[30] ranging from 5% to 30% polymer. For rodlike/flexible coil blends, this concentration is generally lower due to phase separation problems. Flory recently proposed an athermal theory of the statistical thermodynamics of a rodlike polymer, a flexible coil polymer, and an isodiametrical solvent system.[32] A brief description of this theory is useful here.

Figure 2 illustrates an idealized solution morphology of the three component system.[33] Below the critical concentration for the isotropic

$C \ll C_{cr}$

$C \leqslant C_{cr}$

$C > C_{cr}$

Figure 2 Idealized morphology of a ternary rigid rod/flexible coil/ solvent system as a function of concentration (28).

to biphasic transition ($C \ll C_{cr}$), there are essentially no polymer-polymer interactions and the solution behaves in a Newtonian manner. As the concentration approaches the critical concentration ($C < C_{cr}$), interactions become important and non-Newtonian behavior occurs although the solution is still isotropic. At this point, the rigid rod molecules are separated by a highly elastic matrix of flexible polymer. Finally, as the solution exceeds the critical concentration ($C > C_{cr}$), the solution separates into liquid crystalline domains dispersed in an entangled coil matrix. Fibers and films spun from anisotropic dopes are phase-separated. It is therefore necessary that these ternary solutions be processed below the critical concentration, which is generally on the order of 3 to 5 weight percent for the PBT composite systems.[27,34,35] This low concentration prevents the application of dry-jet wet spinning as used for PBT fibers, since the composite solution is not sufficiently viscous to prevent filament breakage.[30]

Wet-spun fibers are stretched in the wet state between corotating rollers in order to increase the orientation and mechanical properties. The fibers, after wet-stretching and drying, possess moderately enhanced properties that can be significantly improved with heat treatment under tension. A thorough investigation of the optimum heat treatment conditions has not been performed but initial results are available.

2. EXPERIMENTAL

a. Materials

Poly (p-phenylene benzobisthiazole), PBT, was synthesized by SRI International.[20] The polymer had an inherent viscosity of 25 dl/g, measured in dilute methane sulfonic acid. The weight average molecular weight was estimated as 36,400 g/mol using the correlation for polymer chains in the rodlike limit:[36]

$$\{\eta\} = 4.86 \times 10^{20}[d_H^{0.2}/M_L][M_\eta/M_L]^{1.8}$$

$$M_\eta^{1.8} = M_w^{1.8}[1/(h+1)]^{1.8}\ \Gamma(1.8+h+1)/\Gamma(h+1)$$

$$h = [(M_w/M_n) - 1]^{-1}$$

The heterogeneity factor, h, was taken to be 2, the hydrodynamic diameter of a chain element, d_H, to be 7Å, and M_L, the mass per unit length, to be 22 Å.[35] Nylon 6 and Nylon 6,6 were supplied by Polysciences, Inc. and by DuPont. Material properties for the nylons are listed in Table 3.

TABLE 3

MATERIAL PROPERTIES OF NYLON 6 AND NYLON 6,6

MATERIAL	M_n	T_g (°C)	T_m (°C)	SUPPLIER
Nylon 6	14500	50	228	DuPont
Nylon 6	20000	62	228	Polysciences
Nylon 6,6	13700	55	255	DuPont
Nylon 6,6	17500	45	270	Polysciences

As reported by supplier.

Except for drying, the nylons were used as received. PBT was received in a polyphosphoric acid "dope" and was extracted in water before use. The extraction process consisted of coagulating a flat sheet of PBT in water, chopping this sheet of PBT into small strips and boiling the strips in methanol for several days. The strips were then washed for several days and dried. The solvent, 98% methane sulfonic acid, MSA, was used as received.

b. Mixing

The ternary solutions were formed by mixing predetermined weight concentrations of PBT and nylon in MSA. The mixing apparatus, shown in Figure 3, consisted of a variable speed stirring rod in a glass flask. The stirring speed was approximately 8 to 10 revolutions per minute. The system was kept under a dry nitrogen atmosphere for the duration of the mixing process, which ranged from two to three weeks.

The critical concentration was determined by slow titration of an initially anisotropic phase separated solution until the solution became isotropic. This was determined by optical microscopy under crossed polars. A drop of solution was placed between a glass slide and cover glass and sealed with paraffin to prevent moisture contamination. The sample was heated briefly on a hot plate to relax any shearing stresses that occurred during the mounting then examined under the microscope. A lack of birefringence was taken to indicate optically isotropic solutions under 200X magnification. Approximately two days of stirring were allowed between successive titrations to ensure complete mixing.

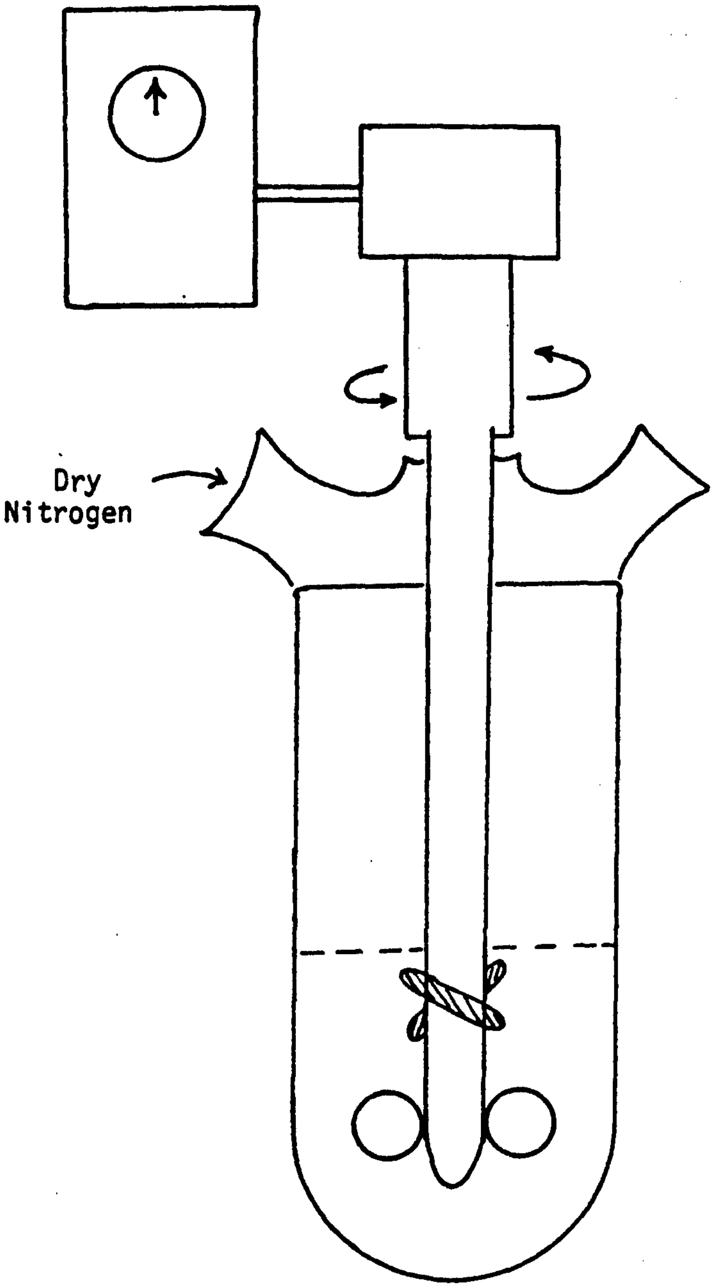


Figure 3 Composite mixing apparatus.

Composite concentrations were limited to 30 weight percent PBT for two reasons. First, this concentration was found to yield the best properties for the ABPBI and ABPBT systems.[27] Secondly, we desired to study the influence of various processing parameters on mechanical properties. Thus it was necessary to keep fiber composition constant. A systematic study of mechanical properties as a function of PBT concentration for the nylon matrix composites is an area recommended for future study.

c. Fiber spinning

Fibers were spun from a piston and ram apparatus shown in Figure 4. The barrel and plunger were constructed of teflon since MSA is corrosive for most stainless steels. The fibers were extruded through a single, 13-mil-diameter die hole. All solutions were filtered during the spinning process with a 7X Dynalloy micromesh filter.

Although the solutions were not highly viscous, it was necessary to deaerate them prior to spinning. This was done by placing the dopes within the barrel with the plunger intact and inverting the barrel in a vacuum oven at approximately 50°C for one to two days. This step was critical to the spinning process, because air bubbles in the dope result in voids and breaks in the fibers.

The fiber spinning apparatus is shown in Figure 5. The motor was a variable speed type, although a ram speed of 1.5 cm/hr was used exclusively. The fibers were spun directly into the water coagulation bath (pH approximately 7.0), which was slightly below ambient

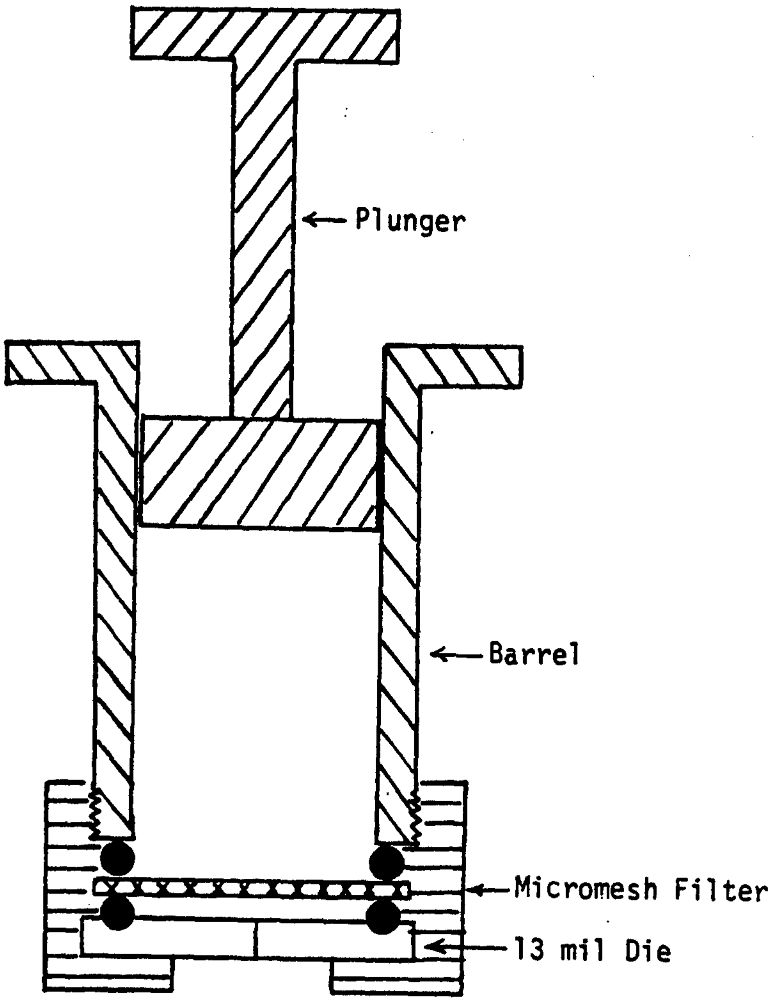


Figure 4 Fiber spinning barrel set-up.

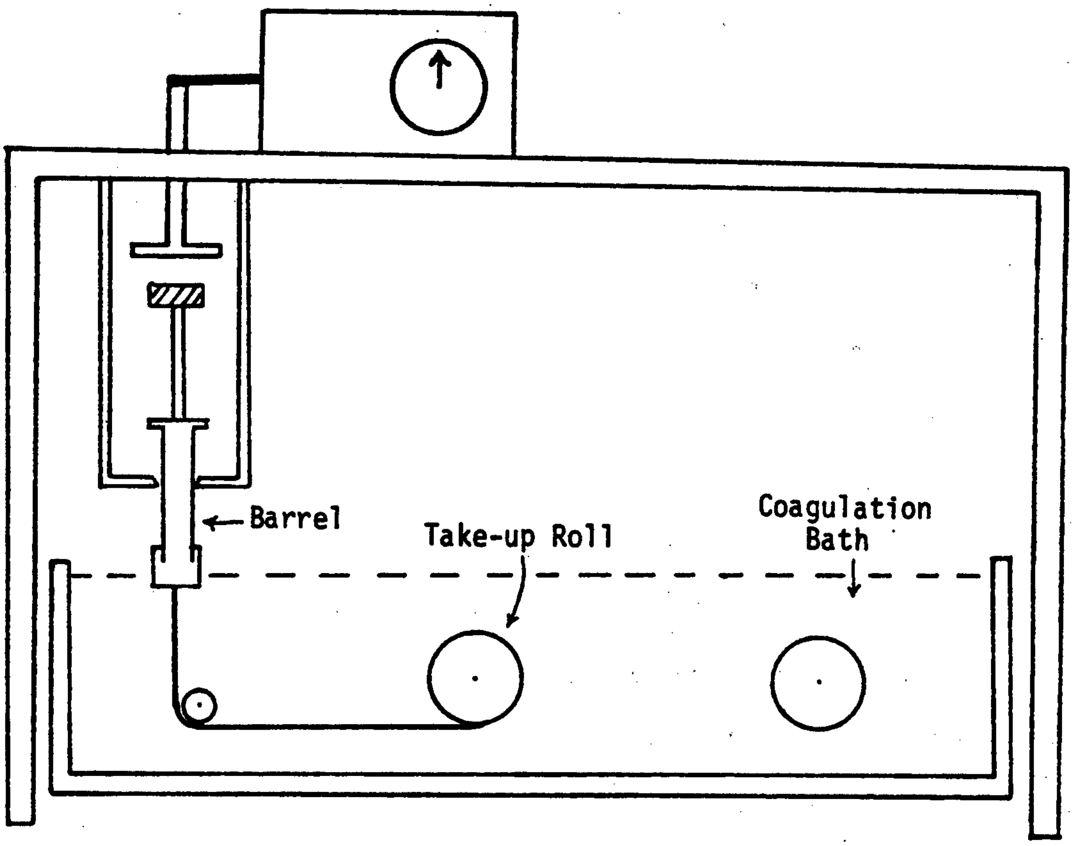


Figure 5 Fiber spinning apparatus.

temperatures (15-20°C). No tension was applied during take-up.

Orientation of the fibers was induced by post-coagulation wet-stretching between corotating rollers. The stretch was measured as an area reduction (D_o/D) . This was on the order of 1.1 to 2.0 for the nylon composites studied. The stretched fibers were subsequently air dried on the take-up roller without tension.

d. Heat treatment

Heat treatment was performed under a dry nitrogen atmosphere at various temperatures (215°C, 255°C, 295°C), oven residence times (0.5, 1, 2 minutes) and applied tensions (10 - 100 MPa). The heat-treatment apparatus, devised by Allen,[37] is shown in Figure 6. The nitrogen was preheated to prevent excessive temperature fluctuations within the oven which were reported to be on the order of 10 - 15°C. The temperature was monitored by a thermocouple and was controlled to 5°C. The tension was controlled by a Dynamometer (MAGTROL HD-500-1), and the torque readings were checked by dead weight calibration. Oven residence times were controlled be a multiratio gear motor (APCOR 2202) and a ten-speed transmission (APCOR 2415).

Fiber samples, gage length of 30 mm, were tensile tested on an Instron Universal Testing Machine at a crosshead speed of 0.1 cm/min, under ambient conditions. Samples were mounted on paper tabs with Devcon 5-Minute Epoxy which was allowed to cure overnight. Diameters were measured with an optical microscope under 200X magnification. The

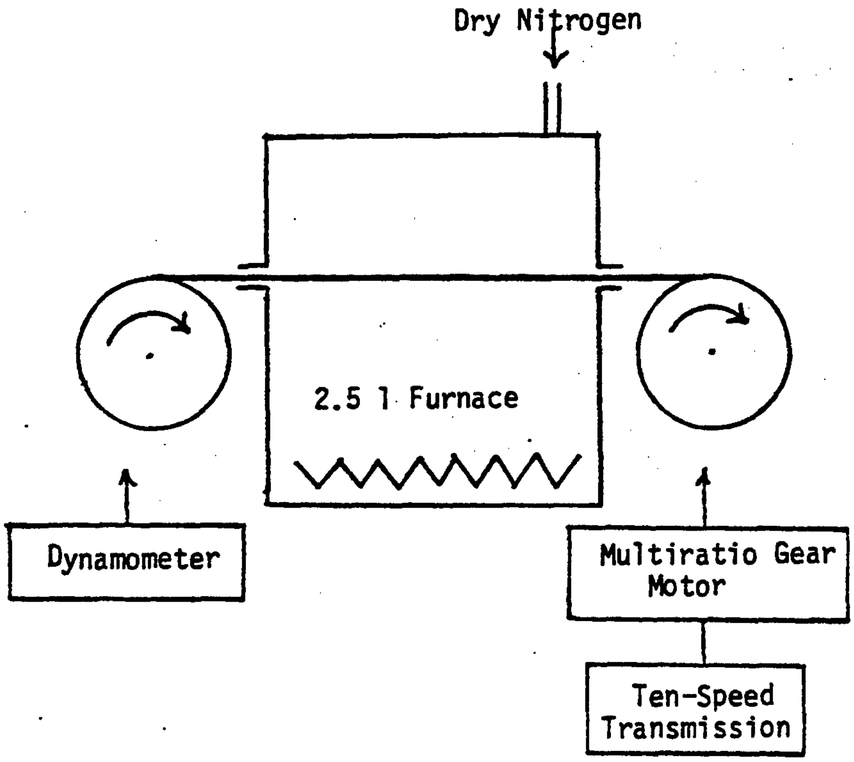


Figure 6 Heat-treatment apparatus (37).

mechanical data reported are the average of seven samples.

DSC measurements were performed over a temperature range of 300 - 600 K with a heating rate of 40 K/min.

3. RESULTS AND DISCUSSION

a. Basic parameters

The mechanical properties of PBT composites were found to depend on several processing variables. A thorough investigation of the influence of every variable is beyond the scope of this work, and some results from earlier studies were applied. The mechanical properties were previously found to depend on the rod-to-coil proportion,[27] with a 30/70 weight ratio yielding the best properties, and this work was limited to this ratio.

The properties are also a function of the spinning solution concentration. The most desirable concentration is one slightly below the isotropic to biphasic transition concentration.[33-35,39,57] Nylon/PBT composites were spun from such concentrations, which were 3.7 weight percent for the Nylon 6,6 composites and 3.5 weight percent for the Nylon 6 composites. The higher dope temperature was found to lower the viscosity and simplify spinning of the PBT dopes.[38] Nylon/PBT/MSA solutions were sufficiently viscous at room temperature such that the application of heat was not necessary. Cool water coagulant baths ($15^{\circ}C$ - $20^{\circ}C$) were used although studies have shown higher (2X) mechanical properties and lower void fractions for nylon fibers coagulated in slightly acidic media.[43,44] The effect of extrusion speed, i.e., shear rate, was not investigated here. A constant extrusion rate of 2.8 cm^3/hr was used (linear fiber velocity of 13 cm/min).

Several post-spinning processing variables which induce orientation within the fiber were studied. The influence of wet-stretching, heat treatment time, heat treatment tension and temperature on the mechanical properties were investigated. We also studied the effect of matrix molecular weight on the tensile properties.

b. Wet-stretching

Wet-spun fibers generally exhibit low mechanical properties as compared with dry-jet wet-spun fibers or melt spun fibers.[30,43] This is because the wet-spun fibers lack sufficient viscosity to be drawn during the spinning process. For this reason, no stretching is applied to the nylon composite fibers during the wet spinning process. However, wet-stretching provides an orienting step in these composites. Table 4 shows the properties of nylon/PBT composites as-spun and after wet-stretching. Figure 7 shows the stress versus strain curves of the Nylon 6,6/PBT (14500) as-spun and wet-stretched fibers. The degree of wet-stretching is measured as an area decrease, (D_o/D), where D_o is the as-spun fiber diameter.

The modulus and tensile strength show substantial increases as a result of wet stretching. The Nylon 6,6/PBT fibers were subjected to a low degree of wet-stretching, yet increases of 32% to 38% are seen in

TABLE 4

EFFECT OF WET-STRETCHING ON NYLON COMPOSITE MECHANICAL PROPERTIES

	E (GPa)	TS (MPa)	ε (%)
Nylon 6,6/PBT (13700)			
As spun	5.3	102.3	30.8
Wet-stretched (DR=1.4)	7.0	156.0	21.4
% Increase	32	53	- -
Nylon 6,6/PBT (17500)			
As spun	6.1	113.5	23.3
Wet-stretched (DR=1.1)	8.4	150.2	20.2
% Increase	38	32	- -
Nylon 6/PBT (14500)			
As spun	3.2	64.5	2.6
Wet-stretched (DR=2.0)	5.2	127.5	37.9
% Increase	63	98	- -
Nylon 6/PBT (20000)			
As spun	2.9	63.5	2.9
Wet-stretched (DR=2.0)	5.9	141.2	17.0
% Increase	103	122	- -

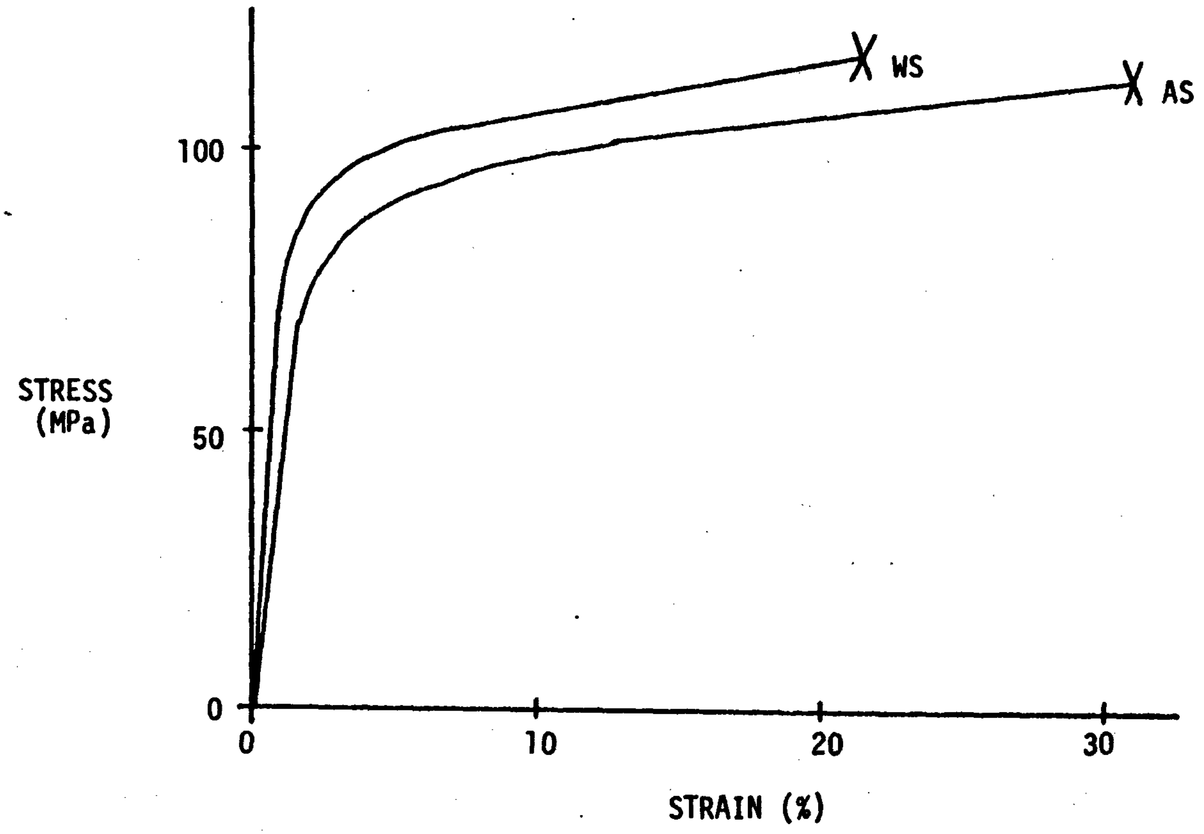


Figure 7 Stress-strain curves for Nylon 6,6/PBT (14500) as-spun and wet-stretched fibers.

the moduli and 32% to 53% in the tensile strengths. The elongation at break drops by 10% to 30% as a result of wet-stretching, indicating a greater amount of orientation within the fibers. Nylon 6/PBT composite fibers were subjected to a high degree of wet-stretching as measured by an area reduction of one half. Significant increases, from 63% - 123 %, are achieved in the moduli and tensile strengths as a result. The as-spun Nylon 6/PBT composites exhibit extremely low (2.6% and 2.9%) elongations at break as compared to the wet-stretched fibers (37.9% and 17.0%) and to the Nylon 6,6/PBT fibers (20% to 30% elongations at break). In these as-spun composite fibers, the PBT does not provide reinforcement but rather causes the fibers to be brittle.

c. Heat treatment

Solution-spun fibers generally exhibit poor properties in comparison to melt-spun fibers, and heat treatment provides an effective method of improving the mechanical properties. Heat treatment is used commercially to achieve a stabilization of fiber geometry, enhance structural order, improve mechanical properties and sometimes to chemically alter the fibers. Heat treatment creates a more perfect and stable structure through the relaxation of internal stresses.[30,31] The degree to which heat treatment can achieve these ends is governed by several processing parameters. Heat-treatment temperature, residence time, and applied tension play key roles in the achievement of desirable finished properties.

The influence of residence time was studied for the nylon/PBT composite fibers heat-treated at 215°C, 255°C and 295°C. Fibers were heat treated under tension for residence times of one half, one and two minutes. Tension was applied at increasing values until the limiting value, that of fiber breakage, was reached. Standard deviation of the data is on the order of 5% to 7%.

The mechanical properties as a function of heat-treatment time and tension for the high (17500) and low (13700) molecular weight Nylon 6,6 composites heat-treated at 255°C are shown in Figures 8 and 9. The Nylon 6,6/PBT (13700) fibers show greater sensitivity to oven residence time than do the Nylon 6,6/PBT (17500) fibers (Figure 8). Heat treatment for 0.5 minutes results in a 25% to 30% improvement in modulus over heat treatment for 1 minute or 2 minutes. However, the 1 and 2 minute times result in 5% to 10% higher tensile strength values. The Nylon 6,6/PBT (17500) composite fibers were not heat-treated for 2 minutes, and were heat-treated under limited tension for one minute (Figure 9). The modulus values are comparable to the Nylon 6,6/PBT (13700) values, while the tensile strengths are approximately 40% lower. The low tensile strengths can be partially attributed to the fact that these fibers were not heat-treated at 2 minutes and only slightly at 1 minute, the times which seem to show the higher tensile strength values.

Mechanical properties for the Nylon 6,6/PBT composites heat treated at 295°C are shown in Figures 10 and 11. The higher molecular weight (17500) Nylon 6,6 composites show less sensitivity to oven residence time than the lower molecular weight (13700) Nylon 6,6 composites. In fact, the modulus and tensile strength are identical within the experimental error at the three residence times studied (Figure 11). The Nylon 6,6/PBT (13700) fibers show the best moduli and

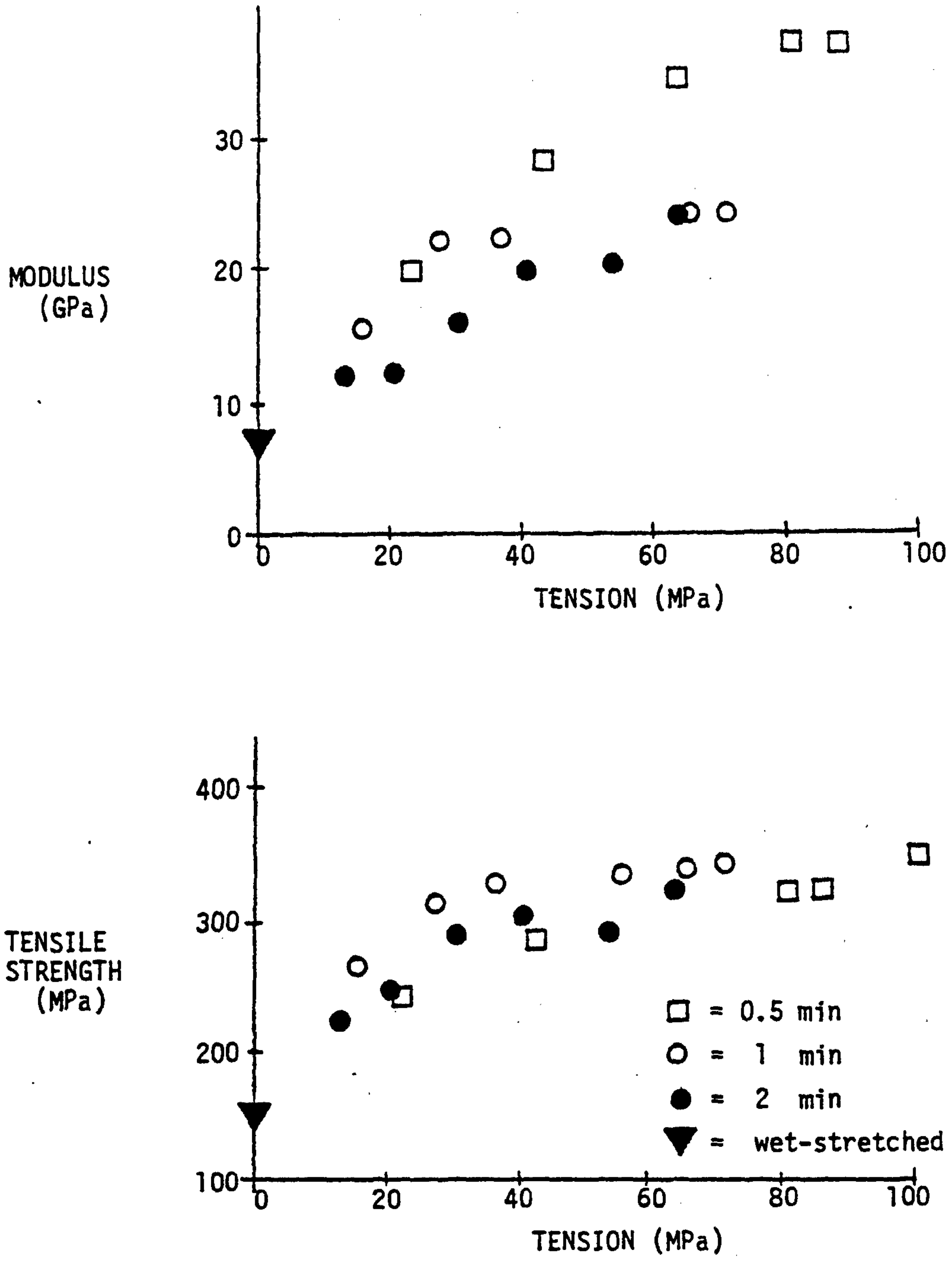


Figure 8 Mechanical properties as a function of heat-treatment time and tension for Nylon 6,6/PBT (13700) fibers heat-treated at 255°C.

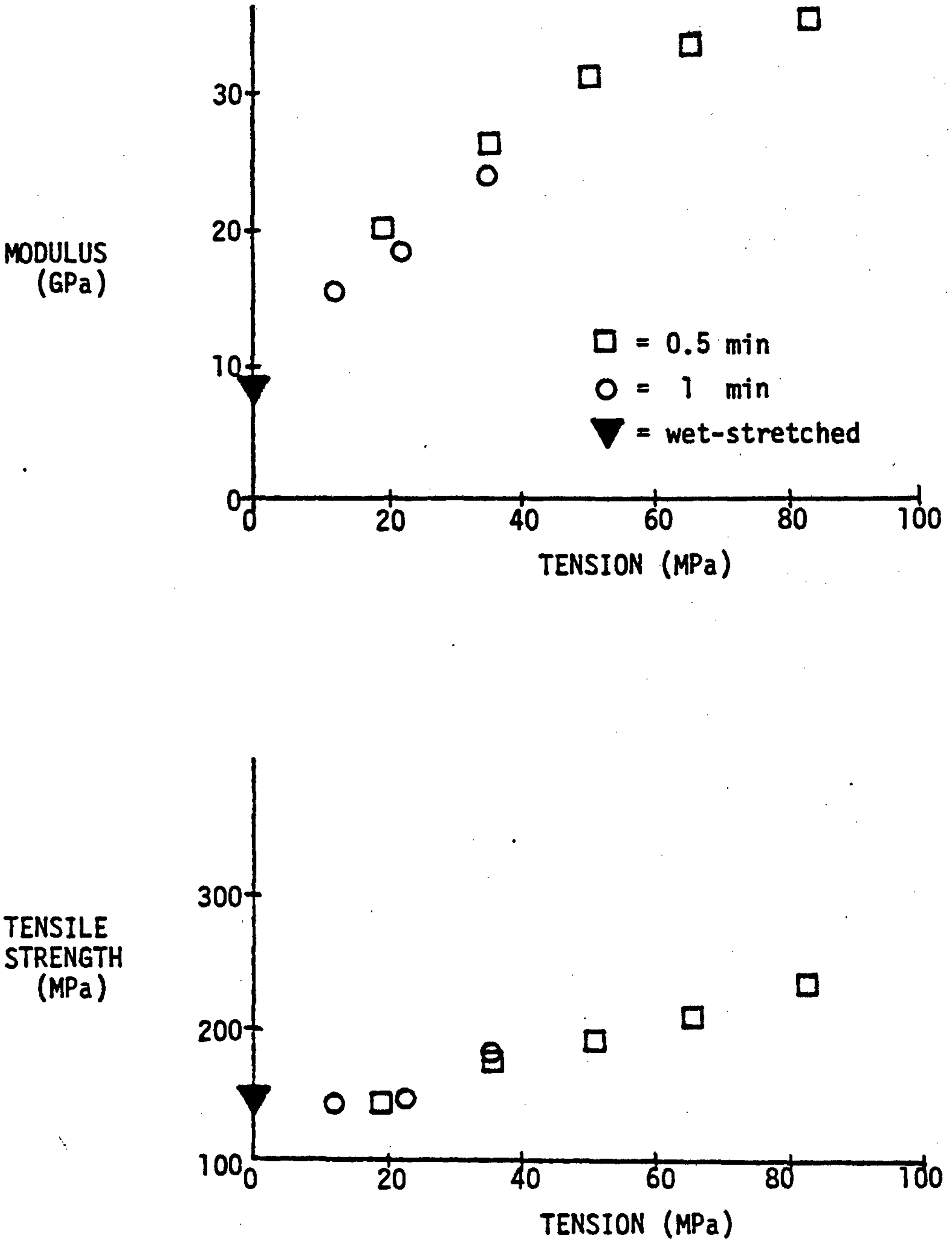


Figure 9 Mechanical properties as a function of heat-treatment time and tension for Nylon 6,6/PBT (17500) fibers heat-treated at 255°C.

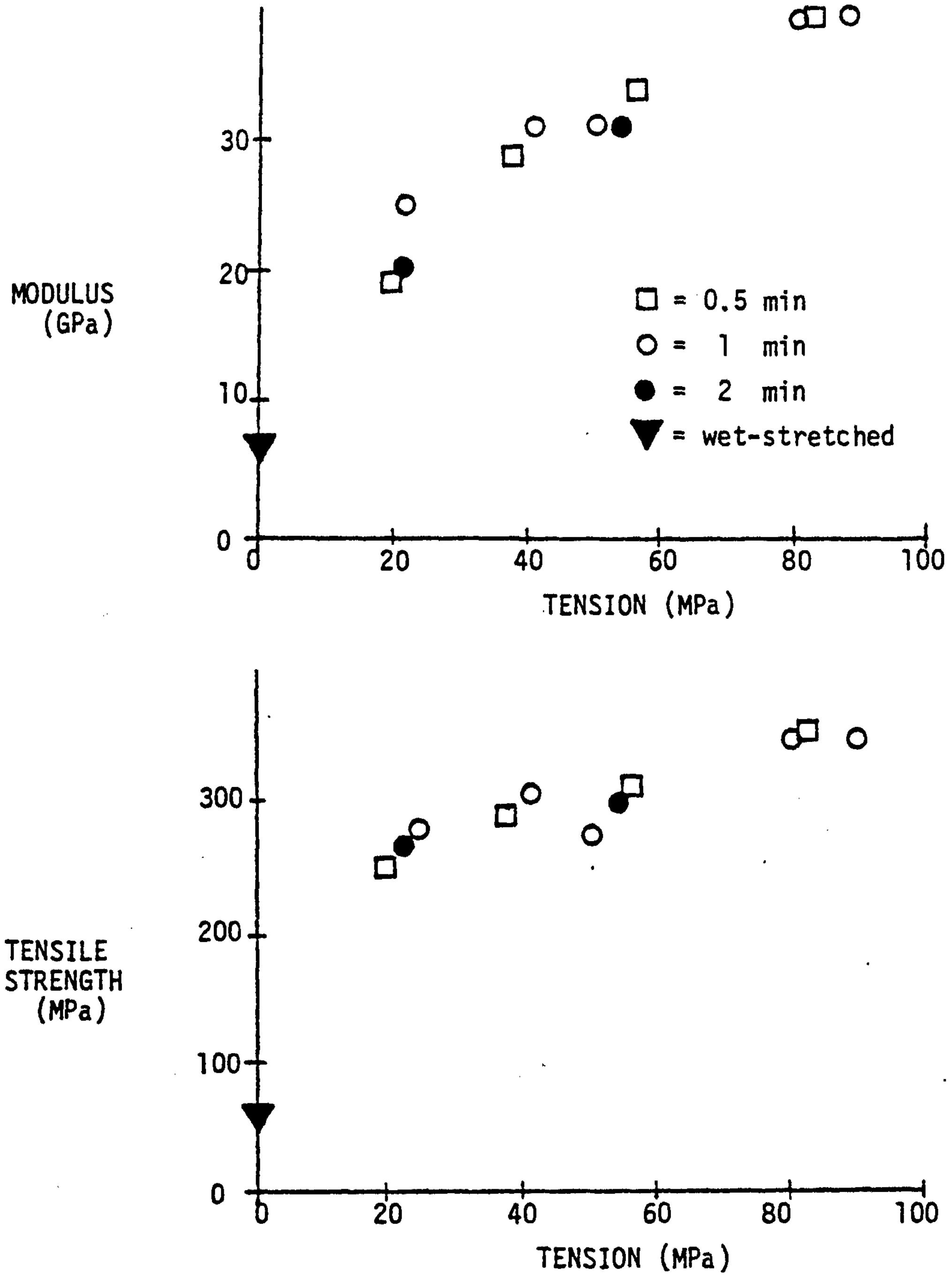


Figure 10 Mechanical properties as a function of heat-treatment time and tension for Nylon 6,6/PBT (13700) fibers heat-treated at 295°C.

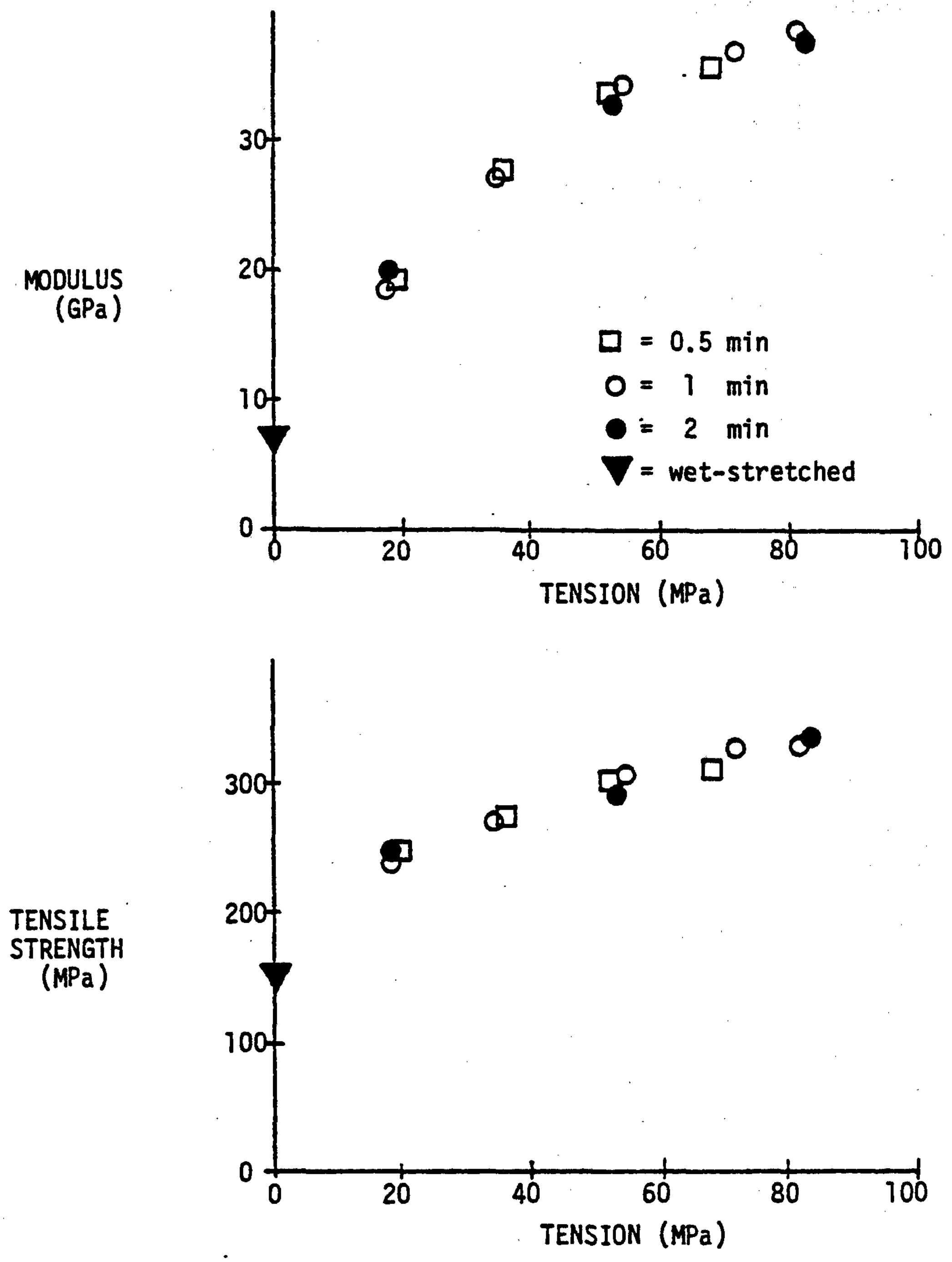


Figure 11 Mechanical properties as a function of heat-treatment time and tension for Nylon 6,6/PBT (17500) fibers heat-treated at 295°C.

tensile strengths at the 0.5 minute and 1-minute times. These times allow the fiber to be tensioned at a higher value (90 MPa), giving the highest properties.

The mechanical properties as a function of heat-treatment time and tension for the high (20000) and low (14500) molecular weight Nylon 6 composites heat-treated at 215°C are shown in Figures 12 and 13. Like the Nylon 6,6 composites, the higher molecular weight (20000) Nylon 6 composite properties are not a strong function of oven-residence time for the two times studied (Figure 13). The Nylon 6/PBT (14500) fibers, however, have a 5% to 10% better modulus at the 2-minute residence time and a 5% to 10% better tensile strength at the 1 minute time.

The mechanical properties for the Nylon 6/PBT fibers heat-treated at 255°C are shown in Figures 14 and 15. Both the high (20000) and low (14500) molecular weight composite fibers are sensitive to oven-residence time at this temperature. In both cases, the modulus is 5% to 15% higher at the 0.5 minute time. The tensile strengths, as with the Nylon 6,6 composites, are 5% to 15% higher at the 2- and 1-minute times than at the 0.5 time.

Tensioning during heat treatment most drastically improves the modulus and less dramatically the tensile strength compared to the wet stretched values. The modulus and tensile strength values level off with increasing heat-treatment tension, increasing at a decreasing rate. The tensile properties are not a strong function of oven residence time for the higher molecular weight nylons.

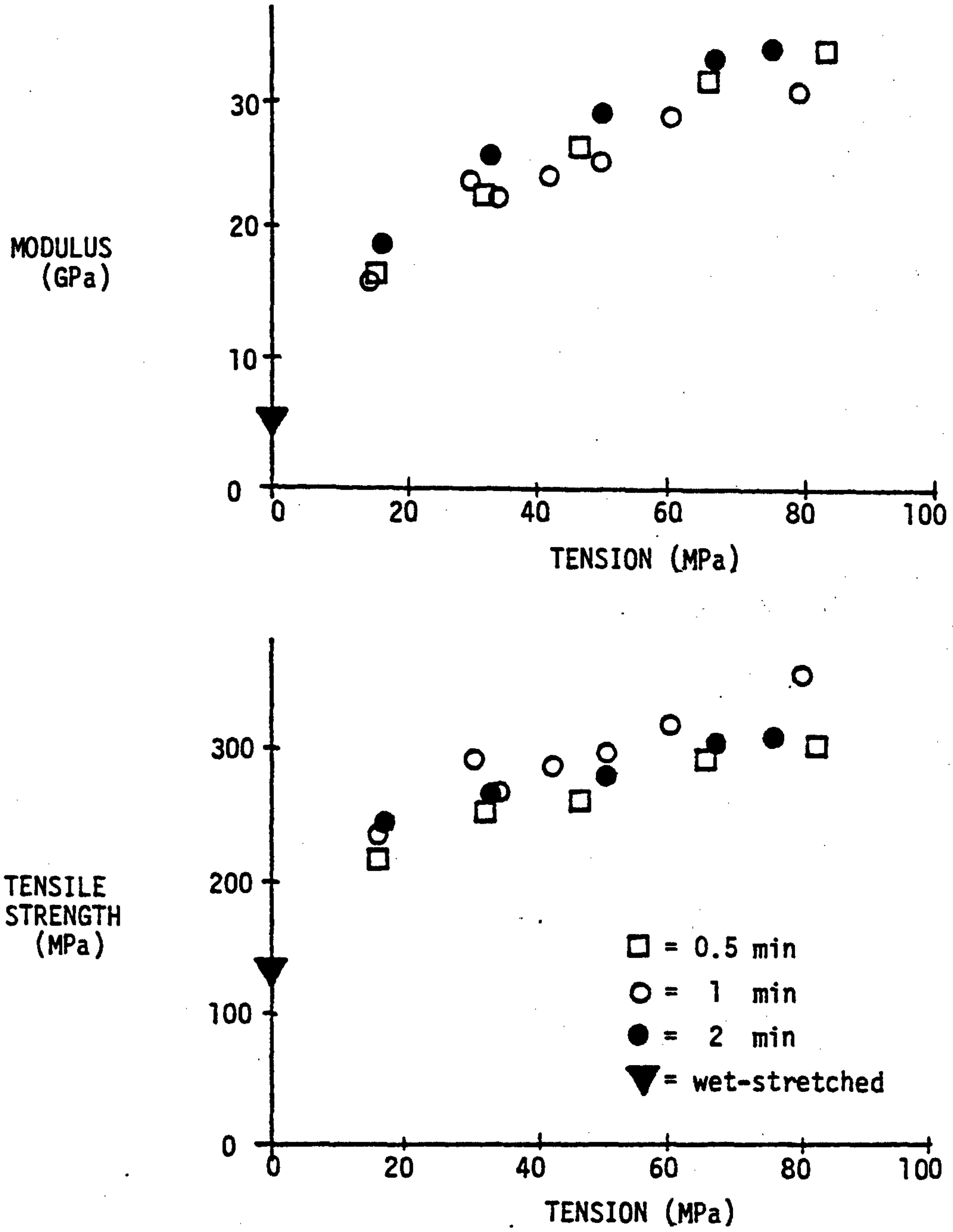


Figure 12 Mechanical properties as a function of heat-treatment time and tension for Nylon 6/PBT (14500) fibers heat-treated at 215°C.

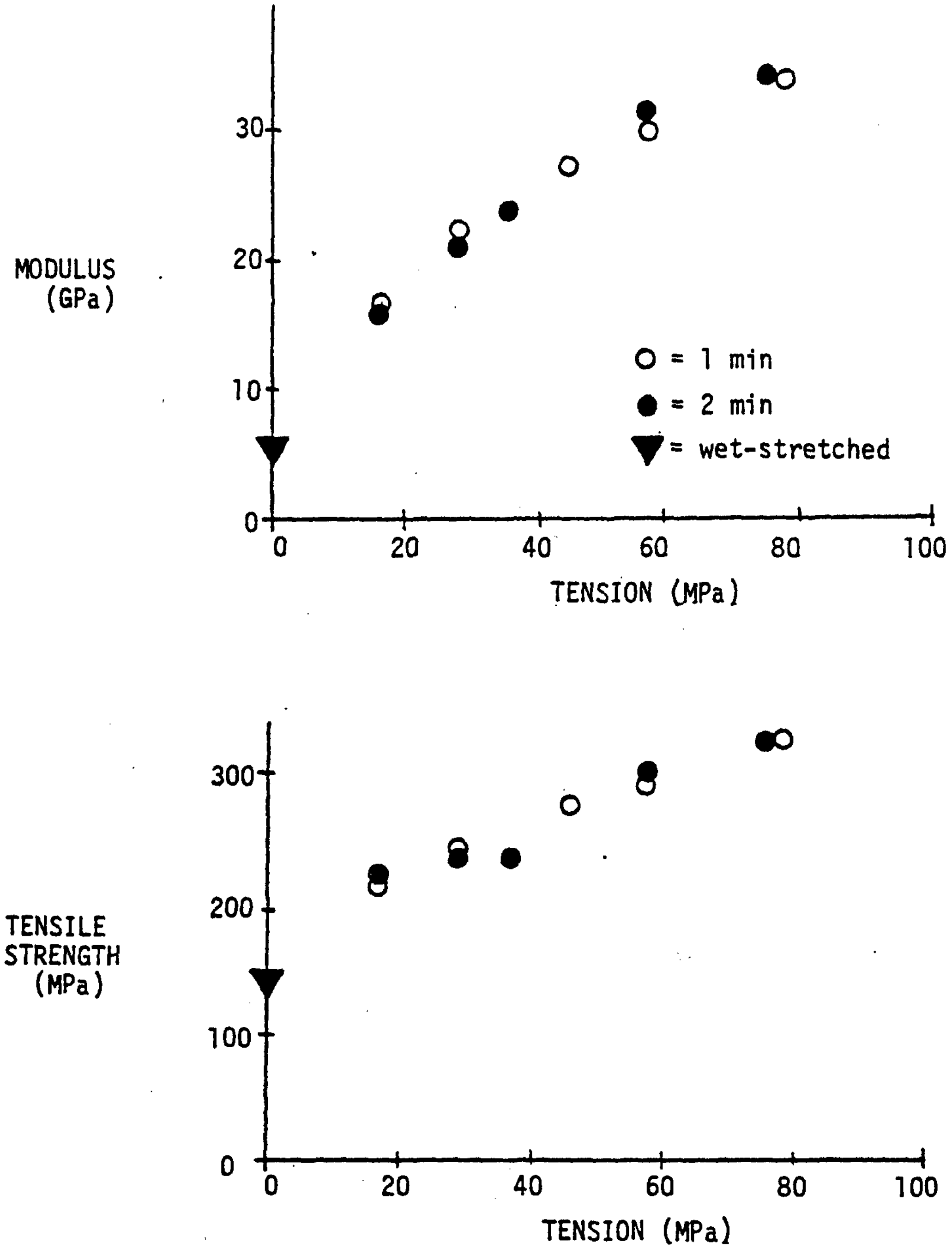


Figure 13 Mechanical properties as a function of heat-treatment time and tension for Nylon 6/PBT (20000) fibers heat-treated at 215°C.

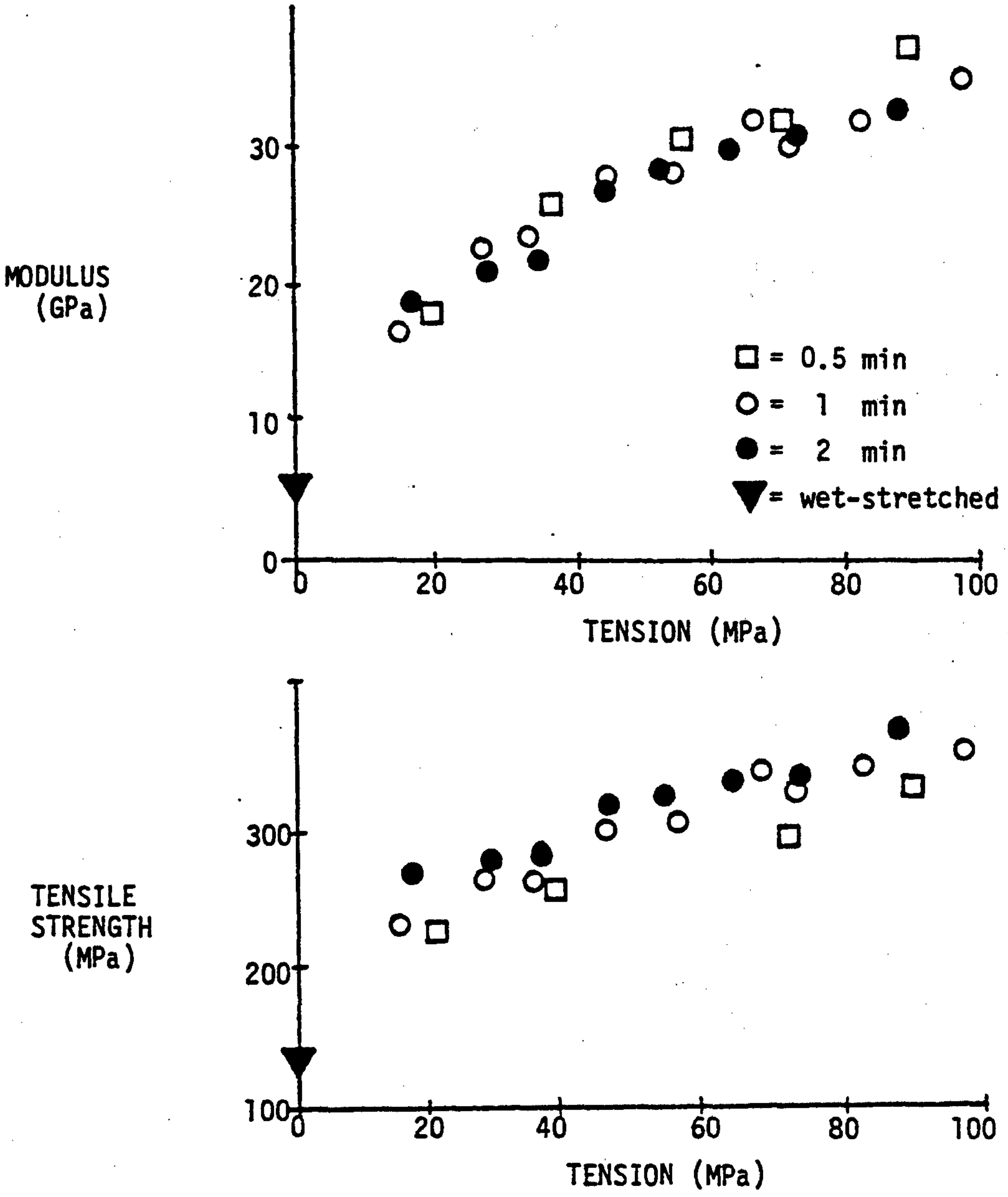


Figure 14 Mechanical properties as a function of heat-treatment time and tension for Nylon 6/PBT (14500) fibers heat-treated at 255°C.

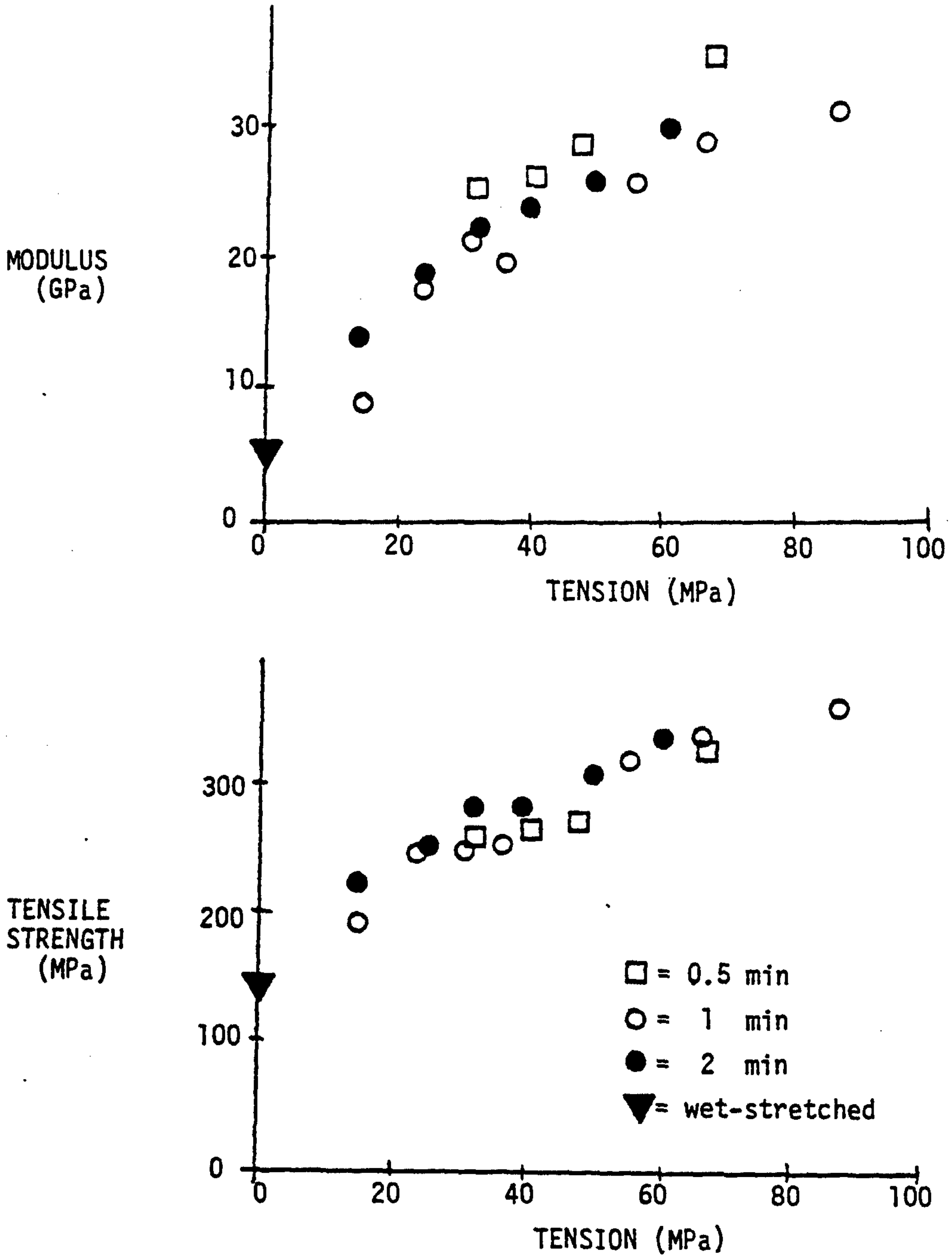


Figure 15 Mechanical properties as a function of heat-treatment time and tension for Nylon 6/PBT (20000) fibers heat-treated at 255°C.

However, the modulus tends to be higher at lower residence times, while the tensile strength tends to be better at higher residence times. The highest tensile strengths, though, are achieved by high tensioning during heat treatment which occurs at the lower residence times.

Little background information was available on heat-treatment temperature for nylon/PBT composites. PBT/ABPBI composites, which show no melting point, were heat-treated at temperatures slightly below the point of degradation. Commercial nylon fibers are heat-treated at temperatures of 50°C to 70°C lower than the melting point. An appropriate temperature for heat treatment, in keeping with PBT composite systems studied previously, is one slightly below the melting point of the matrix material. For Nylon 6,6, this temperature was 255°C and for Nylon 6, this temperature was 215°C. For comparison, the Nylon 6,6 composites were also heat treated at 295°C and the Nylon 6 composites at 255°C. Typical mechanical property data for Nylon 6/PBT (14500 and 20000) fibers heat-treated for one minute and Nylon 6,6/PBT (13700 and 17500) fibers heat-treated for one-half minute are plotted in Figures 16 through 19. Standard deviation of the data is 5% to 7%.

The composite mechanical properties are not a strong function of heat treatment temperature for the residence times and the oven temperatures studied. The properties are somewhat higher at the higher temperatures, that is 255°C for the Nylon 6 composites and 295°C for the Nylon 6,6 composites. This is perhaps unexpected because these

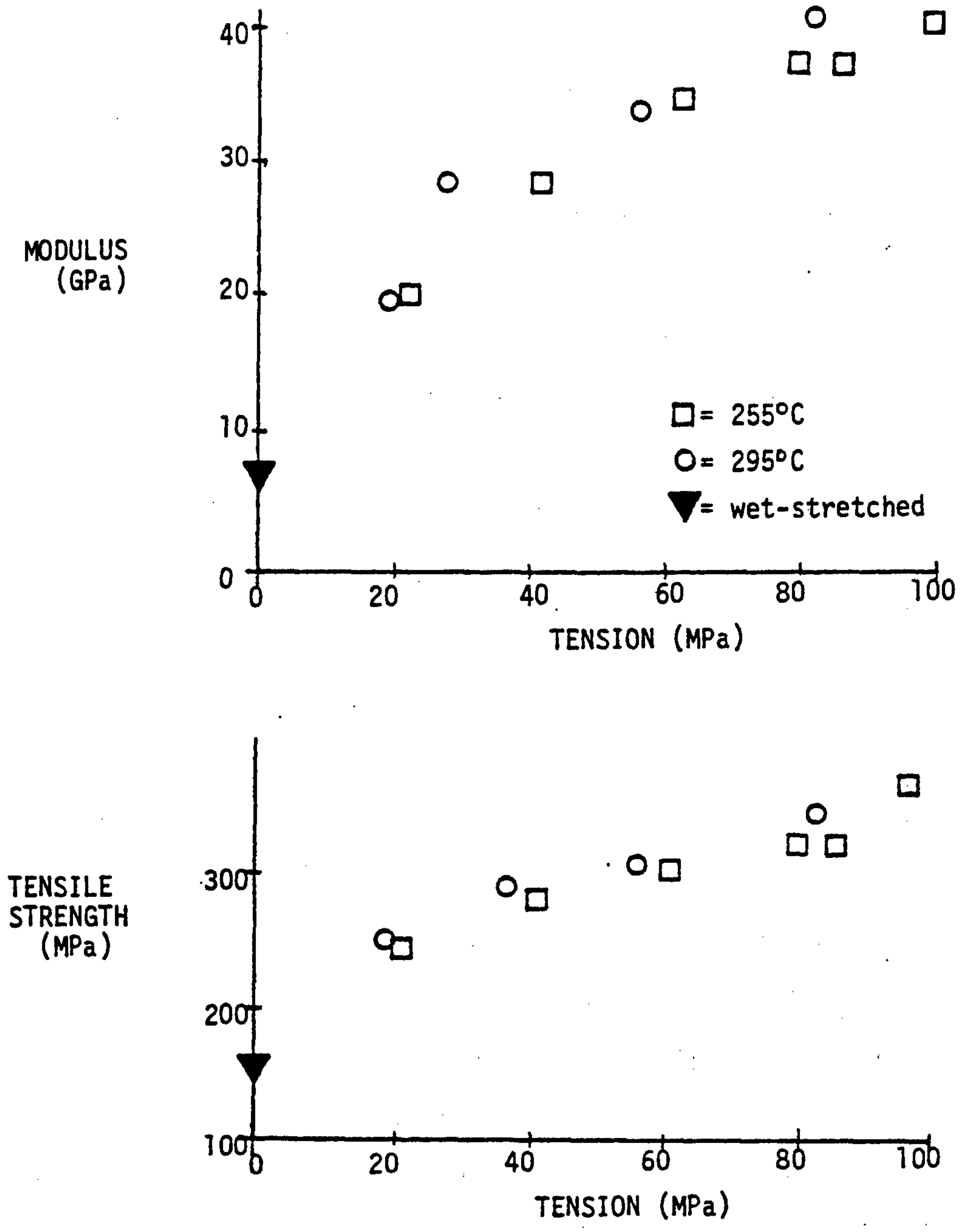


Figure 16 Mechanical properties as a function of heat-treatment temperature and tension for Nylon 6,6/PBT (13700) fibers heat-treated for 0.5 minutes.

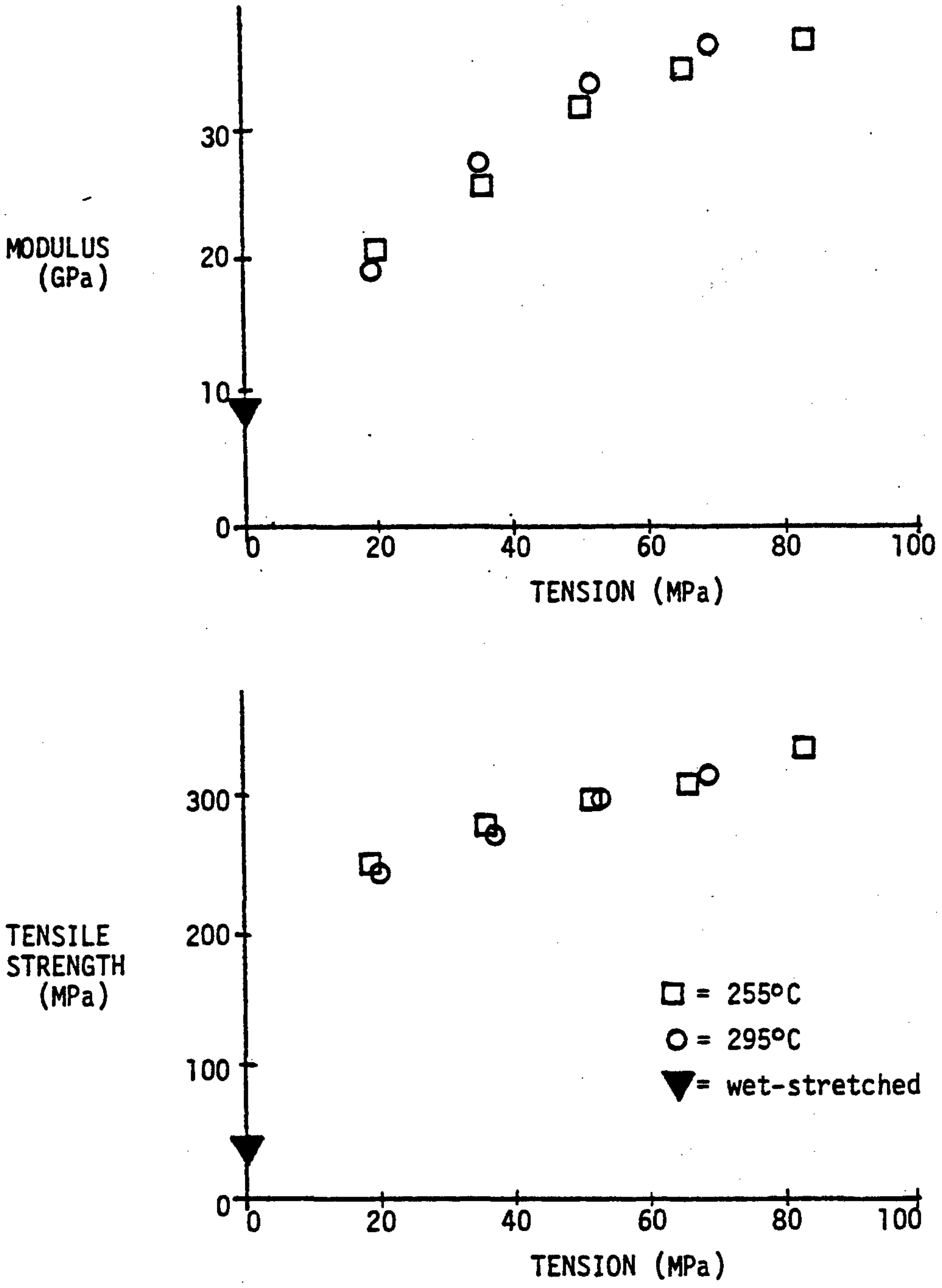


Figure 17 Mechanical properties as a function of heat-treatment temperature and tension for Nylon 6,6/PBT (17500) fibers heat-treated for 0.5 minutes.

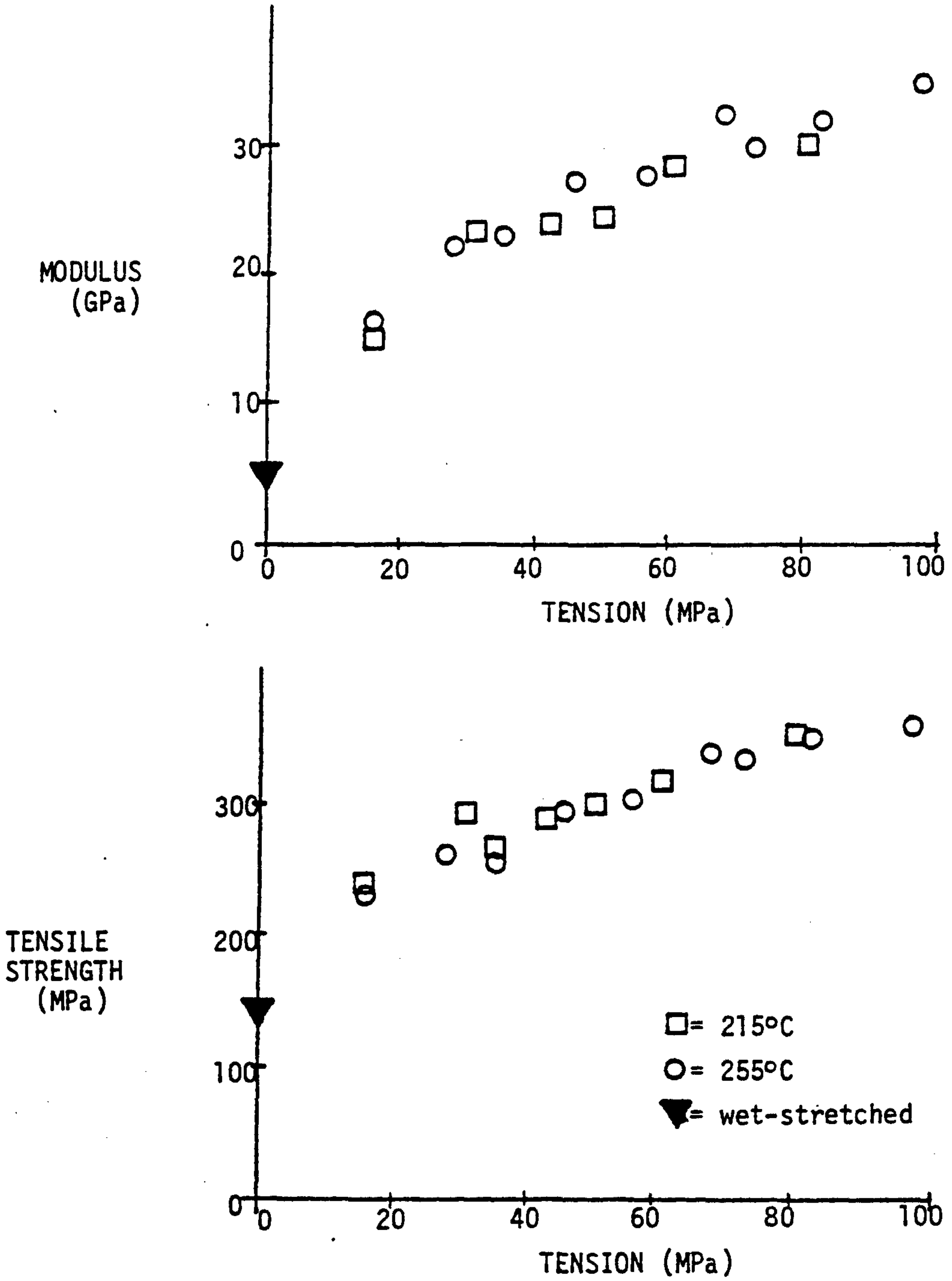


Figure 18 Mechanical properties as a function of heat-treatment temperature and tension for Nylon 6/PBT (14500) fibers heat-treated for 1 minute.

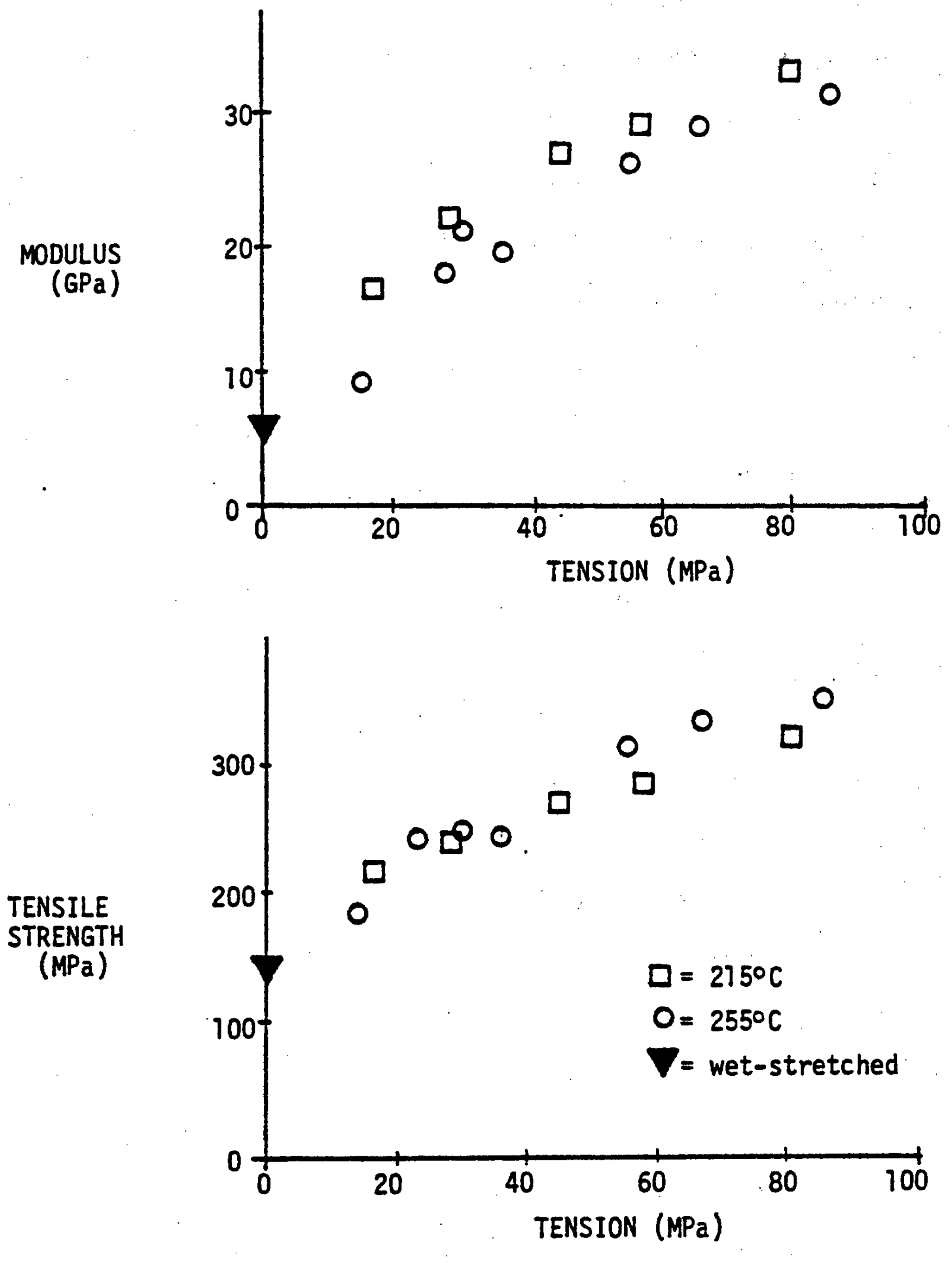


Figure 19 Mechanical properties as a function of heat-treatment temperature and tension for Nylon 6/PBT (20000) fibers heat-treated for 1 minute.

temperatures are approximately 40°C higher than the melting point of both Nylon 6 and Nylon 6,6.

Differential scanning calorimeter (DSC) thermograms (Figures 20 and 21) of the neat nylons and of the nylon/PBT composites were studied to determine the thermal transitions of the composites. The thermograms indicate composite melting points lower than the melting points of the neat matrix materials. The Nylon 6,6/PBT (13700) composites melt 32°C below the Nylon 6,6 (13700) polymer and the Nylon 6,6/PBT (17500) composites melt 16°C below the Nylon 6,6 (17500) polymer. Similarly, the Nylon 6/PBT (14500) composites melt 11°C below the Nylon 6 (14500) polymer and the Nylon 6/PBT (20000) composites melt 6°C below the Nylon 6 (20000) polymer. This melting temperature is not ascribed to the melting of the entire composite but rather to the melting of the nylon within the composite. This is an example of melting point depression that occurs in polymer-polymer mixtures in which one of the polymers is crystalline. The PBT is hindering the crystallinity of the Nylon 6 and Nylon 6,6, resulting in a lower melting temperature. In addition, the composites do not flow at the indicated melting temperature. The nylon can be seen to melt, yet the fiber remains mechanically intact.

d. Matrix molecular weight

Varying the material properties of the matrix polymer naturally affects the mechanical properties of the composite. The influence of matrix molecular weight on the composite properties was investigated for

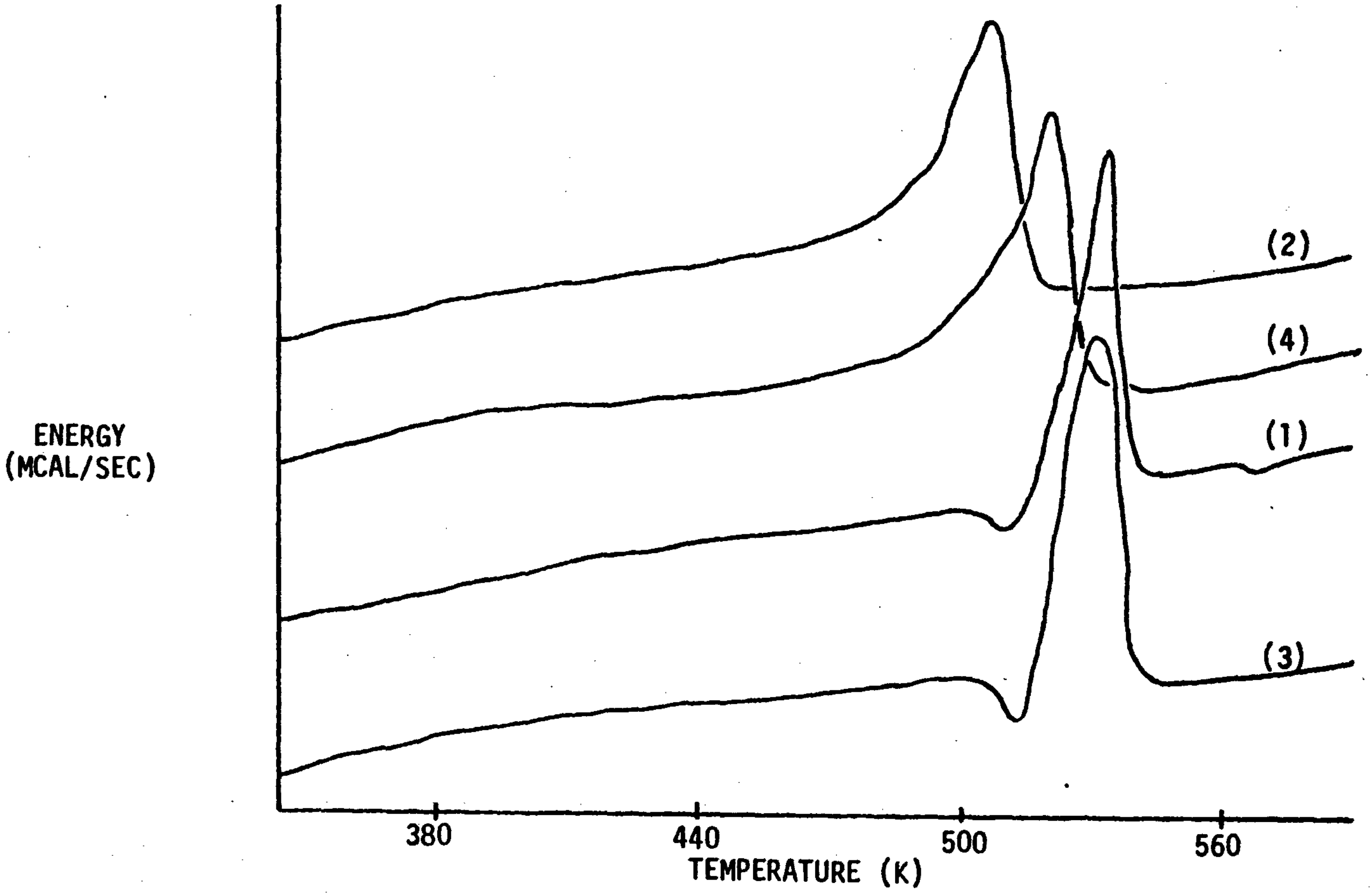


Figure 20 DSC thermograms for Nylon 6,6 (13700) (1), Nylon 6,6/PBT (13700) (2), Nylon 6,6 (17500) (3), Nylon 6,6/PBT (17500) (4).

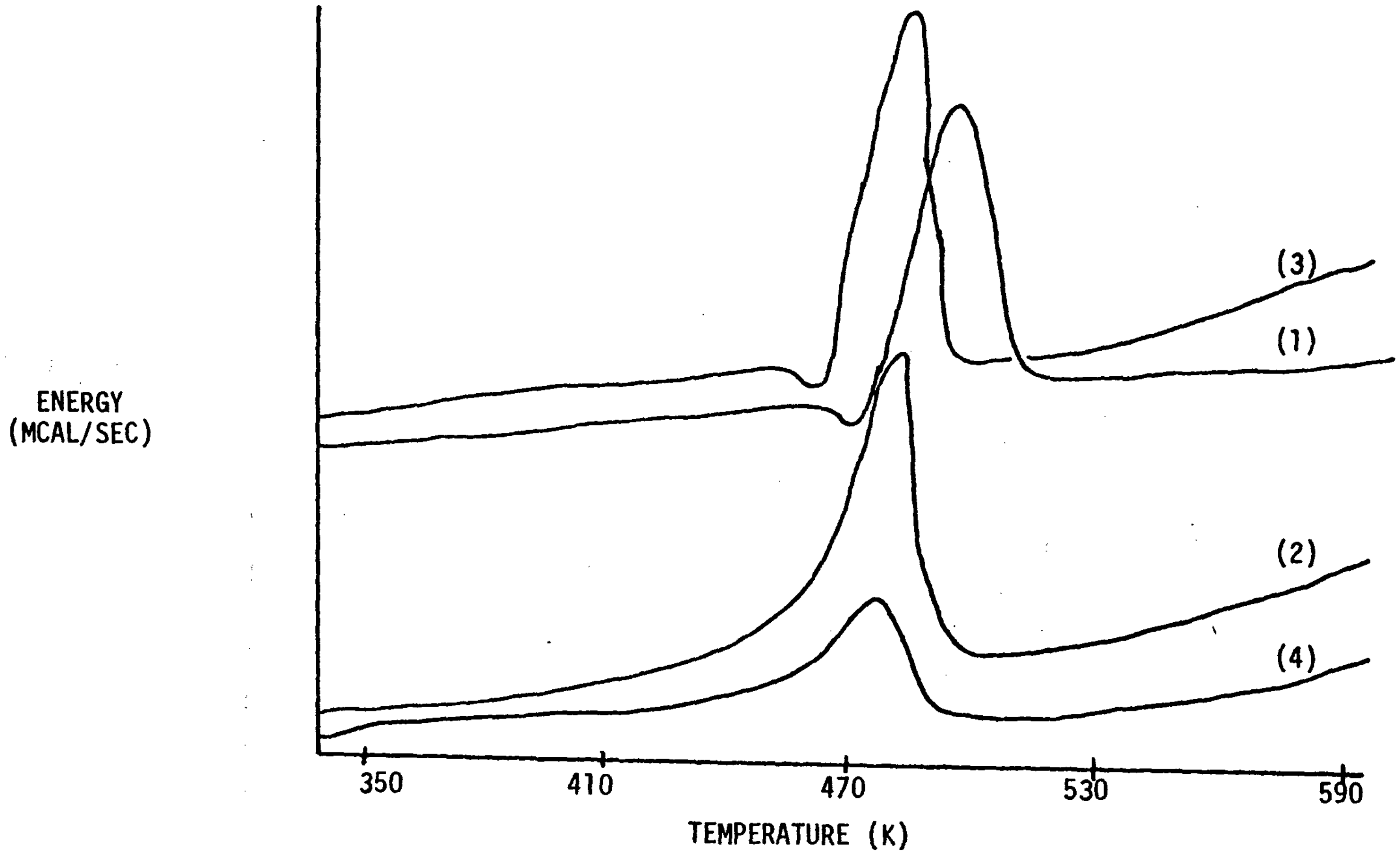


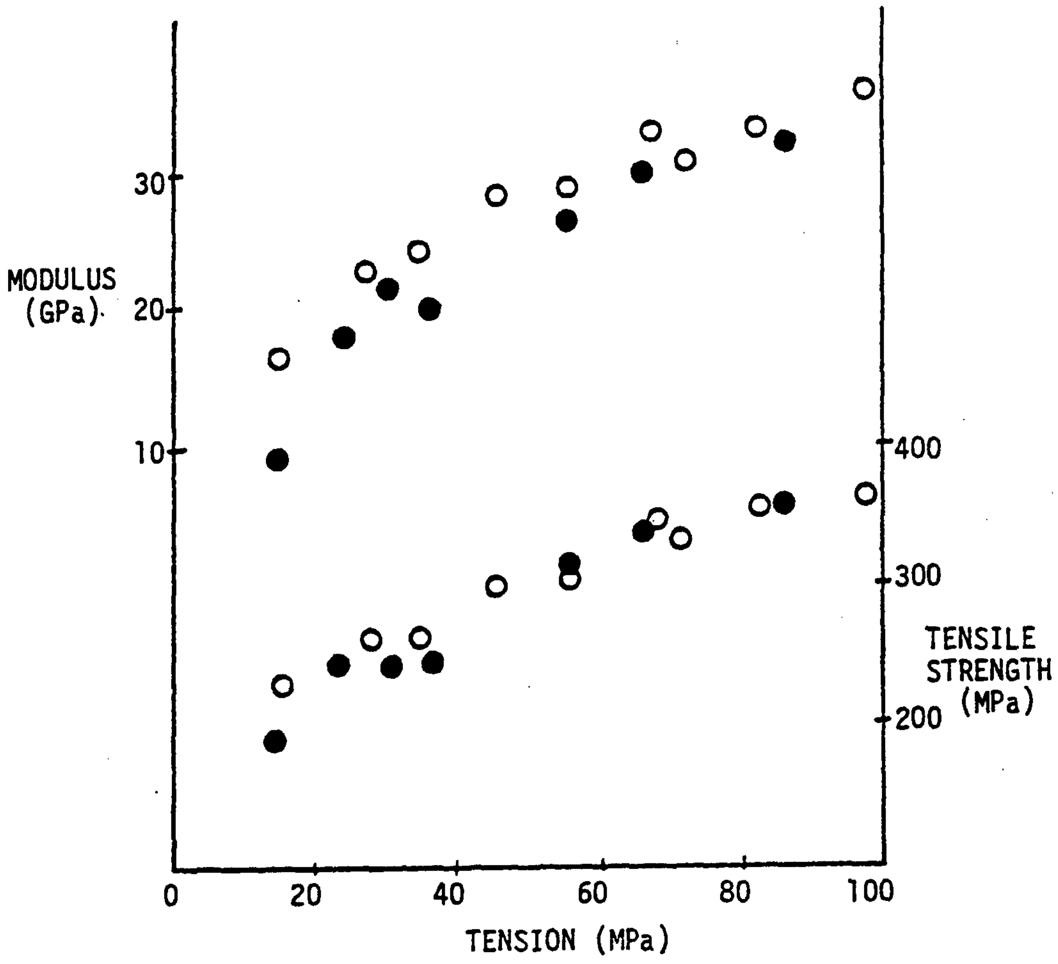
Figure 21 DSC thermograms for Nylon 6 (14500) (1), Nylon 6/PBT (14500) (2), Nylon 6 (20000) (3), Nylon 6/PBT (20000) (4).

the Nylon 6 and Nylon 6,6 systems. Recall that the Nylon 6 samples had number average molecular weights of 14,500 and 20,000 and the Nylon 6,6 samples had number average molecular weights of 13,700 and 17,500.

The tensile strength and modulus of Nylon 6/PBT and Nylon 6,6/PBT fibers are plotted as a function of matrix molecular weight and heat-treatment tension in Figures 22 and 23. The results are surprising. The properties of the lower molecular weight matrix polymer composite are equivalent or slightly higher than for the high molecular weight matrix polymer composite. The Nylon 6/PBT (14500) fibers show equivalent or better properties than the Nylon 6/PBT (20000) fibers at each heat treatment tension. The tensile properties of the low and high molecular weight Nylon 6,6/PBT composite fibers are equivalent. However, the lower molecular weight matrix composite fibers can be tensioned at a higher value and thereby achieve the highest properties. Notice again how the modulus and tensile strength level off with increasing applied tension.

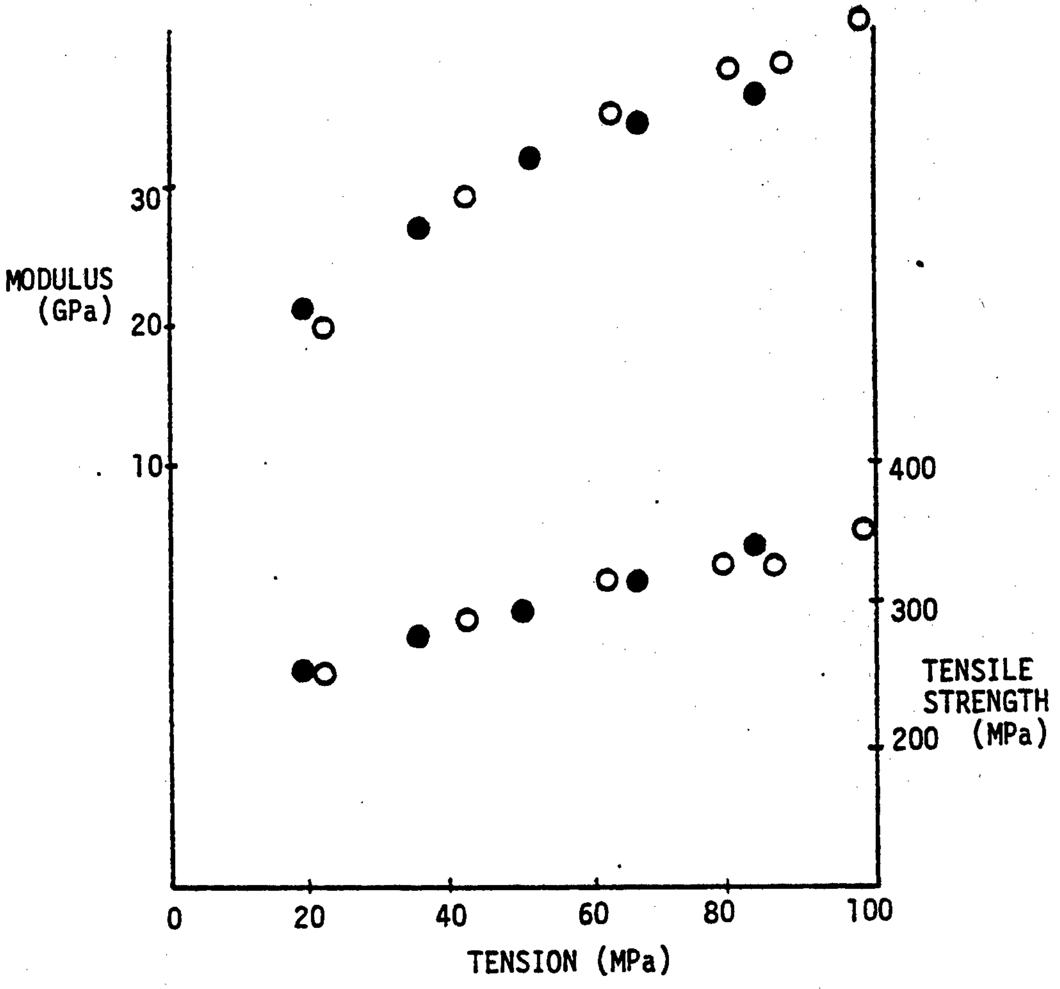
e. Molecular composites versus chopped fiber composites

This sectio[Bwould not be complete without a comparison of nylon/PBT compositeB with nylon/chopped fiber composites. Although cost data is not available, PBT represents a high performance material and as such is more costly than commercial fibers. Thus, a comparison based on costs would overwhelmingly favor the chopped fiber composites at this stage of development. It is on mechanical properties, however, that a comparison will be made.



○ = 14500 g/mole
● = 20000 g/mole

Figure 22 Mechanical properties as a function of matrix molecular weight and tension for Nylon 6/PBT fibers heat-treated at 255°C for 2 minutes.



○ = 13700 g/mole
● = 17500 g/mole

Figure 23 Mechanical properties as a function of matrix molecular weight and tension for Nylon 6,6/PBT fibers heat-treated at 255°C for 0.5 minutes.

Before one can judge the degree of reinforcement attained, it is necessary to know the properties of the pure matrix material. Nylons are not generally solution processed since melt processed fibers possess much better properties. Table 5 compares commercial melt spun Nylon 6 and Nylon 6,6 fibers to MSA solution spun fibers. The solution spun fibers were not wet stretched or heat-treated. However, with these additional processing steps it is doubtful whether properties equivalent to the melt spun fibers would be achieved. Melt spinning is the preferred method.

Table 1 showed the properties of a Nylon 6 and a Nylon 6,6 fiber with glass fiber reinforcement. The modulus and tensile strength increased significantly with 30% to 40% added glass fibers. Yet those values were substantially lower than values achieved for 30 weight percent PBT in Nylon 6 and in Nylon 6,6. The best properties for a 30 weight percent nylon/PBT fiber were approximately 40 GPa modulus and 375 MPa tensile strength as compared to a modulus of 6.6 GPa and tensile strength of 151.7 MPa for the 30 weight percent glass fiber/nylon fiber, and a modulus of 9.0 GPa and tensile strength of 185 MPa for the 33 weight percent glass fiber reinforced Nylon 6,6. It is evident that nylon/PBT composites show superior properties over chopped glass fiber composites.

TABLE 5

MECHANICAL PROPERTIES OF MELT SPUN NYLONS AND SOLUTION SPUN NYLONS

	E (GPa)	TS (MPa)	ε (%)
COMMERCIAL MELT SPUN (10)			
Nylon 6	2.4	81.4	50-200
Nylon 6,6	3.0	86.2	40-80
SOLUTION SPUN (H_2SO_4) (43)			
Nylon 6 (30 wt%)	--	10.5	--
Nylon 6,6 (25 wt%)	--	7.7	--
SOLUTION SPUN (MSA)			
Nylon 6 (14500, 13 wt%)	0.2	5.2	27.2
Nylon 6 (20000, 12.6 wt%)	0.2	5.1	59.0
Nylon 6,6 (13700, 15 wt%)	0.2	3.7	5.0
Nylon 6,6 (17500, 12.5 wt%)	0.2	4.3	10.9

4. CONCLUSIONS

We reached several conclusions regarding wet stretching, heat-treatment tension, heat-treatment temperature and time for the nylon/PBT composites. (1) Wet stretching, with high degrees of stretch, can double the modulus and tensile strength. (2) Tensioning during heat-treatment has the most significant influence on mechanical properties, increasing the wet-stretched modulus by a factor of 7 and the tensile strength by a factor of 3. (3) The modulus and tensile strength values level off with increasing tensioning, increasing at a decreasing rate. (4) The tensile properties are not a strong function of residence time or oven temperature for the times (0.5, 1, 2 minutes) and temperatures (215°C, 255°C, 295°C) studied. Higher temperatures, however, allow the fibers to be tensioned at a higher value which provides the best properties. (5) The mechanical properties are not a strong function of matrix molecular weight for the range studied, although the lower molecular weight matrix composite has the higher final values. (6) The composites exhibit a melting transition at a temperature below the melting point of the nylon matrix material. The melting points of Nylon 6,6 13700 and 17500 composites are depressed 32°C and 16°C, respectively, and the melting points of Nylon 6 14500 and 20000 composites are depressed 11 °C and 6°C, respectively. This is attributed to the hinderence of nylon crystallinity by the PBT. The composites do not flow when brought to the melting temperature.

These conclusions support the idea that, at this composition, a molecular composite of PBT in the nylons is not achieved, but that a network of PBT exists within the composite fibers. Thus, one would expect the mechanical properties to have a limiting value as imposed by the PBT network. Likewise, the lower molecular weight matrix may, by its reduced viscosity, allow the PBT network to perfect and thus give the better properties. Most importantly, a PBT network allows the fibers to be heat-treated above the melting temperature of the nylon matrix without fiber breakage. At these temperatures, the molten nylon may allow further perfection of the network, giving the better properties at higher heat-treatment temperatures. The fact that the composites exhibit a melting point but do not flow further supports the network idea.

III. EXTENDED HEAT TREATMENT

1. INTRODUCTION

Nylon 6,6 is formed by the condensation of adipic acid and hexamethylene diamine. The reaction is carried out by removing water to shift the equilibrium to favor high molecular weights. The last stage of the reaction is a melt polymerization.[45] The molecular weight of Nylon 6,6 can be further increased by a solid-state polymerization (61). Reaction times are on the order of 12 - 15 hours at temperatures below the nylon melting temperature and reduced pressures for water removal. Although we have no reports of Nylon 6 undergoing a solid-state polymerization, it would seem possible to drive the polymer to a higher molecular weight through a process similar to the Nylon 6,6 solid-state polymerization.

The idea of solid-state polymerization has been applied to the nylon/PBT composite fibers. Despite the results of Chapter II, the use of a higher molecular weight matrix polymer should result in a stronger composite fiber. One method of achieving this higher molecular weight matrix is by solid-state polymerization of the matrix within the composite fiber. Thus, composites comprised of relatively low molecular weight matrix materials and PBT can be improved by polymerizing the matrix after processing to a higher molecular weight.

2. EXPERIMENTAL

Composite fibers of Nylon 6/PBT (14500) and Nylon 6,6/PBT (13700) and solution spun fibers of Nylon 6 and Nylon 6,6 were used for extended heat treatment studies. The composite fibers were solution spun, wet-stretched and heat-treated under tension before being exposed to extended heat treatment. The MSA solution spun nylons were tested as-spun. Bulk Nylon 6 and Nylon 6,6 were heat-treated along with the fibers with inherent viscosity used as a measure of solid-state polymerization. Half of the nylon pellets were boiled in water for two hours and dried at 100°C before being solid-state polymerized, and the other half were used as-received. The water boiling was to simulate the removal of any residual monomer that would typically be removed in the acid spinning process.

Two reaction conditions were studied. Oven temperatures of 170°C and 220°C were used for the Nylon 6,6 samples and oven temperatures of 160°C and 225°C were used for the Nylon 6 samples. The Nylon 6,6 and composite fibers were placed in the vacuum oven under high vacuum for 12 hours while the Nylon 6 and composite fibers were placed in the oven for 17 - 19 hours. We attempted to keep the fibers under tension during extended heat treatment, but were not successful. The oven was flushed with dry nitrogen before evacuation, and dry nitrogen was used to fill the oven when the vacuum was removed. The fibers were tensile-tested as described earlier.

3. RESULTS AND DISCUSSION

Stress-strain curves for Nylon 6,6/PBT and Nylon 6/PBT fibers before and after extended heat treatment are shown in Figures 24 and 25. In both cases, the extended heat treatment results in a higher modulus and a greater tensile strength without significant changes in the elongation at break. For the Nylon 6,6/PBT fibers (Figure 25), the lower temperature of 170°C results in higher tensile properties as compared to the fibers treated at 220°C and those not extended heat-treated.

The corresponding mechanical property data for Nylon 6 and Nylon 6,6 fibers and the composite fibers are shown in Tables 6 and 7. The standard deviation of the data is 5% to 7%. The moduli and tensile strengths increased as a result of the extended heat-treatment process. The moduli are most significantly affected, increasing from 20 % to 50% for the composites and 47% to 63% for the neat nylon fibers. The tensile strength shows little change (1-3% for the Nylon 6,6 composites and 5-14% for the Nylon 6 composites) as a result of extended heat treatment. The neat nylon fibers reflected the greatest changes in the moduli and tensile strengths.

A question naturally arises as to what physical changes may occur during this extended heat treatment. Is a solid-state polymerization occurring, or is the heat treatment causing an increase in crystallinity which in turn improves the properties? A sample of nylon pellets was heat-treated with the fibers in order to test these ideas. The inherent viscosity of the nylon pellets (88% formic acid, Fisher Chemical Co.)

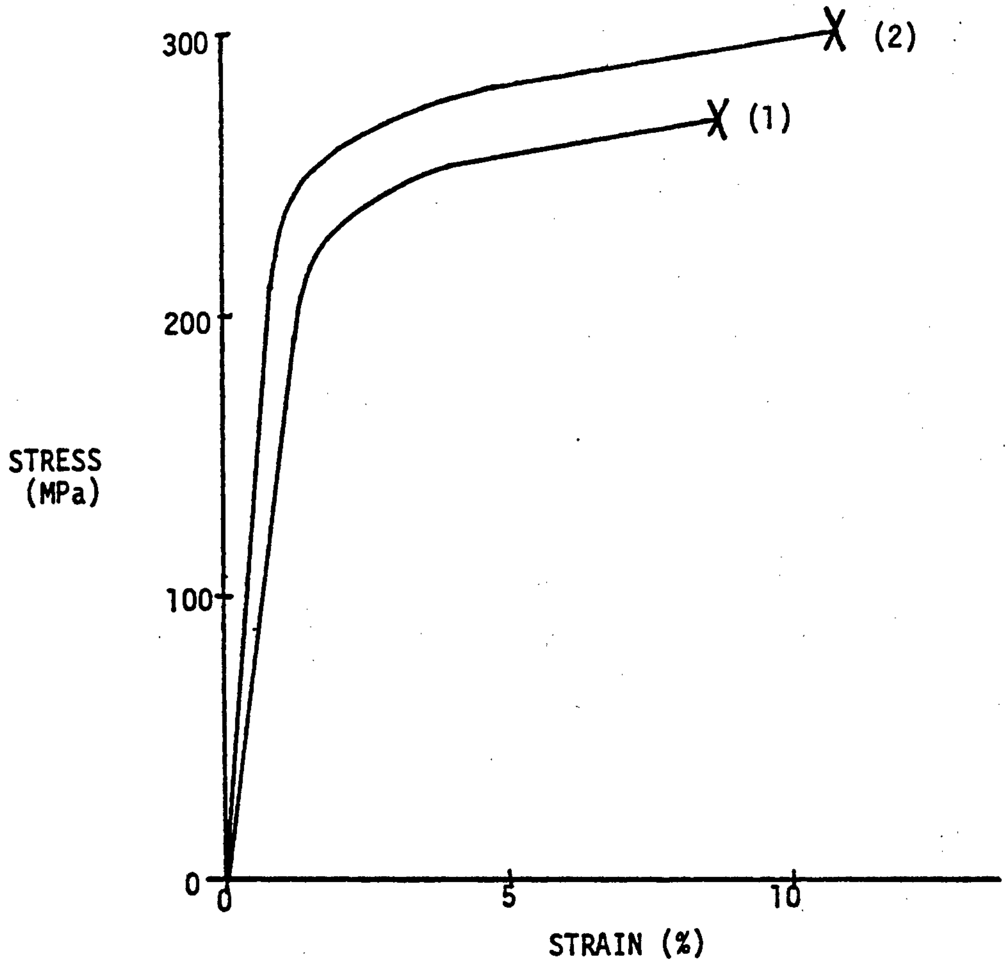


Figure 24 Stress-strain curves for extended heat treatment of Nylon 6/PBT (14500) fibers at 220°C for 17 hours; (1) heat-treated at 255°C for 2 minutes and 16.7 MPa tension; (2) extended heat-treatment fibers.

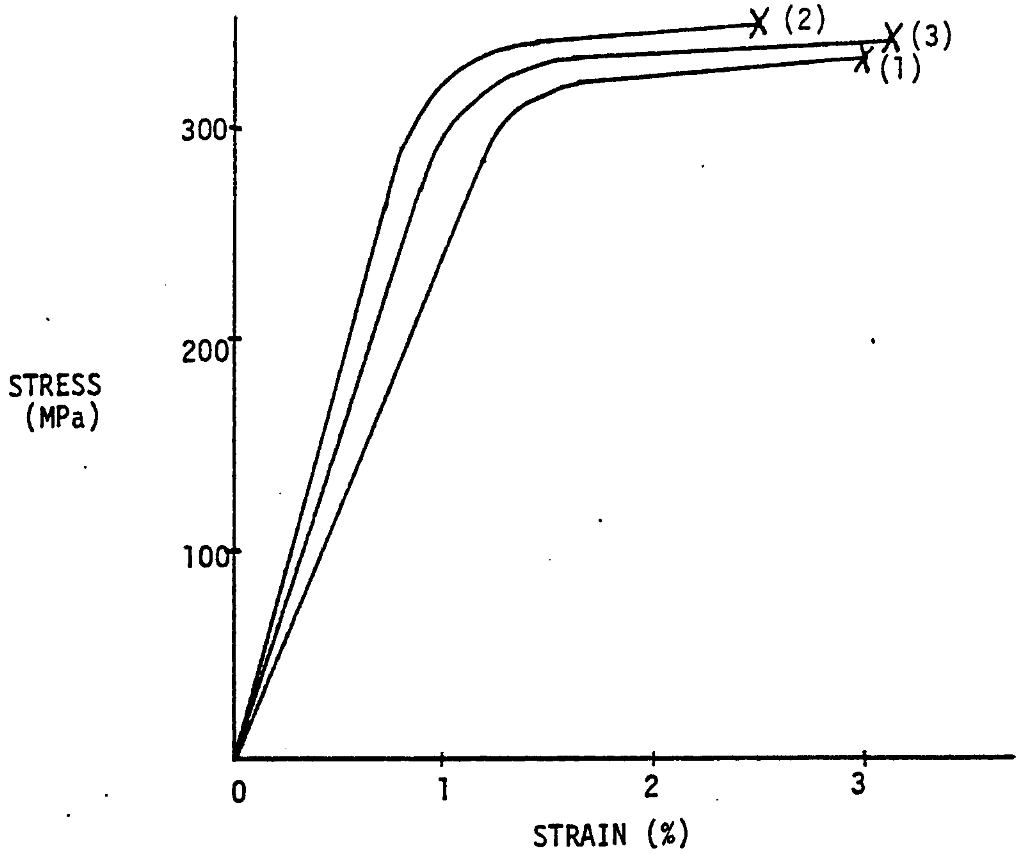


Figure 25 Stress-strain curves for extended heat treatment of Nylon 6,6/PBT (13700) fibers at 220°C for 12 hours and 170°C for 12 hours; (1) heat-treated at 255°C for 1 minute at 70.9 MPa tension; (2) extended heat-treated at 170°C; (3) extended-heat treated at 220°C.

TABLE 6

SOLID-STATE POLYMERIZATION OF NYLON 6,6 COMPOSITE FIBERS

		E (GPa)	TS (MPa)	ε (%)
Nylon 6,6	Before	0.2	3.7	5.0
	After (170°C,12 hrs)	0.3	4.8	4.9
% Increase		47	29	- -
Nylon 6,6/PBT	Before	24.0	338.3	3.0
	After (170°C,12 hrs)	35.7	349.2	2.5
% Increase		49	3	- -
Nylon 6,6/PBT	Before	24.0	338.3	3.0
	After (220°C,12 hrs)	30.4	341.9	3.1
% Increase		23	1	- -

TABLE 7

SOLID-STATE POLYMERIZATION OF NYLON 6 COMPOSITE FIBERS

		E (GPa)	TS (MPa)	ε (%)
Nylon 6	Before	0.2	5.2	27.2
	After (160°C,19 hrs)	0.3	7.0	24.5
% Increase		63	34	- -
Nylon 6/PBT	Before	18.7	269.0	8.7
	After (220°C,17 hrs)	21.9	298.3	10.7
% Increase		17	11	- -
Nylon 6/PBT	Before	31.9	352.3	1.2
	After (160°C,19 hrs)	39.0	366.0	1.2
% Increase		22	14	- -
Nylon 6/PBT	Before	29.7	334.6	1.3
	After (160°C,19 hrs)	35.7	350.6	1.4
% Increase		20	5	- -

was measured and compared to the inherent viscosity of the pellets which had undergone extended heat treatment. If the molecular weight of the nylon was increasing as a result of the extended heat treatment, the inherent viscosity would increase. Increased crystallinity would not be reflected in inherent viscosity data. The viscosity results are shown in Table 8.

The nylon pellets treated at 220°C show an inherent viscosity that is nearly double that of the untreated pellets, while the pellets treated at 160°C and 170°C show a lower increase in inherent viscosity. Two points are noted. First, we interpret this increase in inherent viscosity as evidence for the occurrence of solid state polymerization. Secondly, the results for Nylon 6,6 are consistent with what has been shown earlier, namely that the lower molecular weight matrix polymer has the better tensile properties. Apparently, the higher temperature results in a higher matrix molecular weight (greater increase in inherent viscosity) yet these fibers exhibit lower modulus and tensile strengths when compared to those treated at 170°C.

DSC measurements were made on the nylon pellets and the composite fibers exposed to extended heat treatment, with the results shown in Figures 26 and 27. The melting points of the pellets increase, by 1°C for Nylon 6,6 and by 22°C for Nylon 6, while the composite melting points increase by 10°C for the Nylon 6 composite and 4°C for the Nylon 6,6 composite. This increase in melting point indicates that a change occurs in the nylons during extended heat treatment, although this change may not be entirely due to an increase in molecular weight.

TABLE 8

SOLID-STATE POLYMERIZATION OF NYLON 6 AND NYLON 6,6

	INHERENT VISCOSITY (25°C) (Formic Acid, dL/g)	
	BEFORE	AFTER
220°C, 16 hrs		
Nylon 6, as received	1.14	2.07
Nylon 6, boiled	1.10	2.29
220°C, 12 hrs		
Nylon 6,6, as received	0.95	1.96
Nylon 6,6, boiled	0.93	2.04
160°C, 16 hrs		
Nylon 6, as received	1.10	1.32
170°C, 12 hrs		
Nylon 6,6, as received	0.99	1.11

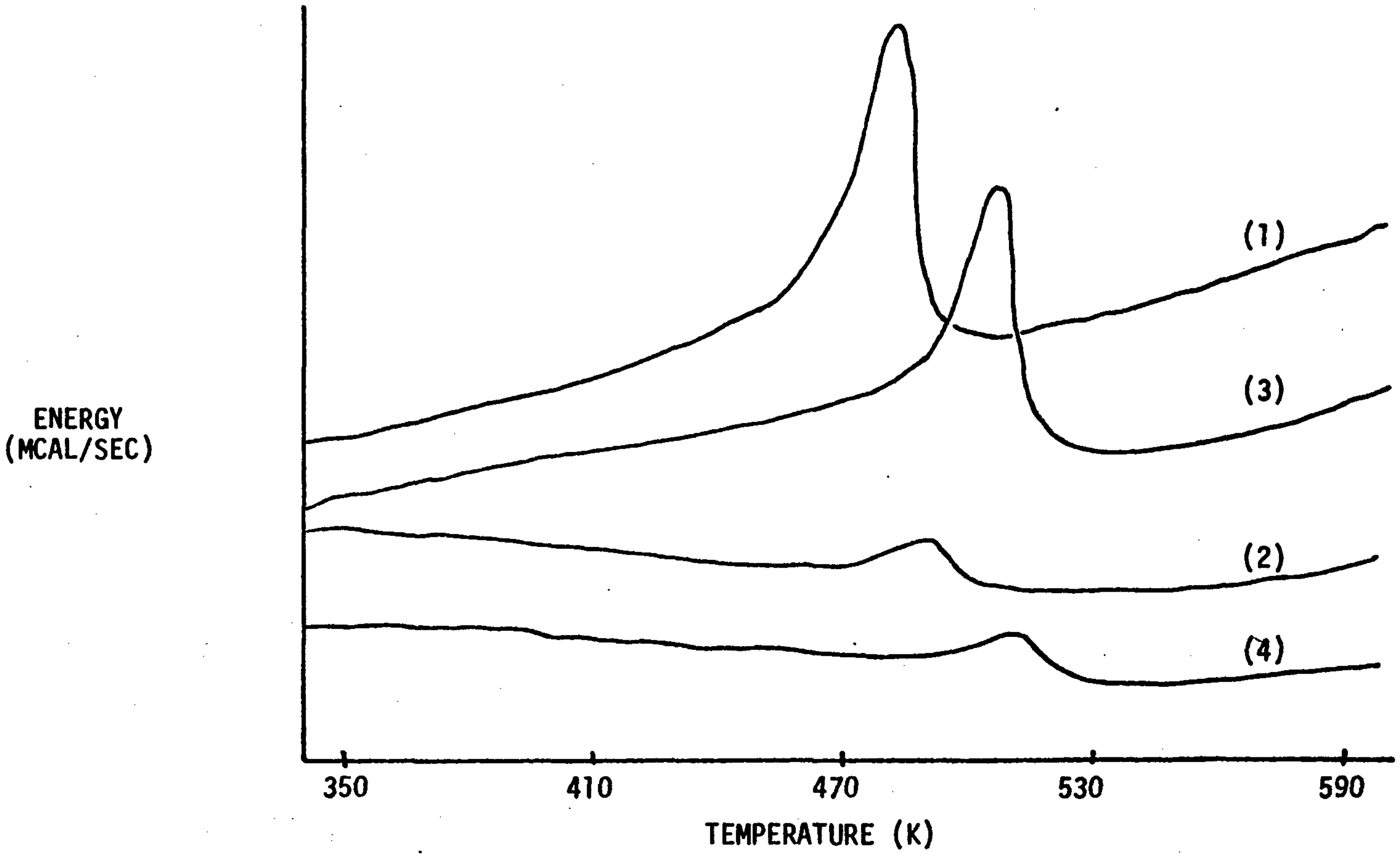


Figure 26 DSC thermograms for extended heat treatment of Nylon 6/PBT (14500) fibers and Nylon 6,6/PBT (13700) fibers; (1) Nylon 6/PBT (14500), before; (2) Nylon 6/PBT (14500), after; (3) Nylon 6,6/PBT (13700), before; (4) Nylon 6,6/PBT (13700), after.

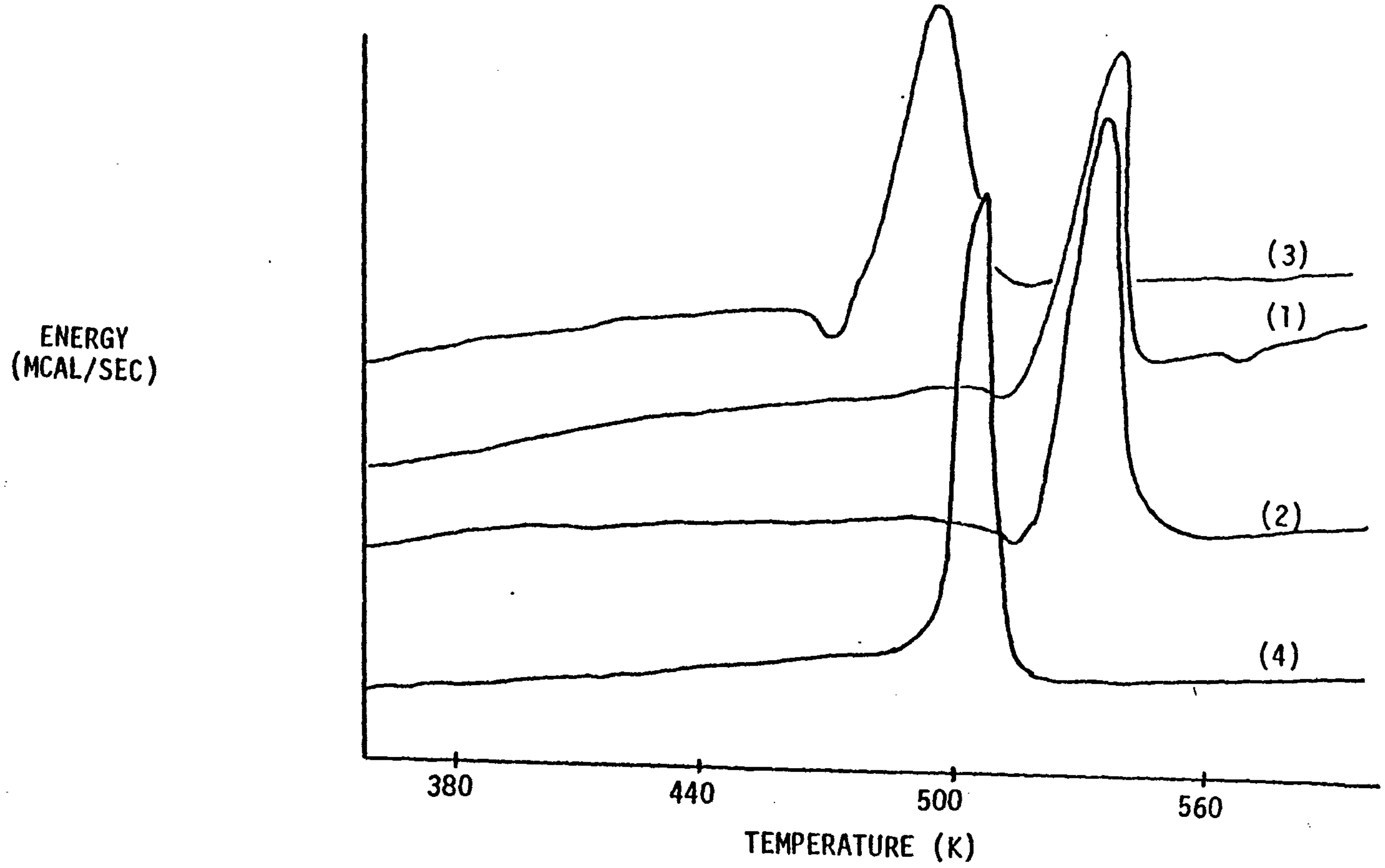


Figure 27 DSC thermograms for extended heat treatment of Nylon 6,6 pellets and Nylon 6 pellets; (1) Nylon 6,6; (2) Nylon 6,6 extended heat treated; (3) Nylon 6; (4) Nylon 6 extended heat-treated.

Increased crystallization may also occur as a result of extended heat treatment.

4. CONCLUSIONS

Several conclusions can be drawn from the extended heat-treatment data. (1) Composite fibers subjected to extended heat treatment show improved mechanical properties, most notable in the modulus (20 % - 50 % improvement) and less so in the tensile strength (3% -15 % improvement). (2) The nylon fibers show greater improvement in mechanical properties as a result of extended heat treatment, with a 50 % - 60% increase in the modulus and a 30 % - 35 % increase in the tensile strength. (3) In addition to a change in the mechanical properties, the melting temperature of the matrix increases with extended heat treatment by 4 to 10°C. (4) There is evidence that the extended heat treatment is actually solid-state polymerization (inherent viscosity data for the bulk polymers before and after extended heat treatment). (5) The mechanical property data combined with inherent viscosity data is consistent with the results of Chapter II; namely that the lower molecular weight matrix composite has the higher mechanical properties.

IV. PBT COMPOSITE STRUCTURE

1. INTRODUCTION

A molecular level composite of PBT within a nylon matrix would be expected to have tensile properties which follow the linear "rule of mixture." For the Nylon 6 and Nylon 6,6 composites considered in this study and also for the amorphous nylon composites of Hwang et al.,[14] this level of reinforcement was not attained. The composites in this study were 30 weight percent PBT, which corresponds to a volume percent of approximately 24 (PBT density of 1.5; nylon density of 1.1). Using a PBT modulus of 300 GPa and tensile strength of 3 GPa[37] and a nylon modulus of 2 GPa and tensile strength of 80 MPa,[9,10] the "rule of mixture" predicts a composite modulus of 74 GPa and a tensile strength of 780 MPa. These calculated values are significantly higher than the best values attained in this study, which were approximately 40 GPa modulus and 375 MPa tensile strength for the heat treated composites. Hwang et al.[14] attained comparable tensile properties for the amorphous nylon/PBT composites of 36 GPa and 345 MPa tensile strength.

A thermoplastic molecular composite must also melt and flow when brought to the melting temperature of the matrix. Differential scanning calorimeter thermograms indicate a melting point for the PBT composites that is close to the melting point of the nylons. However, the composites do not flow when raised above this temperature.

The question thus arises as to whether a molecular composite of PBT in nylon is formed at the composition studied. Various theories predict the onset of a network of the rodlike molecule as the filler concentration reaches a critical level.[12,46-48] Chain forming theory correlates the formation of a continous network of the reinforcing fiber with the length-to-diameter (L/D) ratio and volume fraction of the reinforcing fiber.[46] The higher the L/D value, the smaller the volume fraction necessary to obtain a continuous network. For cylindrical reinforcing fibers with an L/D ratio of 100, a volume fraction of approximately 1% should yield a network formation.[46] Although PBT rods have been found to be lath- or ribbon- shaped rather than cylindrical,[37] a network should be formed at some concentration less than the 30 weight percent used in this study.

A rather simple experiment, that of placing the composite fiber in a solvent for the matrix, may indicate whether a molecular composite exists or whether a network is formed. If the fiber were a composite on the molecular level, placing it in a solvent for the matrix should result in the destruction of the fiber. The matrix would dissolve, leaving molecules of PBT isolated within the solvent. On the other hand, if a network of PBT exists, placing the fiber in a solvent for the matrix would result in the extraction of the matrix while the fiber remained intact. The remaining fiber would be essentially pure PBT.

The extraction process has been found by other authors to be successful for isolating the fiber phase from blends.[59,60] However, it is important to mention an opposing argument for the extraction process. If the solvent for the nylon is a non-solvent for the PBT, perhaps the dissolution process is actually a coagulation process for the PBT molecules. The molecularly dispersed PBT molecules may coalesce when placed in the solvent and form a network during the extraction process. We believe this is not what is occurring, and that a network exists a priori.

2. EXPERIMENTAL

The extraction process was performed on Nylon 6/PBT (20000) fibers which were previously tension heat-treated for one minute at 255 C. Two samples were tested, a fiber heat-treated under tension at 86 MPa and a fiber heat-treated under tension at 55 MPa. The solvent was 95-98% sulfuric acid (Fisher Chemical Co.), a solvent for nylon but not for PBT.[49] The composite fiber heat treated at 86 MPa was placed in a beaker of sulfuric acid, allowed to remain for 12 days, and then washed in water for 2 days. It was held under tension while air-dried. The composite fiber which had been heat-treated at 55 MPa was held under tension during extraction for 7 days. The fiber broke when placed in a water wash but was held under tension while air-dried.

Fiber diameters were measured with an optical microscope at 200X magnification. Tensile tests were performed on 30-mm fiber segments as described previously. DSC measurements were performed over a temperature range of 300 - 600 K with a heating rate of 40 K/min. Scanning electron microscope pictures were taken using an ETEC Autoscan operated at 20 kV. Samples were first sputter coated with a 350 A layer of gold in a Polaron E5100 SEM coating apparatus.

3. RESULTS AND DISCUSSION

The Nylon 6/PBT fibers, when placed in the sulfuric acid bath did not break up as expected for a molecular composite of PBT in nylon. The fibers remained intact, presenting evidence for the existence of a network of PBT within the nylon matrix. A color change was noted in the sulfuric acid bath which can be attributed to the dissolution of nylon, and a reduction of 30% to 40 % in fiber diameter occurred as a result of extraction. The extracted fibers were tensile-tested and observed under the scanning electron microscope.

The stress-strain curves for the Nylon 6/PBT (20000) fibers heat-treated under 86 MPa tension, before and after extraction are plotted in Figure 28 and the corresponding numerical results are given in Table 9. The modulus after extraction is lower than the modulus before extraction, while the tensile strength after extraction is increased. The lower modulus may be explained by the fact that the fiber was not held in tension during the extraction and washing process, allowing the PBT to become less oriented as the nylon was removed. This is further supported by a much larger elongation at break after extraction, indicating a less oriented fiber.

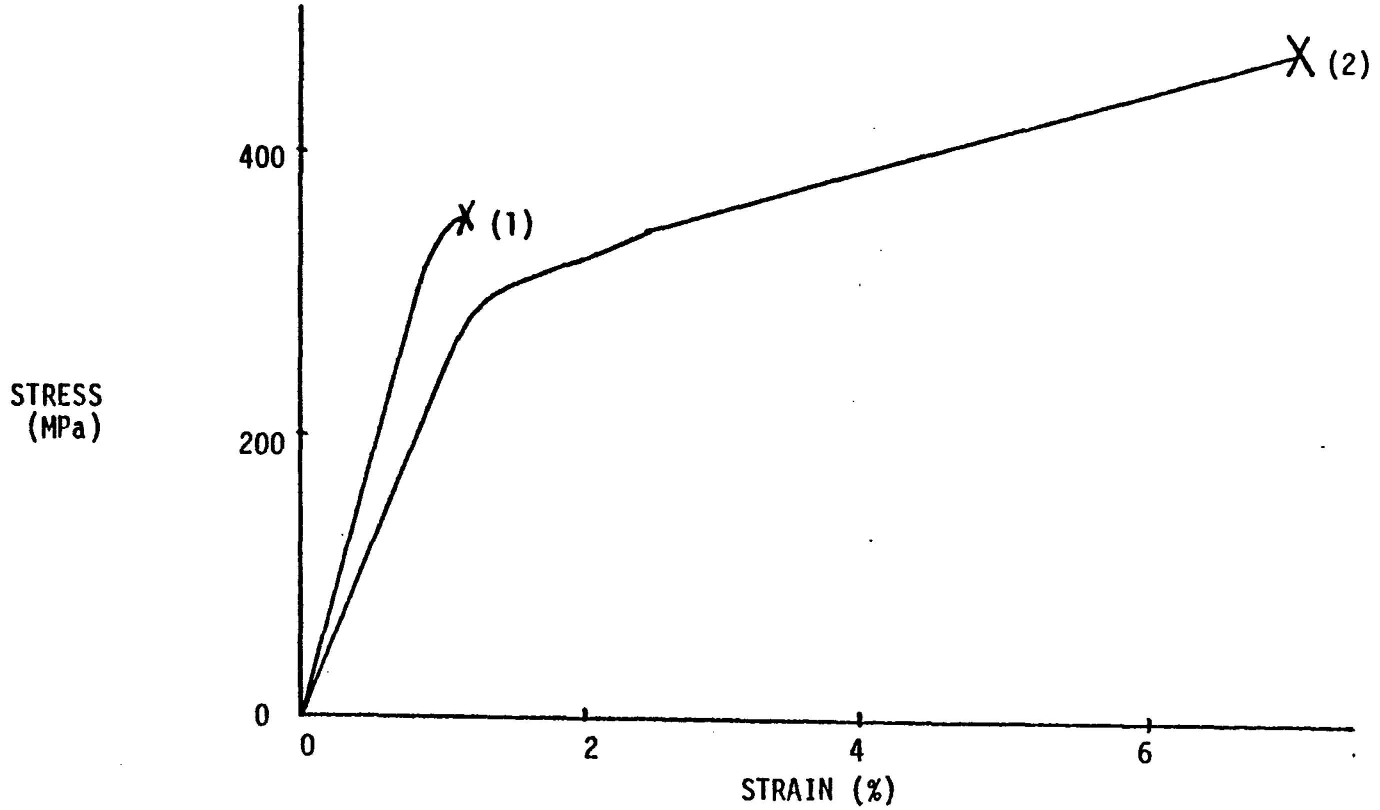


Figure 28 Stress-strain curves for Nylon 6/PBT (20000) fibers before and after sulfuric acid extraction; (1) heat-treated at 255°C for 1 minute and 86 MPa tension; (2) extracted in sulfuric acid without tension.

TABLE 9

MECHANICAL PROPERTIES OF NYLON 6/PBT (20000) FIBERS* BEFORE AND AFTER EXTRACTION IN SULFURIC ACID

	FIBER DIAMETER	E (GPa)	TS (MPa)	ε (%)
86 MPa Tensioned Fiber, BEFORE	62.9	31.2	354.9	1.2
AFTER (no tension extraction)	43.3	25.2	467.4	7.1
55 MPa Tensioned Fiber, BEFORE	67.2	26.0	314.2	1.4
AFTER (tensioned extraction)	41.8	39.3	418.6	1.4

* heat-treated at 255°C for 1 minute.

The stress-strain curves for the Nylon 6/PBT (20000) fibers which were heat-treated at 55 MPa tension before and after extraction are shown in Figure 29 and the corresponding numerical results are given in Table 9. This fiber was held in tension during extraction, and both the modulus and tensile strength are higher. The fiber was held under tension as the nylon was removed, preventing the PBT from becoming less oriented. The higher modulus values and the constant elongation at break values support this interpretation.

Although the extracted fibers are believed to be pure PBT, they do not exhibit the high modulus and tensile strength, 300 GPa and 3 GPa respectively,[37] of spun PBT fibers. The PBT fiber spinning procedure imparts a high degree of orientation to the PBT fibers, much superior to the orientation imparted in the composite spinning procedure. Thus PBT fibers show substantially higher mechanical properties than the extracted fibers.

Scanning electron micrographs of the extracted fibers are shown in Figure 30. The top photographs refer to the fibers from Figure 28 (no tension extraction) and the bottom photographs refer to the fibers from Figure 29 (tension extraction). Note the highly fibrillar nature of the extracted fibers and oriented appearance. The surface appears grooved and the fibrils seem loosely held together, as though collapse was incomplete after removal of the nylon. In addition, the extracted fibers exhibited no large (> 10%) nonuniformities in diameter.

The extracted fibers were tested in a differential scanning calorimeter to detemine if the nylon was removed from the composite

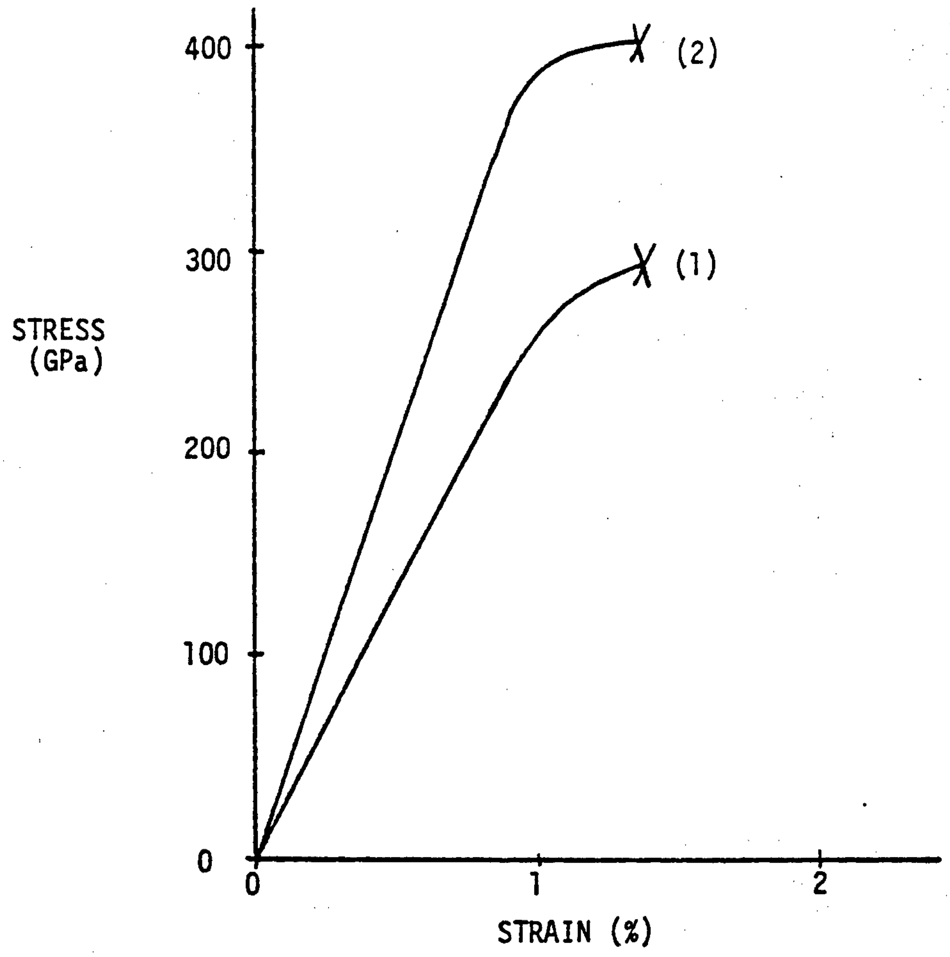
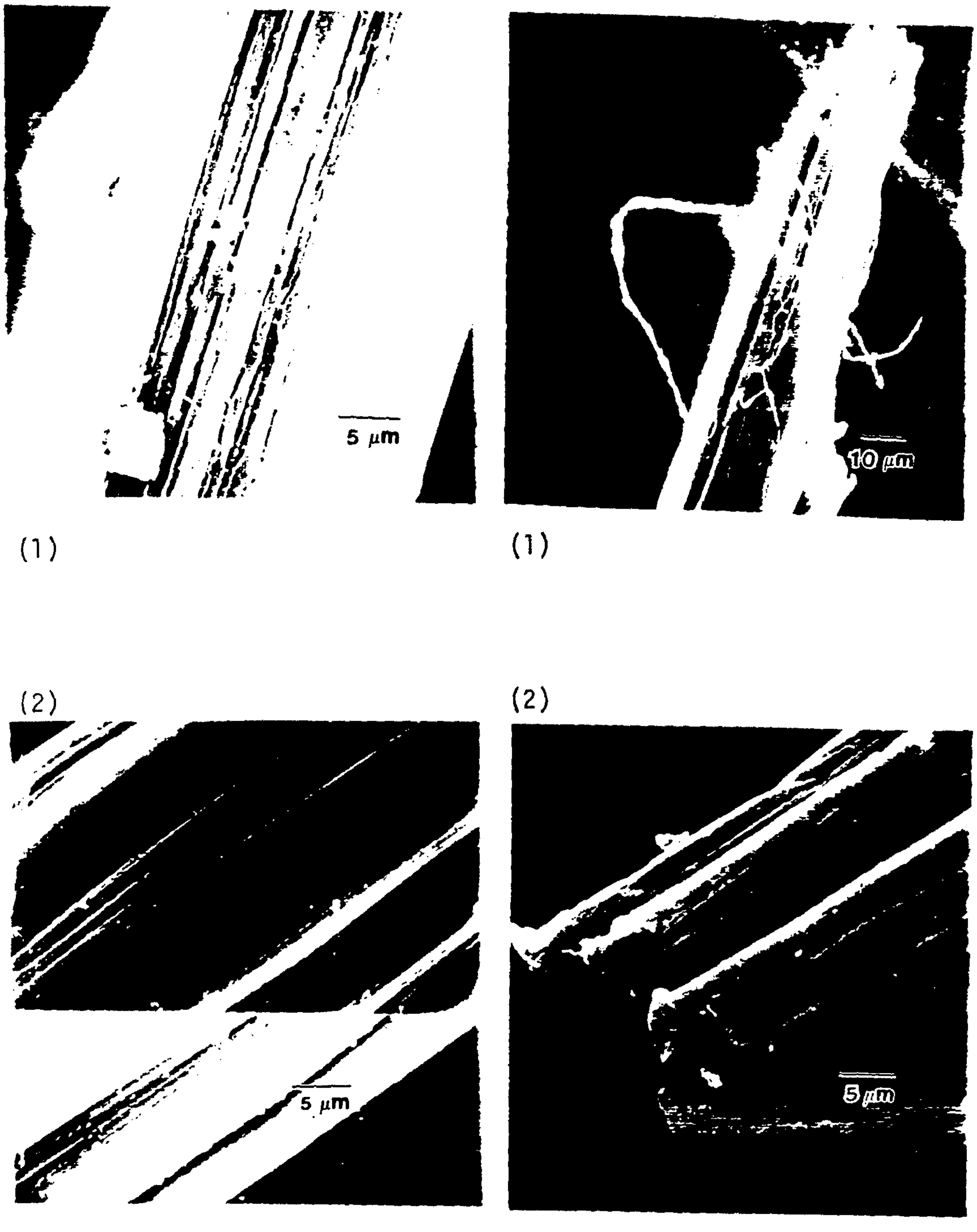


Figure 29 Stress-strain curves for Nylon 6/PBT (20000) fibers before and after sulfuric acid extraction; (1) heat-treated at 255°C for 1 minute and 55 MPa tension; (2) extracted in sulfuric acid with tension.



(1) (1)

(2) (2)

Figure 30 Scanning electron microscope photographs of sulfuric acid extracted Nylon 6/PBT (20000) fibers; (1) fibers extracted without tension; (2) fibers extracted with tension.

fiber (Figure 31). A pure PBT fiber was tested for comparison. It appears as though essentially complete removal of the nylon occurs, as the PBT DCS thermogram is nearly identical to the extracted composite fiber DCS scan. No nylon peak is exhibited.

4. CONCLUSIONS

(1) A molecular level composite of PBT in nylon, at 30 weight percent PBT, has not been achieved. (2) The mechanical properties of the composites do not follow the "rule of mixture" as would be expected of a molecular composite, nor do the composites flow when placed above the melting temperature of the nylon. (3) The composite fibers, when placed in sulfuric acid, remain intact, supporting the existence of a network of PBT within the composite. (4) DSC thermograms for the extracted fibers exhibit no nylon peak and are not unlike the thermograms for PBT, indicating that the extracted fiber is indeed pure PBT.

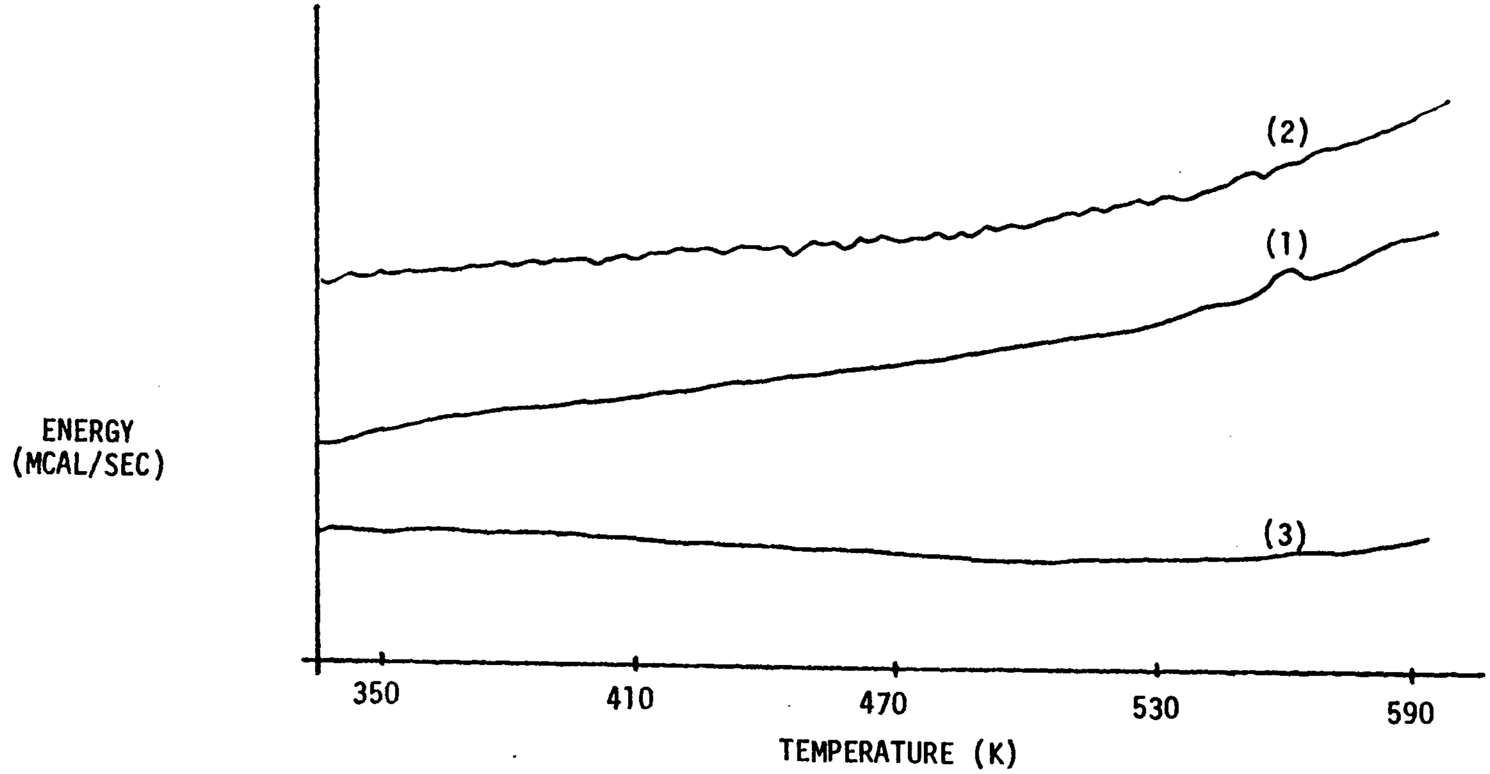


Figure 31 DSC thermograms of Nylon 6/PBT (20000) fibers extracted in sulfuric acid and PBT fibers; (1) extracted fibers; (2) PBT; (3) baseline.

V. CONCLUSIONS AND RECOMMENDATIONS

1. CONCLUSIONS

a. Nylon/PBT composites

As spun nylon/PBT fibers have low mechanical properties that can be more than doubled by wet-stretching. Further increases can be obtained by heat treatment under tension. The wet-stretched modulus increases by a factor of seven and the tensile strength increases by a factor of three during tensioned heat treatment. The mechanical properties are not a strong function of oven residence time for the times studied (0.5, 1, 2 minutes), although the modulus tends to be slightly higher at low residence times and the tensile strength at higher residence times. The highest tensile strengths are achieved with high tensioning which occurs at the low residence times. Similarly, the mechanical properties are not a strong function of heat-treatment temperature (215°C, 255°C, 295°C) or matrix molecular weight. However, a higher heat-treatment temperature tends to result in better properties as does a lower molecular weight matrix material. DSC thermograms indicate that the higher temperature is above the melting point of the nylon.

b. Extended heat treatment

Extended heat treatment has been found to improve the composite mechanical properties, most notably the modulus. The modulus of fibers extended heat-treated increases by 20 % to 50 % and the tensile strength improves modestly by 3 % to 15 %. In addition, this process produces a change in the melting point of the matrix, increasing it from 5°C to 10°C. Studies of bulk nylons subjected to extended heat treatment show an increase in the inherent viscosity as a result of the process, indicating that solid-state polymerization occurs. Fibers that were extended heat-treated at the lower temperature have the lower increase in inherent viscosity (lowest increase in molecular weight), yet have the better properties. This is consistent with previous results in that the lower molecular weight matrix has the better properties.

c. PBT composite structure

A molecular composite of PBT in nylon (30/70 weight ratio) has not been achieved. The "rule of mixture" reinforcement is not obtained, despite wet-stretching, heat treatment and extended heat treatment. In addition, when the composite fibers are placed in sulfuric acid, a solvent for nylon, the fibers remain intact. DSC curves indicate this remaining fiber is essentially pure PBT.

d. Summary

These results strongly support the idea that a network of PBT is formed during processing within the 30/70 PBT/nylon composite fibers. Thus, the lower molecular weight matrix, with a lower viscosity, allows the network to perfect more than does the higher molecular weight matrix. The mechanical properties are therefore better for the lower molecular weight matrix. Likewise, the higher heat treatment temperature allows the network to perfect which results in improved properties over the lower heat-treatment temperature. In addition, the fibers do not break at the higher heat-treatment temperature even though it is above the melting point of the nylon. The composites melt, but do not flow.

Further support of the network idea is found in the mechanical property data. The modulus and tensile strength do not follow the "rule of mixture" and tend to level off with applied tension during heat treatment. The mechanical properties may be limited by the properties of the PBT network within the composite fibers. Extended heat treatment improves the mechanical properties, but the "rule of mixture" is still not achieved.

The sulfuric acid extraction process adds further support to the idea of a PBT network within the nylon composites.

2. RECOMMENDATIONS

Based on the above conclusions, several recommendations for future work can be made.

(1) A network of PBT is formed during processing within the 30/70 PBT/nylon composites. It would be useful to study various compositions of PBT in nylon to determine at what point a network is formed. An investigation of the composite at a composition just below that of network formation would be useful for molecular composite studies.

(2) Results seem to indicate that the network is formed due to an ease of mobility of the PBT molecules within the nylon matrix. Perhaps a very high molecular weight nylon as a matrix would prevent the formation of a PBT network, even at the 30/70 composition. A theory by

Graessley and Edwards[50] shows the necessity of having a sufficiently high molecular weight matrix to prevent the occurrence of a network.[51,52] A study of very high molecular weight nylons as matrix materials is therefore indicated.

REFERENCES

1. W.B. Goldsworthy, "Economic Advantages of Reinforced Plastics/Composites in High Volume Applications," Kevlar Composites, SPE (1980).
2. P.R. Langston, "Overview of Kevlar Composites: Properties and Uses," Kevlar Composites, SPE (1980).
3. Composite Materials, Volume 3, Chapter 1, B.R. Noton Editor, Academic Press, New York (1974).
4. L.E. Nielson, "Mechanical Properties of Particulate-Filled Systems," J. Composite Materials, 1, 100 - 119 (1967).
5. J.L. Kardos, "Structure Property Relations in Short-Fiber Reinforced Plastics," CRC Critical Reviews in Solid State Sciences, 419 - 450 (August, 1973).
6. S.W. Tsai, J.C. Halpin and N.J. Pagano Editors, Composite Materials Workshop, Technomic Publishing Co., Connecticut (1968).
7. B.W. Rosen, "Mechanics of Composite Strengthening," Fiber Composite Materials, American Society of Metals (1978).
8. SPI Handbook of Technology and Engineering of Reinforced Plastics/Composites, Second Edition, J.G. Mohn, S.S. Oleesky, G.D. Shook and L.S. Meyer Editors, Van Nostrand Reinhold, Co., New York, 15 - 35 (1973).
9. "Polyamides (Fibers)," Kirk-Othmer Encyclopedia of Chemical Technology, Volume 18, Wiley and Sons, New York, 372 - 422 (1978).

REFERENCES (Continued)

10. "Polyamide Fibers", Encyclopedia of Polymer Science and Technology: Plastics, Resins, Rubbers and Fibers, Volume 10, Wiley and Sons, New York, 418 - 581 (1969).

11. G.S. Holster and C. Thomas, Fibre Reinforced Materials, Elsevier Publishing Co., LTD (1966).

12. D.M. Bigg, "Mechanical, Thermal and Electrical Properties of Metal Fiber-Filled Polymer Composites," Polym. Eng. Sci., 19(16), 1188 - 1192 (1979).

13. J.L. Kardos and J. Raisoni, "The Potential Mechanical Response of Macromolecular Systems - A Composite Analogy," Polym. Eng. Sci., 15(3), 183 - 190 (1975).

14. W.-F. Hwang, D.R. Wiff, T.E. Helminiak and W.W. Adams, "Molecular Composites of Rigid Rod Poly (p-phenylene benzobisthiazole) (PPBT) in Thermoplastic Matrices," Org. Coat. Plast. Chem. Preps., ACS Div. Org. Coat. Plast., 48, 929 - 931 (1983).

15. T.E. Helminiak, C.L. Benner, F.E. Arnold and G.E. Husman, "Aromatic Heterocyclic Polymer Alloys and Products Produced Therefrom," U.S. Patent 4,207,407 (1980).

16. T.E. Helminiak, "The Air Force Ordered Polymers Research Program: An Overview," ACS Div. Org. Coat. Plasts. Chem. Papers, 40, 475 - 478 (1979).

17. J. Preston, "High-Strength/High-Modulus Organic Fibers," Polym. Eng. Sci., 15(3), 199 - 206 (1975).

18. A. Ciferri, "Ultra-High-Modulus Fibers From Solution Spinning," Polym. Eng. Sci., 15(3), 191 - 198 (1975).

REFERENCES (Continued)

19. A. Ciferri and B. Valenti, "Solution Spinning of Rigid and Semi-Rigid Polymers," Ultra-High Modulus Polymers, A. Ciferri and I.M. Ward Editors, Applied Science Publishers, 203 - 226 (1979).

20. J.F. Wolfe, B.H. Loo and F.E. Arnold, "Thermally Stable Rod-Like Polymers: Synthesis of an All-Para Poly (benzobisthiazole)," Polym. Preps., ASC Div. Polym. Chem., 19(2), 1 - 6 (1978).

21. S.R. Allen, A.G. Filippov, R.J. Farris and E.L. Thomas, "Microstructure and Mechanical Behavior of Fibers of Poly (p-phenylene benzobisthiazole)," J. Appl. Polym. Sci., 26, 291 - 301 (1981).

22. J.R. Minter, K. Shimamura and E.L. Thomas, "Microstructural Study of As-Extruded and Heat Treated Ribbons of Poly (p-phenylene benzobisthiazole)," J. Mater. Sci., 16, 3303 - 3308 (1981).

23. J.A. Odell, A. Keller, E.D.T. Atkins and M.J. Miles, "Structural Studies of Poly (p-phenylene benzobisthiazole) Films," J. Mater. Sci., 16, 3309 - 3318 (1981).

24. G.C. Berry, P.C. Metzger, S. Venkatramen and D.B. Cotts, "Properties of Rod-like Polymers in Solution," ACS Div. Polym. Chem., Polym. Preps., 20(1), 42 - 44 (1979).

25. J.E. Ashton, J.C. Halpin and P.H. Petit, Primer on Composite Materials: Analysis, Progress in Materials Science, Volume III, Technomic Publishing Co., Connecticut (1969).

26. J.C. Halpin and R.L. Thomas, "Ribbon Reinforcement of Composites," J. Comp. Mater., 2(4), 488 - 497 (1968).

27. W.-F. Hwang, D.R. Wiff, C.L. Benner and T.E. Helminiak, "Composites on a Molecular Level: Phase Relationships, Processing

and Properties," J. Macromol. Sci. - Phys., B22(2), 231 - 257 (1983).

28. T.T. Tsai and F.E. Arnold, "Acetylene Containing Aromatic Benzothiazole Resins," Polym. Preps., ACS Div. Polym. Chem., 23(1), 1 (1982).

29. M. Takayanagi, "Polymer Composites of Rigid and Flexible Molecules," Pure Appl. Chem., 55(5), 819 - 832 (1983).

30. A. Ziabicki, Fundamentals of Fiber Formation, Chapter 4, Wiley and Sons, New York (1976).

31. A.E. Zachariades and R.S. Porter, The Strength and Stiffness of Polymers, Chapter 3, Marcel Dekker, Inc., New York, 121 (1983).

32. P.J. Flory, "Statistical Thermodynamics of Mixtures of Rodlike Particles. 5. Mixtures with Random Coils," Macromol., 11(6), 1138 - 1141 (1978).

33. W.-F. Hwang, D.R. Wiff, C. Verschoore, G.E. Price, T.E. Helminiak and W.W. Adams, "Solution Processing and properties of Molecular Composite Fibers and Films," Polym. Eng. Sci., 23(14), 784 - 788 (1983).

34. W.-F. Hwang, D.R. Wiff and C. Verschoore, "Phase Relationships of Rigid Rod Polymer/Flexible Coil Polymer/Solvent Ternary Systems," Polym. Eng. Sci., 23(14), 789 - 791 (1983).

35. T.E. Helminiak, M. Wellman, W.-F. Hwang, D.R. Wiff, V. Rodgers and C. Benner, "Critical Processing Conditions of a Specific Ternary System - Molecular Composites," AFWAL-TR-80-4163 (1980).

REFERENCES (Continued)

36. G.C. Berry, E.F. Casassa, P. Metzger and S. Venkatramen, "Physical - Chemical Properties of Complex Aromatic Heterocyclic Polymers," AFML-TR-78-164 (1979).

37. S. Allen, "Mechanical and Morphological Correlations in Poly (p-phenylene benzobisthiazole) Fibers," PhD Thesis, Polymer Science and Engineering, University of Massachusetts (May, 1983).

38. E.C. Chenevey, "Processing of Rod-Like Polymers, Part III," AFWAL-TR-80-4142 (1982).

39. W.-F. Hwang,D.R. Wiff and T.E. Helminiak, "Solution Behavior of a Ternary System - ABPBI/PBT in a Mixed Acidic Solvent," Org. Coat. Plast. Chem., 44, 32 - 37 (1981).

40. D.R. Wiff, "Polymeric Materials for Advanced Aircraft and Aerospace Vehicles," AFWAL-TR-80-4124 (1980).

41. D.R. Wiff, "Polymeric Materials for Advanced Aircraft and Aerospace Vehicles," AFWAL-TR-81-4156 (1981).

42. S.R. Allen, A.G Filippov, R.J. Farris, E.L. Thomas, C.P. Wong, G.C. Berry and E.C. Chenevey, "Mechanical Studies of High-Strength, High-Modulus Poly (p-phenylene benzobisthiazole) Fibers," Macromol., 14, 1134 - 1138 (1981).

43. T.A. Hancock, J.E. Spruiell and J.L White, "Wet Spinning of Aliphatic and Aromatic Polyamides," J. Appl. Polym. Sci., 21, 1227 - 1247 (1977).

44. J.R. Minter, "Structural Investigation of Fibers and Films of Poly (p-phenylene benzobisthiazole)," PhD Thesis, Polymer Engineering and Science, University of Massachusetts (1982).

REFERENCES (Continued)

45. G. Odian, *Principles of Polymerization*, Second Edition, Wiley and Sons, New York, 105 - 107 (1981).

46. D.E. Davenport, "Metalloplastics - The Art of Infinite Chains," Paper Presented at the 55th Annual Meeting of the Society of Rheology (1983).

47. B. Abeles, H.L. Pinch and J.I Gittleman, "Percolation Conductivity in w-Al O Granular Metal Films," Phys. Rev. Letters, **35**(4), 247 (1975).

48. W.Y. Hsu, J.R. Barkley and P. Meakin, "Ion Percolation and Insulator-to-Conductor Transition in Nafion Perfluorosulfonic Acid Membranes," Macromol., **13**, 198 - 200 (1980).

49. D.C. Bonner, "Determination of Solvents for Thermally Stable Polymers," AFML-TR-77-73 (1977).

50. W.W. Graessley and S.F. Edwards, "Entanglement Interactions in Polymers and the Chain Contour Concentration," Polymers, **22**, 1329 - 1334 (1981).

51. S. Middleman, *The Flow of High Polymers; Continuum and Molecular Rheology*, Interscience Publishers, New York (1968).

52. R.B. Bird, R.C. Armstrong and O. Hassager, *Dynamics of Polymeric Liquids*, Volume 1: Fluid Mechanics, Wiley Interscience, New York (1977).

53. G. Husman, T.E. Helminiak, W. Adams, D. Wiff and C. Benner, "Molecular Composites - Rodlike Polymer Reinforcing an Amorphous Polymer Matrix," ACS Div. Org. Coat. Plast., Org. Coat. Plast. Chem. Preps., **40**, 797 - 802 (1979).

54. G. Husman, T.E. Helminiak, M. Wellman, W. Adams, D. Wiff and C. Benner, "Molecular Composites - Rodlike Polymer Reinforcing an Amorphous Polymer Matrix," AFWAL-TR-80-4034 (1980).

55. T.E. Helminiak, "An Approach to a Molecular Composite - Rodlike Polymer Reinforcement of an Amorphous Polymer Matrix, ABPBI/PBT," Proceedings of the 1981 Science and Engineering Symposium, AFSC/NMC, Volume 2, 275 - 282 (1981).

56. W.W. Adams, T.E. Helminiak, A. Viswanathan, W.-F. Hwang and D.R. Wiff, "Molecular Composites: The Morphology of Rigid Rod/Random Coil Polymer Blends," IUPAC Proceedings MACRO 82, 828 (July 12-16, 1982/Amherst, MA).

57. T.E. Helminiak and R.C. Evers, "Tailoring Polymer Molecules for Specific Fiber and Ribbon Properties," Polymeric Materials Science and Engineering, 49, 689 - 693 (1983).

58. M. Takayanagi, "New Aspects of Aramid as Reinforcement in Composites," IUPAC Proceedings MACRO 82, 480 (July12-16, 1982/Amherst, MA).

59. M. Takayanagi, T. Ogata, M. Mirikawa and T. Kai, "Polymer Composites of Rigid and Flexible Molecules: System of Wholly Aromatic and Aliphatic Polyamides," J. Macromol. Sci. - Phys., B17(4), 591 - 615 (1980).

60. J.A. Duiser and J.A. Copper, "Matrix/Fibril Fibers from Cellulose Acetate and Acrylonitrile Copolymer," Fibre Sci. Tech., 6, 119 - 124 (1973).

61. H.R Allcock and F.W. Lampe, Contemporary Polymer Chemistry, Prentice-Hall, Inc., New Jersey, 110 - 115 (1981).

APPENDIX A

MECHANICAL PROPERTIES OF NYLON 6,6/PBT (13700) COMPOSITE FIBERS

	E (GPa)	TS (MPa)	ε (%)
As-Spun Fibers	5.5 ± 0.5	116.8 ± 7.3	37.6 ± 3.5
Wet-Stretched Fibers	6.2 ± 0.4	143.2 ± 10.6	28.1 ± 1.3
Heat-Treated at 255°C for 0.5 Minutes			
21.9 MPa	19.9 ± 0.9	246.8 ± 10.6	14.4 ± 2.0
41.6 MPa	28.6 ± 2.2	282.3 ± 12.3	5.3 ± 0.4
61.7 MPa	34.5 ± 2.6	309.3 ± 12.0	2.4 ± 0.3
79.3 MPa	37.4 ± 2.4	320.7 ± 15.8	1.4 ± 0.1
86.4 MPa	37.5 ± 1.3	321.0 ± 10.8	1.2 ± 0.1
98.9 MPa	40.6 ± 2.1	347.3 ± 15.6	1.1 ± 0.1
Heat-Treated at 255°C for 1 Minute			
15.3 MPa	15.4 ± 0.7	263.1 ± 27.3	12.0 ± 0.8
26.6 MPa	22.2 ± 1.4	311.9 ± 10.6	10.0 ± 1.4
36.3 MPa	22.0 ± 0.8	326.1 ± 9.4	7.7 ± 1.3
55.4 MPa	18.9 ± 1.3	332.6 ± 0.8	5.3 ± 0.9
64.5 MPa	23.9 ± 1.0	336.7 ± 3.3	3.0 ± 0.5
70.9 MPa	24.0 ± 1.6	338.3 ± 15.8	3.0 ± 0.5
Heat-Treated at 255°C for 2 Minutes			
12.4 MPa	11.6 ± 0.8	225.4 ± 14.3	16.1 ± 2.1
19.7 MPa	11.8 ± 1.1	246.2 ± 15.1	15.4 ± 2.7
29.4 MPa	15.7 ± 1.6	289.6 ± 20.7	7.7 ± 1.7
39.5 MPa	19.7 ± 2.4	301.9 ± 22.7	6.2 ± 0.6
53.4 MPa	20.0 ± 0.8	291.4 ± 4.2	7.1 ± 2.3
63.3 MPa	23.9 ± 1.7	321.1 ± 23.4	2.9 ± 0.2
Heat-Treated at 295°C for 0.5 Minutes			
19.4 MPa	19.7 ± 0.6	249.0 ± 11.1	14.4 ± 1.9
37.2 MPa	28.3 ± 1.0	288.3 ± 4.4	7.9 ± 0.4
56.1 MPa	33.7 ± 2.4	309.2 ± 20.3	2.6 ± 0.3
82.5 MPa	40.3 ± 1.2	349.3 ± 3.6	1.2 ± 0.1

NYLON 6,6/PBT (13700) COMPOSITE FIBERS (CONTINUED)

	E (GPa)	TS (MPa)	ε (%)
Heat-Treated at 295°C for 1 Minute			
22.3 MPa	24.7 ± 1.1	278.8 ± 12.1	6.9 ± 0.5
40.8 MPa	31.2 ± 2.7	303.4 ± 23.5	4.1 ± 0.4
49.4 MPa	31.1 ± 2.5	270.9 ± 15.6	2.0 ± 0.1
79.3 MPa	39.4 ± 2.6	342.4 ± 21.1	1.1 ± 0.2
95.2 MPa	40.2 ± 3.2	342.4 ± 15.4	1.0 ± 0.1
Heat-Treated at 295°C for 2 Minutes			
20.8 MPa	20.6 ± 1.8	264.9 ± 14.1	15.0 ± 1.4
54.0 MPa	32.4 ± 1.5	294.3 ± 12.4	2.1 ± 0.3

MECHANICAL PROPERTIES OF NYLON 6,6/PBT (17500) COMPOSITE FIBERS

	E (GPa)	TS (MPa)	ε (%)
As-Spun	6.1 ± 0.4	113.5 ± 9.0	23.3 ± 5.7
Wet-Stretched	8.4 ± 1.1	150.2 ± 10.3	20.2 ± 4.7
Heat-Treated at 255°C for 0.5 Minutes			
18.6 MPa	20.8 ± 1.1	247.7 ± 9.5	9.4 ± 0.5
34.7 MPa	26.7 ± 1.4	273.4 ± 20.4	5.5 ± 0.3
50.3 MPa	31.4 ± 1.6	293.2 ± 13.1	2.1 ± 0.2
65.8 MPa	33.9 ± 0.7	310.7 ± 9.8	1.8 ± 0.2
83.3 MPa	36.0 ± 0.9	333.6 ± 6.7	1.2 ± 0.1
Heat-Treated at 255°C for 1 Minute			
12.1 MPa	15.5 ± 1.6	246.8 ± 12.3	11.4 ± 2.2
22.4 MPa	18.4 ± 2.7	248.9 ± 17.0	7.7 ± 2.4
35.2 MPa	24.2 ± 2.3	273.3 ± 19.6	4.9 ± 1.4
Heat-Treated at 295°C for 0.5 Minutes			
19.1 MPa	18.9 ± 0.7	244.6 ± 8.8	12.1 ± 1.0
35.9 MPa	27.5 ± 1.7	270.4 ± 14.3	3.9 ± 1.0
52.1 MPa	33.4 ± 0.8	296.5 ± 8.8	1.4 ± 0.2
68.2 MPa	35.5 ± 0.4	310.6 ± 7.8	1.1 ± 0.1
Heat-Treated at 295°C for 1 Minute			
18.2 MPa	18.6 ± 1.8	232.4 ± 17.7	11.1 ± 1.8
34.7 MPa	26.9 ± 0.9	267.3 ± 10.8	2.5 ± 0.5
55.0 MPa	34.5 ± 1.7	306.2 ± 11.3	1.4 ± 0.2
72.1 MPa	36.6 ± 1.7	324.5 ± 13.1	1.1 ± 0.1
81.6 MPa	37.7 ± 2.9	329.8 ± 28.3	1.1 ± 0.1
Heat-Treated at 295°C for 2 Minutes			
19.1 MPa	19.2 ± 0.2	247.5 ± 1.8	14.1 ± 1.1
53.0 MPa	32.8 ± 2.2	289.5 ± 16.5	1.8 ± 0.1
83.2 MPa	37.5 ± 2.0	331.9 ± 29.5	1.1 ± 0.1

MECHANICAL PROPERTIES OF NYLON 6/PBT (14500) COMPOSITE FIBERS

	E (GPa)	TS (MPa)	ε (%)
As-Spun	3.2 ± 0.1	64.5 ± 3.2	2.6 ± 0.2
Wet-Stretched	5.2 ± 0.4	127.5 ± 12.0	37.9 ± 7.8
Heat-Treated at 215°C for 0.5 Minutes			
17.6 MPa	16.1 ± 0.8	220.4 ± 13.4	16.4 ± 0.7
32.4 MPa	22.3 ± 0.8	249.2 ± 8.0	10.6 ± 0.9
46.1 MPa	25.9 ± 3.1	261.0 ± 6.9	6.2 ± 0.7
65.8 MPa	30.8 ± 1.0	287.1 ± 9.8	2.1 ± 0.2
81.9 MPa	32.4 ± 1.3	299.2 ± 12.2	1.4 ± 0.1
Heat-Treated at 215°C for 1 Minute			
14.5 MPa	15.4 ± 0.5	236.9 ± 9.2	12.2 ± 0.2
29.8 MPa	23.4 ± 0.9	294.0 ± 9.5	3.0 ± 0.5
34.1 MPa	21.8 ± 1.9	267.7 ± 9.7	5.0 ± 0.8
41.6 MPa	23.8 ± 0.9	285.6 ± 8.0	5.3 ± 1.1
50.3 MPa	24.7 ± 0.8	298.4 ± 10.6	3.0 ± 0.4
59.6 MPa	28.1 ± 1.3	320.6 ± 16.7	1.6 ± 0.1
80.1 MPa	29.8 ± 1.5	351.9 ± 17.1	1.4 ± 0.1
Heat-Treated at 215°C for 2 Minutes			
18.2 MPa	18.4 ± 1.1	246.4 ± 12.4	16.1 ± 1.5
33.4 MPa	25.1 ± 1.1	268.1 ± 9.9	8.7 ± 0.6
49.4 MPa	28.3 ± 1.0	277.4 ± 11.8	4.1 ± 0.4
67.0 MPa	32.4 ± 1.0	304.0 ± 9.5	1.8 ± 0.2
75.9 MPa	33.0 ± 0.3	307.2 ± 0.7	1.4 ± 0.1
Heat-Treated at 255°C for 0.5 Minutes			
19.4 MPa	17.9 ± 1.1	227.4 ± 6.8	12.5 ± 1.6
36.6 MPa	26.2 ± 1.3	256.7 ± 11.7	5.3 ± 1.4
56.1 MPa	30.6 ± 2.1	284.2 ± 11.1	2.0 ± 0.2
70.7 MPa	31.7 ± 2.0	296.5 ± 13.8	1.5 ± 0.1
88.1 MPa	36.7 ± 2.0	331.8 ± 15.1	1.1 ± 0.1

NYLON 6/PBT (14500) COMPOSITE FIBERS (CONTINUED)

	E (GPa)	TS (MPa)	ε (%)
Heat-Treated at 255°C for 1 Minute			
14.5 MPa	16.2 ± 0.9	233.0 ± 14.0	21.4 ± 3.9
27.2 MPa	22.7 ± 1.6	263.1 ± 18.9	9.8 ± 2.7
33.9 MPa	23.6 ± 1.6	261.8 ± 7.3	5.6 ± 0.7
44.8 MPa	27.6 ± 1.4	299.0 ± 13.8	3.4 ± 0.8
54.8 MPa	27.9 ± 1.2	306.9 ± 13.8	2.0 ± 0.3
67.0 MPa	32.4 ± 2.4	342.2 ± 14.3	1.4 ± 0.9
71.6 MPa	29.7 ± 1.3	334.6 ± 11.8	1.3 ± 0.1
82.3 MPa	31.9 ± 1.6	352.3 ± 14.7	1.2 ± 0.1
97.0 MPa	34.8 ± 1.0	360.6 ± 9.8	1.2 ± 0.1
Heat-Treated at 255°C for 2 Minutes			
16.7 MPa	18.7 ± 0.5	269.0 ± 9.4	8.7 ± 1.6
27.7 MPa	21.1 ± 1.7	278.0 ± 16.6	9.5 ± 0.8
34.7 MPa	21.8 ± 1.4	280.6 ± 11.8	8.9 ± 1.7
45.5 MPa	27.2 ± 0.7	318.8 ± 2.1	3.4 ± 0.5
53.1 MPa	28.3 ± 0.5	326.6 ± 4.2	2.3 ± 0.2
62.9 MPa	29.7 ± 1.7	338.9 ± 6.3	1.8 ± 0.1
73.4 MPa	31.3 ± 1.1	339.0 ± 4.2	1.4 ± 0.1
88.1 MPa	34.7 ± 1.0	373.2 ± 6.4	1.2 ± 0.1

MECHANICAL PROPERTIES OF NYLON 6/PBT (20000) COMPOSITE FIBERS

	E (GPa)	TS (MPa)	ε (%)
As-Spun	2.9 ± 0.4	63.5 ± 2.6	2.9 ± 0.4
Wet-Stretched	5.9 ± 0.3	141.2 ± 7.4	16.9 ± 1.3
Heat-Treated at 215°C for 1 Minute			
15.8 MPa	16.6 ± 1.2	219.5 ± 19.8	12.2 ± 1.4
28.2 MPa	22.0 ± 1.5	242.6 ± 12.1	5.1 ± 1.4
44.5 MPa	26.9 ± 1.1	274.0 ± 1.8	2.4 ± 0.5
57.3 MPa	29.1 ± 0.5	290.4 ± 1.7	1.4 ± 0.1
77.7 MPa	33.1 ± 1.5	326.6 ± 11.5	1.2 ± 0.1
Heat-Treated at 215°C for 2 Minutes			
16.3 MPa	16.1 ± 1.5	220.5 ± 19.1	13.9 ± 1.5
28.0 MPa	20.8 ± 1.4	232.4 ± 8.4	7.7 ± 0.6
35.7 MPa	23.6 ± 1.8	236.6 ± 16.2	2.7 ± 0.6
57.3 MPa	31.0 ± 1.3	298.7 ± 10.4	1.4 ± 1.5
75.2 MPa	33.7 ± 1.3	326.0 ± 10.3	1.2 ± 0.1
Heat-Treated at 255°C for 0.5 Minutes			
31.1 MPa	25.5 ± 2.7	251.3 ± 17.8	6.3 ± 2.4
40.0 MPa	26.6 ± 2.0	260.1 ± 21.3	3.3 ± 0.6
46.9 MPa	28.5 ± 3.5	263.6 ± 25.5	1.6 ± 0.3
67.0 MPa	35.3 ± 1.8	319.1 ± 22.0	1.0 ± 0.1
Heat-Treated at 255°C for 1 Minute			
14.0 MPa	9.2 ± 0.6	189.4 ± 9.4	25.8 ± 3.5
23.5 MPa	17.8 ± 0.8	244.5 ± 6.6	3.1 ± 0.3
29.7 MPa	21.3 ± 1.0	245.2 ± 13.6	3.1 ± 0.5
36.2 MPa	19.4 ± 1.5	246.1 ± 12.9	3.2 ± 0.8
55.2 MPa	26.0 ± 1.0	314.2 ± 10.9	1.4 ± 0.1
66.1 MPa	28.8 ± 1.0	337.1 ± 18.9	1.4 ± 0.1
86.1 MPa	31.1 ± 1.4	354.9 ± 14.0	1.2 ± 0.1

NYLON 6/PBT (20000) COMPOSITE FIBERS (CONTINUED)

	E (GPa)	TS (MPa)	ε (%)
Heat-Treated at 255°C for 2 Minutes			
13.5 MPa	13.9 ± 0.7	220.8 ± 13.1	12.7 ± 0.7
24.1 MPa	18.9 ± 0.5	248.2 ± 7.0	5.5 ± 0.7
31.5 MPa	22.1 ± 0.7	279.5 ± 5.5	3.5 ± 0.6
39.0 MPa	23.3 ± 1.0	279.8 ± 8.6	2.0 ± 0.2
49.0 MPa	26.0 ± 0.3	305.9 ± 7.3	1.8 ± 0.1
59.7 MPa	30.0 ± 0.5	333.0 ± 5.8	1.4 ± 0.1

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