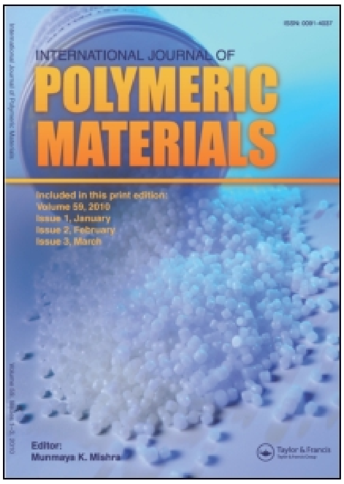

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Microfibrillar-Reinforced Nylon-6/PET Fibers with Interfacial Bonding

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Microfibrillar-reinforced fibers (MRF's) with a majority of poly (ϵ-caprolactam) (Nylon-6) and a minority of poly(ethylene terephthalate) (PET) were melt spun. When triphenylphosphite (TPP) was masterbatched into the PET (PET MB) prior to spinning, some block polyamide/polyester copolymers were formed during the spinning, serving to bond the nylon matrix to the PET microfibrils. The mechanical and processing properties of such fibers were consistently better than those of comparable fibers of the same composition but without interfacial bonding. Fibers containing PET microfibrils have higher modulus than the corresponding nylon-6 blanks; and fibers containing bonded PET microfibrils have a modulus much higher than those containing unbonded PET microfibrils. At 3:1 draw ratio, the highest modulus approached 60 g/den and the highest strength was about 4.0 g/den. At 5:1 draw ratio, a modulus of over 80 g/den was achieved. Together with improvements in modulus, the glass transition temperature, T_g, of the nylon-6 matrix gradually increased as function of the fibers' draw ratio.

In order for polyamide/polyester bonds to occur, the polyamide must contain at least one primary amine group per chain. The PET must be masterbatched with ca. 1.5% TPP, increasing its intrinsic viscosity (I.V.) from 0.69 to not higher than 0.80 dL/g. Fibers containing up to 30% PET MB could be easily spun and drawn to 3:1 and 5:1 either immediately or after time-lagging. MRF's containing 15%, 20%, 25% and 30% PET MB were processed and performed reasonably well. MRF's with 25% PET MB performed about as well as those with 30% PET MB, but were easier to spin and draw. Fibers containing 45% PET MB had poorer mechanical properties than MRF's containing 30% PET MB and showed large property, performance and processing fluctuations due to massive phase inversions randomly taking place in them. During the melt spinning, time and temperature dependence are interdependent. The best conditions with our equipment were found to be: barrel temperatures of 271–288°C, residence time of about 150 seconds, and spinnerette temperature of 260–266°C. Under these conditions, high levels of interfacial bonding, constant intrinsic viscosity, and filament uniformity were achieved.

Keywords: Microfibrils; Nylon-6; PET; Interfacial bonding; grafting; mechanical properties; fibers

INTRODUCTION

Aliphatic polyamide fibers have excellent tenacity, durability and dyeability but their initial modulus and stiffness are less than desirable. On the other hand, polyester fibers have high modulus and stiffness but their dyeability is poor. For these reasons, attempts have been made to create fibers possessing the better properties of both polyamide and polyester, while being free of the less desirable ones. These attempts consisted of preparing block copolymers of polyamide and polyester [1] and melt spinning the product into fibers, of intensively mixing polyamide and polyester in the molten state and then spinning fibers out of the molten mixture [2,3], and of the preparation of microfibrillar-reinforced composites (MRC's) created by annealing oriented blends below the melting temperature of the higher-melting semi-crystalline polymer present in the composite [4–7]. None of the above approaches combined a sufficient improvement in fiber properties without deleterious effects with technological and economical feasibility useful in the fibers industry: the block copolymers were prepared by a very lengthy solid-state procedure, the spun mixtures resulted in no or very poor bonding between the majority polyamide fiber matrix phase and the minority polyester microfibrillar phase, and the MRC's were prepared in film and not in fiber form.

The present work is limited to fibers only. Even though several aliphatic polyamides and several polyesters were used in various combinations and degrees of success, we limit ourselves in this work to discuss only the pair of poly (ϵ-caprolactam) (nylon-6) and poly(ethylene terephthalate) (PET). Additional details may be found in the U.S. Patent of Aharoni and Morgan [8] which was issued in 1990 on the basis of applications dating back as early as 1984.

In the present endeavor we expected to improve upon the above [1–7] by causing the formation of some block copolymers during the mixing and spinning of the molten nylon-6 and PET, and by these block polymers remaining in the interface between the two immiscible polymers binding them together and serving as interfacial bonds between the PET microfibrils and the nylon-6 matrix. It was felt that in this fashion many of the weaknesses previously observed [2,3] and thought to be caused by polymer-polymer interface debonding, would be overcome. Our approach was to build upon our previous experience with "phosphite technology" [9–17], using aryl phosphites to chain extend polyesters and aliphatic polyamides and to create block and graft copolymers by conducting the reactions when the polymer is in the molten state in the extruder. For the purpose of performing the chemistry during melt spinning of *fibers*, the procedure had to be adapted to the special requirement of keeping the melt viscosity of the polyamide about the same as it is in the absence of chain extending reactions and, at the same time, maximizing the creation of block copolymer molecules which are expected to concentrate in the nylon-6/PET interface and serve as an interfacial bonding agent. The combined desirable results were achieved by incorporating the appropriate amounts of aryl phosphite in the least reactive polymer in the system to be blended (PET in the present case). This procedure is usually called masterbatching. The most frequently used phosphite was triphenylphosphite (TPP), but other phosphites were found to perform in equal or lesser success. Examples of the combinations prepared and evaluated were given in the patent of Aharoni and Morgan [8], covering nylon-6/PET and several other polyamide/polyester pairs. In all instances below, the designation MB indicates that TPP was masterbatched by melt blending into the PET prior to mixing of the polyester with nylon-6 and melt spinning of the mixture.

In the Experimental section, detailed procedures of masterbatch preparation, fiber spinning and drawing, characterization, fractionation and block copolymer estimation (interfacial bonding) are given for nylon-6/PET MRF's. The tensile results and the observations of the morphological and interfacial adhesion studies will be discussed in the following Results and Discussion section. Then conclusions will be drawn in a brief Conclusion section.

EXPERIMENTAL

Predetermined weights of pelletized PET, having about equal number of carboxyl and hydroxyl chain ends, a weight average molecular weight, M_W, of 46,000 and intrinsic viscosity (I.V.) of 0.68–0.70 dL/g in 60/40 phenol/tetrachloroethane solvent mixture, were dried for 16 hrs at about 155°C in a vacuum oven maintaining 1.0 mm of less mercury pressure prior to all subsequent handling. The dried pellets were immediately transferred to hermetically sealed glass jars where they were allowed to cool to room temperature. Based on the weight of the PET, there were added 1.5 wt/wt % TPP to the polymer in the jars, the vessels immediately resealed, and then tumble mixed to coat the PET pellets with TPP. Various amounts of TPP, in the range of 0.5 to 2.5 wt/wt %, were evaluated, but it was found that for PET pellets the amount of 1.5% gave the most desirable balance of consistent results and ease of handling.

The tumble-mixed PET/TPP mixture was then extruded at nominal barrel temperature of $285 \pm 5^\circ$C in a single screw Wayne extruder equipped with an L/D = 24, 5:1 single stage mixing screw. The optimal residence time in the extruder was found to be 150 seconds. The extrudate strand was cooled in a trough filled with ambient temperature water, from whence it transferred to a chopping machine in which the strand was chopped to pellets. The collected pellets of the PET containing the TPP (called PET masterbatch, or PET MB) were dried in a vacuum oven as before, but at a temperature of only 120°C. At this point the PET MB was ready for mixing with the desired grade of nylon-6. Best performance was obtained when the intrinsic viscosity of the PET MB was increased by the reaction of the TPP to the interval of 0.75 to 0.80 dL/g, corresponding to $52{,}000 \leqslant M_W \leqslant 57{,}000$. When mixed and then melt spun with the PET MB, all grades of nylon-6 indicated below produced fibers with improved tensile properties, dimensional stability and nylon-6/PET bonding. Best results were obtained when the number concentration of amine end groups of the nylon-6 chains was equal to or higher than the number concentration of carboxyl chain ends. In the present study most work was performed using nylon-6 grades having about equal number of NH_2 and COOH end groups (LSB grade with $M_W = 39{,}200$ and BHS grade with $M_W = 45{,}780$). Precalculated amounts of the pelletized nylon-6 were dried in the vacuum oven at about 110°C for not less than 4 hrs. Then the dried nylon-6 was tumble-mixed in hermetically sealed glass jars with premeasured amounts of the PET MB. The mixture was then fed through a nitrogen-blanketed hopper into a Sterling extruder equipped with a L/D = 21 metering screw, followed in the barrel by a Koch static mixer with L/D $\gtrsim$ 4 and wave amplitudes of either 1/8″ or 1/16″. The optimal residence time in this extruder was found to be about 2 minutes. After emitting from the static mixer the polymeric melt passed through a metering pump maintaining uniform pressure on the polymer melt pool residing on top of a screen pack nestled right on the spinnerette. The exact nominal temperature profile depended on the exact molecular weight of the nylon and its melt viscosity, on the molecular weight of the PET MB (as reflected by its intrinsic viscosity) and on the ratio of nylon-6 to PET MB in the mixture. The temperature range along the extruder barrel was 255–288°C and about 10–22 K higher at the spinnerette. When the amount of PET MB was 15 wt/wt %, then a barrel temperature of about 277°C was found to produce the best results. At 30% loading of PET MB the optimal barrel temperature was about 282°C and at 45% PET MB the optimal barrel temperature reached as high as 288°C.

The shape of the spinnerette reflects the anticipated end-use of the fibers: round holes for industrial or tire-cord applications, and multilobal or other shaped holes for carpets, etc. After passing through the spinnerette, the molten polymer mixture drops down a stack and is partially drawn into fine fibers, prior to being taken up on the take-up roll of a Leesona or similar drawing machine. The use of a hot-sleeve in the stack was found to help the processing on occasion. From the take-up roll the fibers move to a pick-up bobbin for the purpose of time-lagging prior to the final drawing, or are drawn immediately to the desired draw ratio by passing through a sequence of rolls each rotating at higher rpm and each maintained at a different temperature. For industrial yarn the desired draw ratio is 5:1 and for carpeting purposes the desired draw ratio is 3:1. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) observations revealed that the cross section of the PET and PET MB microfibrils in the nylon-6 matrix of each of the filaments in the yarn was about 220 nm and less, independently of whether the fibers were spun and immediately drawn or spun and time-lagged prior to drawing.

Thermal analysis of pelletized nylon-6, PET, their bicomponent blends, and microfibrillar-reinforced fibers (MRF's) was performed in a differential scanning calorimeter (DSC) instrument (duPont Model 9900) with heating and cooling rates of 10 K/min and 20 K/min. The samples, weighing between 10 and 15 mg, were constantly under Ar or nitrogen stream. Prior to thermal scans, the specimens were kept in crimped aluminium pans in sealed desiccators over strong desiccants, such as phosphorus pentoxide or concentrated sulfuric acid, to insure that the specimens will equilibrate with atmosphere approaching 0% relative humidity. Each crimped pan with the sample inside was then rapidly transferred under a blanket of dry nitrogen to the DSC instrument and the heating cycle of the thermal scan immediately started. Other samples, in crimped aluminium pans were equilibrated in another desiccator in which the relative humidity was kept at about 50% by placing in it the appropriate hydrated salts specified in the ASTM procedure. The glass transition temperature, T_g, was measured at the point of inflection, and the first order transitions were defined by the highest point of the respective peaks.

Grafting of nylon-6 onto the surfaces of the PET microfibrils was detected by the following two procedures. Nylon-6 is fully soluble in 2,2,2-trifluoroethanol (TFE) in a matter of hours at room temperature and within minutes at reflux temperature. Nylon-6 and many other nylons dissolve far better and faster in 2:1 or 3:2 vol/vol TFE/$CHCl_3$ [18]. Yarn containing nylon-6/PET was placed in a large excess of TFE or TFE/$CHCl_3$ with agitation and stirred until the yarn fell apart and most of the material dissolved. The suspension was centrifuged at least 35,000 G and the solids filtered off. These solids were again placed in the same solvent and the process repeated in the same manner three times. In the last time, the suspension was heated for 45 minutes at not lower than 50°C prior to centrifugation and filtration. The solids were then collected and subjected to SEM observation and to nitrogen elemental analysis. When the PET contained no TPP, or when the processing temperature was too low for the desired reaction to take place, the PET microfibrils were observed by SEM to be very clean and carry no additional material. Elemental analysis of these microfibrils gave zero nitrogen content, indicating that no grafting of nylon-6 onto the PET, by means of block copolymer formation, took place. It also indicated that our fractionation procedure was appropriate since it did not leave behind any ungrafted nylon-6. When TPP was present in the PET and when the temperature was right for the reaction to proceed (255–288°C in the barrel), then the SEM consistently showed non-fibrillar material firmly attached to and coating the PET microfibrils. Element analysis indicated that the PET with the attached non-fibrillar material contained nitrogen. From the weight percent nitrogen, the amount of nylon attached to the PET microfibrils was calculated. Depending on the temperature profile during spinning, up to 25 weight % nylon was found to be attached to the PET microfibrils. Wide-angle x-ray diffraction patterns obtained from one such sample clearly indicated the presence of crystalline PET and crystalline nylon-6. Since the nylon-6 could not be washed away by procedures that completely washed out ungrafted nylon-6, we have concluded that the nylon-6 is chemically grafted onto the surfaces of the PET microfibrils. Finally, titrations for amine and carboxyl end groups showed that in the instances where chemical bonding was indicated by other analytical techniques, the amounts of unreacted amine and carboxyl groups were drastically reduced. When no grafting was evident by other techniques, the levels of unreacted amine and carboxyl groups remained very close to their levels in blanks containing no TPP at all. Thus, one concludes that in the presence of TPP in the PET and when exposed to the right temperatures for the correct duration, amine end groups from the nylon-6 chains form amide bonds with the carboxyl groups of PET chains on the surfaces of the PET microfibrils, and nylon-6 actually grafts onto the surfaces of these microfibrils.

Tensile tests were performed using an Instron Testing machine following the relevant ASTM Test Methods. Results are tabulated in Table I below, in which specific polymer pairs are listed together with their respective extruder barrel temperature, the final draw ratio, the initial tensile (Young's) modulus in grams per denier, and remarks pertaining to specific processing conditions and observations. Spun and drawn fibers were allowed to equilibrate prior to the test in an environmental cell mounted right on the Instron testing machine and kept at 23°C at essentially zero relative humidity (R.H.). The fibers were tested for their tensile properties while in the environmental cell. Then the cell was altered to maintain an atmosphere of 50% R.H., and other fibers were first equilibrated and then tested in this atmosphere.

RESULTS AND DISCUSSION

Examples of microfibrillar-reinforced fibers preparation, composition, conditions, and their tensile modulus are given in Table I below. The

TABLE I Nylon-6/PET Microfibrillar Reinforced Fibers

Code	*Yarn Composition*	*Barrel Temp. °C*	*Draw Ratio*	*Initial Modulus g/denier*	*Remarks*
A0074-79x	LSB nylon-6 control	266	3:1	20.4	Coarse static mixer
A0397-5A1	LSB nylon-6 control	266	3:1	24.2	Fine static mixer
·	LSB nylon-6 control	266	-	-	No static mixer.Could not be spun.
·	LSB nylon-6 control	266	-	-	Fine static mixer with no hot-sleeve. Drips
-	LSB nylon-6 control	282	-	-	Cannot be spun. Drips
A0397-5B1	LSB/15% PET MB	282	3:1	32.9	Hot-sleeve at ambient temp
A0397-5C1	LSB/15% PET MB	282	3:1	34.9	Hot-sleeve at 150°C
A0397-5D1	LSB/15% PET MB	282	3:1	46.2	Hot-sleeve at 185°C
A0397-5A2	LSB nylon-6 control	266	4.5:1	46.6	No hot-sleeve
A0397-5B2	LSB/15% PET MB	282	4.4:1	66.5	Hot-sleeve at ambient temp
A0397-5C2	LSB/15% PET MB	282	4.7:1	67.2	Hot-sleeve at 150°C
A0397-5D2	LSB/15% PET MB	282	3.9:1	65.7	Hot-sleeve at 185°C
A0397-6G	LSB nylon-6 control	266	3:1	21.8	No hot-sleeve.
A0074-100D	LSB/15% PET MB	282	3:1	49.8	No hot-sleeve for this and all below.
A0074-100B	LSB/15% PET MB	282	3:1	41.3	
–	LSB nylon-6 control	266	3:1	19.2	No time lag.
A0593-5A1	LSB nylon-6 control	266	3:1	24.2	With time lag.
A0593-5B-17	LSB/15% PET no TPP	288	3:1	24.1	No copolymer. No bonding.
A0074-91A	LSB/15% PET MB I.V. = 0.53	282	3:1	30.4	Very low copolymer present
A0074-91B	LSB/15% PET MB I.V. = 0.68	282	3:1	29.0	ditto.
A0074-91C	LSB/15% PET MB I.V. = 0.95	282	3:1	30.2	ditto.
A0074-85B-2	LSB/15% PET on TPP	277	3:1	22.8	No copolymer present.
A0074-88B-1	LSB/15% PET no TPP	277	3:1	26.4	ditto.

A0074-85C	LSB nylon-6 control	255	3:1	18.5	
A0397-6H7	LSB/15% PET MB	282	3:1	40.8	Copolymer present.
A0397-6H8	LSB/15% PET MB	282	3:1	43.1	ditto.
A0074-82B2	LSB/30% PET MB	255	3:1	26.2	Coarse static mixer. No block copolymer formed.
A0074-82B3	LSB/30% PET MB	255	3:1	29.4	Fine static mixer. No copolymer formed.
A0074-79B	LSB/30% PET MB	271	3:1	40.7	Coarse static mixer. Made substant. copolymer amts.
A0593-15-1	LSB/30% PET MB	282	3:1	42.0	Time lag.
A0593-15-2	LSB/30% PET MB	288	3:1	36.5	Spin draw.
A0593-27-3	LSB/30% PET MB	296	3:1	35.9	Spin draw.
A0397-19C1	LSB/30% PET MB	296	3:1	42.4	Time lag.
A0397-19D1	LSB/30% PET MB	291	3:1	44.1	Time lag.
A0074-85A	LSB/30% PET MB	282	3:1	36.8	Spin draw.
A0593-19J1	LSB/45% PET MB	266	3:1	52.7	Time lag.
A0593-19J2	LSB/45% PET MB	266	3:1	59.3	Time lag.
A0074-68A	LSB/5% PET MB	271	3:1	22.5	Spin draw.
A0074-68B	LSB/10% PET MB	271	3:1	37.0	Spin draw.
A0074-68C	LSB/15% PET MB	282	3:1	37.5	Spin draw.
A0593-10-5	BHS/15% PET MB	293	5:1	59.8	Time lag.
A0593-10-6	BHS/15% PET MB	291	5:1	60.9	ditto.
A0593-7	BHS/15% PET MB	288	4.6:1	48.8	ditto.
A0397-15C1	BHS/15% PET MB	282	5:1	65.6	ditto.
A0593-23-1	BHS/30% PET MB	288	2.2:1	23.9	ditto.
A0593-23-2	BHS/30% PET MB	288	2.3:1	27.8	ditto.
A0593-22-1	BHS/45% PET MB	277	5:1	63.9	ditto.
A0593-22-2	BHS/45% PET MB	277	5:1	63.7	ditto.
A0074-55M	LSB/15% PET. TPP on all pellets in polymer mixture.	282	–	–	Could not spin.

last entry in this Table clarifies a very important point: In each and every case where the TPP was applied as a thin coating to all polymer pellets in a mixture containing both nylon-6 and PET, they could not be spun into fibers because the preferential very substantial chain extension of the nylon-6 in such mixtures resulted in significant elevation of the molecular weight of the nylon, a large increase in the melt viscosity of the mixture, and extremely high pressures in the barrel of the extruder. In Table II are presented the intrinsic viscosity results, obtained in m-cresol, of a whole series of polymer mixtures with and without TPP. In the series A0074–55 the TPP was applied to all pellets of the mixed polymers. At the bottom of Table II the results of series A0074–91 are given. In this series, nylon-6 grade 8207 is blended with three grades of PET at 15 wt/wt % loading, but with the TPP previously masterbatched into the PET only. The results clearly indicate that masterbatching the TPP into the polyester keeps the average molecular weight, the intrinsic viscosity and the melt viscosity sufficiently low to facilitate the spinning of microfibrillar-reinforced fibers from the melt. The realization that the phosphite must be masterbatched separately into the pellets of the slower reacting component allowed the routine melt spinning of microfibrillar-reinforced fibers (MRF's) [8].

The mechanical properties of the MRF's depend in a very complicated way on many variables. Among them we have identified the following: (a) The inherent properties of the major components (e.g., nylon-6 LSB *vs.* nylon-6 BHS grades); (b) The amount of the minor phase (at about 45 weight % PET a strong tendency to phase inversion and fluctuations of properties set in); (c) The efficiency of interfacial bonding through the formation of block copolymers, which depends on the concentration of TPP in the initial PET MB; (d) The temperature in the barrel of the extruder and the presence or absence in the stack of a hot-sleeve at optimal temperature; (e) The draw ratio, and (f) The existence or absence of a time lag between spinning and drawing. Tensile modulus results obtained from LSB and BHS grades of nylon-6 fibers reinforced with microfibrils of PET masterbatched with 1.5% TPP are shown in Figures 1 and 2. From Figure 1 we gather that the addition of 25 to 30% PET to nylon-6 results in doubling the modulus of the MRF's drawn to 3:1 draw ratio. In the case of 5:1 drawn MRF's the increase in modulus is by over 50%, and

TABLE II Comparative Intrinsic Viscosity Results of Blends Uniformly Coated with TPP and Blends where the TPP is Masterbatched into the PET

Code	*Composition*	*TPP% Uniform*	*TPP% MB*	*Intrinsic Viscosity, in dL/q.*
A0074-55-A	nylon-6 LSB	none	none	1.47
A0074-55-B	nylon-6 LSB	0.75	–	2.62
A0074-55-L	LSB/15% PET	none	none	1.31
A0074-55-M	LSB/15% PET	0.75	–	Too many microgels to measure soln. viscosity.
A0074-55-N	LSB/5% PET	none	none	1.36
A0074-55-O	LSB/5% PET	0.75	–	2.55
A0074-91A	nylon-6 8207/ 15% PET I.V. = 0.53	–	1.5	1.18
A0074-91B	nylon-6 8207/ 15% PET I.V. = 0.68	–	1.5	1.18
A0074-91C	nylon-6 8207/ 15% PET I.V. = 0.95	–	1.5	1.22
–	PET	none	none	0.70
–	PET masterbatch	–	1.5	0.86

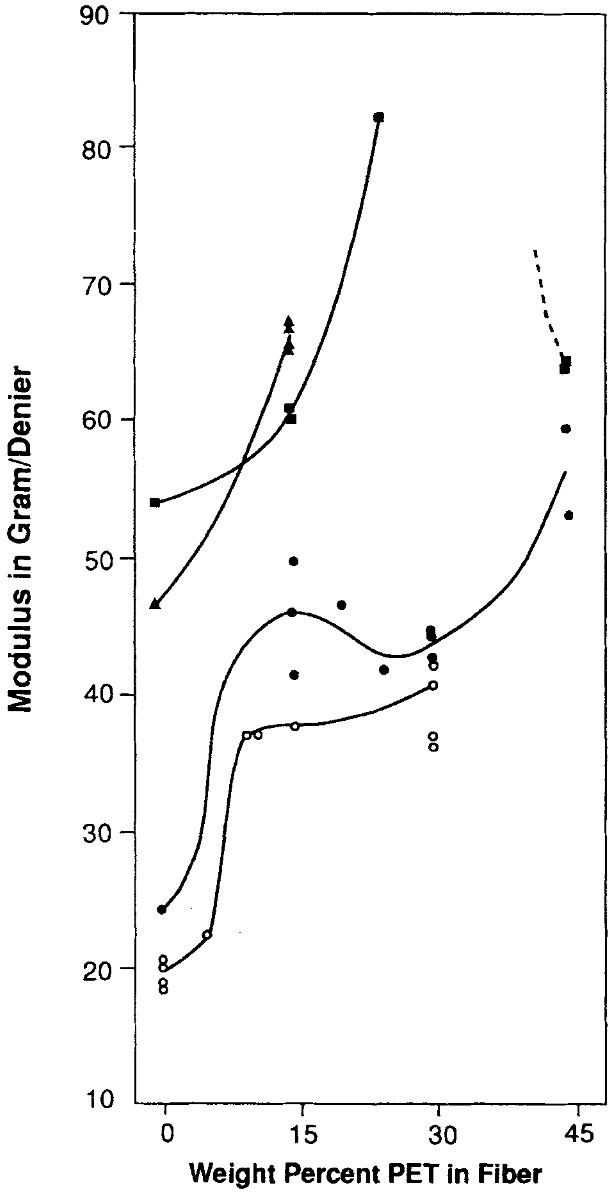


FIGURE 1 Modulus as function of weight percent PET in MRF's. ○–LSB nylon-6, spun and immediately drawn to 3:1 draw ratio. ●–LSB nylon-6, spun, time-lagged, then drawn to 3:1 draw ratio. ▲–LSB nylon-6, spun, time-lagged, then drawn to 5:1 draw ratio. ■–BHS nylon-6, spun, time-lagged, then drawn to 5:1 draw ratio. BHS MRF's with 45% PET underwent substantial phase inversion.

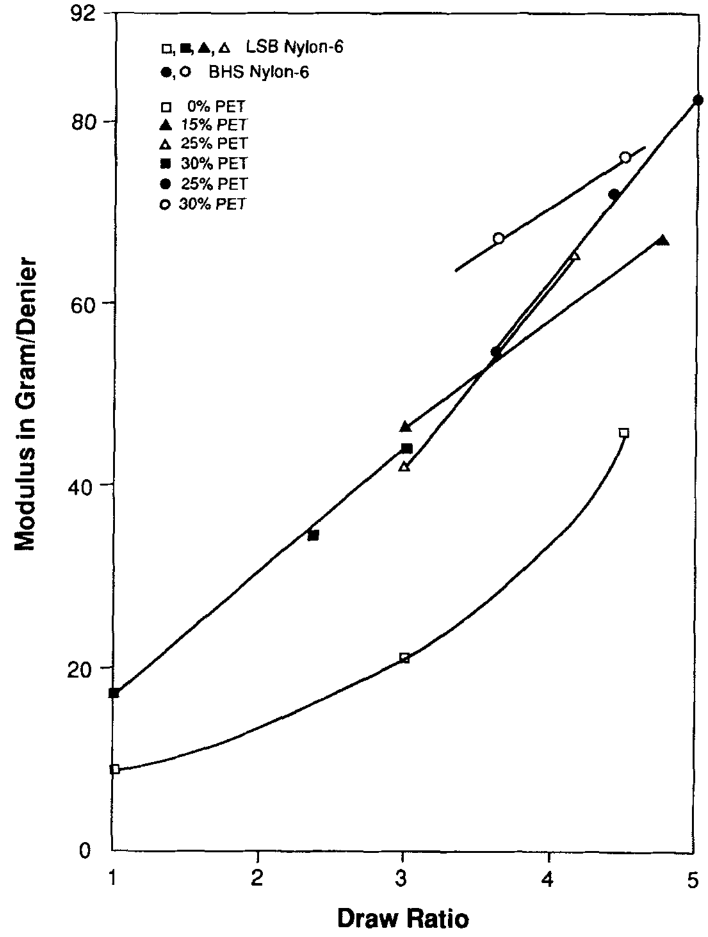


FIGURE 2 Effect of draw ratio on modulus of MRF's. All PET masterbatched with TPP.

the absolute values are impressively high. Fibers with 45% PET in them drawn to 5:1 draw ratio showed a propensity to phase inversion, however, resulting in lower than expected modulus.

The results from both Figures 1 and 2 show that 25% PET MB performed about as well as 30% PET MB. This is important because a reduction in the PET concentration in the MRF's makes it easier to melt spin and process them. In addition to the clear effects of PET reinforcement on the absolute values of the tensile modulus, one also learns from the slopes of the curves in Figure 2 that the increase in modulus with draw ratio shows a weak dependence on the amount of PET in the fibers. Independently of whether the nylon-6 in the MRF's was LSB or BHS grade, the slope for 30% PET MB was essentially the same for all tested systems. The slopes for 25% PET MB were identical to each other but dramatically different from the slope associated with 30% PET MB in the MRF's.

Repeated spinning experiments clearly indicated that MRF's in which block copolymers of nylon-6 and PET served as interfacial bonds were endowed with substantially higher modulus that MRF's of the same polymer composition but devoid of such bonds. A typical example of fibers spun and immediately drawn to 3:1 draw ratio is shown in Figure 3. In Figure 4 results are shown for MRF's spun and time-lagged before being drawn to 3:1 draw ratio. Here again, the advantage of nylon-6/PET block copolymers and interfacial bonding is clear. The scatter in the results of spinning at a given temperature is, to a large extent, a function of the residence time at that temperature, the molecular weight and viscosity of the PET, and the weight percent of TPP in the PET MB. The effects of residence time at temperature are reflected in both the intrinsic viscosity (molecular weight) of the whole fiber, in Figure 5, and in the weight percent nylon-6 actually bonded onto the surfaces of the PET microfibrils in the MRF's in Figure 6.

An additional important point is that in the absence of TPP it was very hard, and often impossible, to spin MRF's because of "raining" and "dripping". In the presence of TPP these processing problems were largely overcome, with "raining" remaining limited to compositions very rich in PET.

The glass transition temperature of the nylon-6 matrix of MRF's was determined using some fibers that were kept dry and others that were equilibrated in atmosphere containing 50% relative humidity (R.H.) In both instances the T_g showed a clear dependence on the draw ratio of the MRF's. The results are shown in Figure 7. For the dry fibers at draw ratios (DR's) of 3 and less, the dependence of T_g on DR followed the relationship:

$$T_g, \text{ in } ^\circ\text{C} = 53 + 3.5(\text{DR} - 1), \quad \text{DR} \leqslant 3 \tag{1}$$

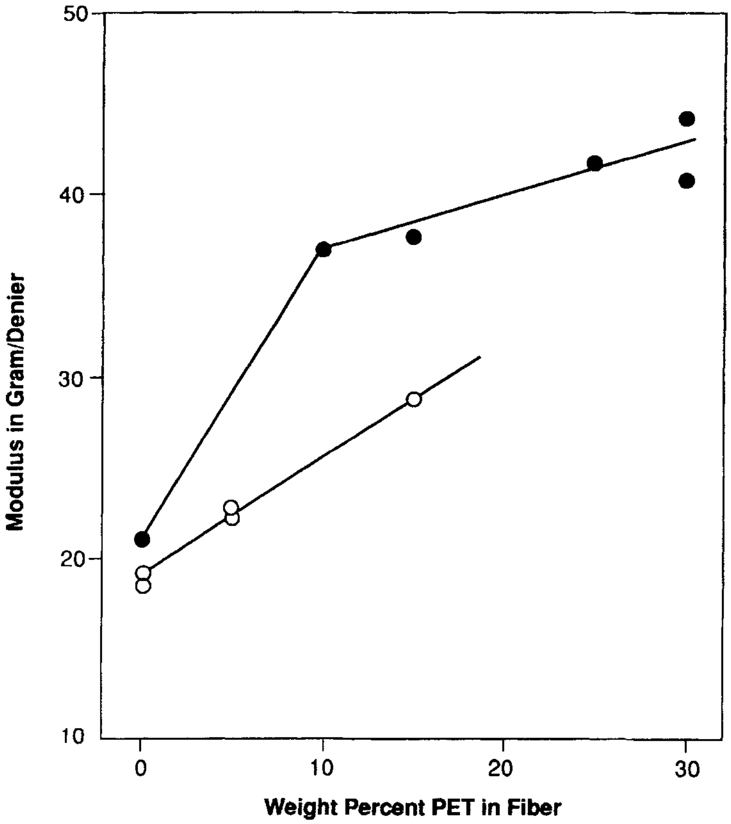


FIGURE 3 Difference in modulus between unbonded and chemically bonded PET microfibrils in MRF's spun and immediately drawn to 3:1 draw ratio ○ – unbounded, ● – chemically bonded.

and for DR's of 3 and higher the dependence was stronger:

$$T_g,\ \text{in } ^\circ\text{C} = 60 + 15(\text{DR} - 3), \quad \text{DR} \geqslant 3 \tag{2}$$

The results for the fibers equilibrated at 50% R.H. were very similar except for their displacement to lower temperatures. In the same Figure 7, results obtained by Murthy *et al.* [19] on neat nylon-6 fibers equilibrated at about 45% R.H. are shown. It is clear that the dependence on draw ratio remains the same as in the case of the MRF's, but the absorbed moisture (about 3% by weight) lowers the transition

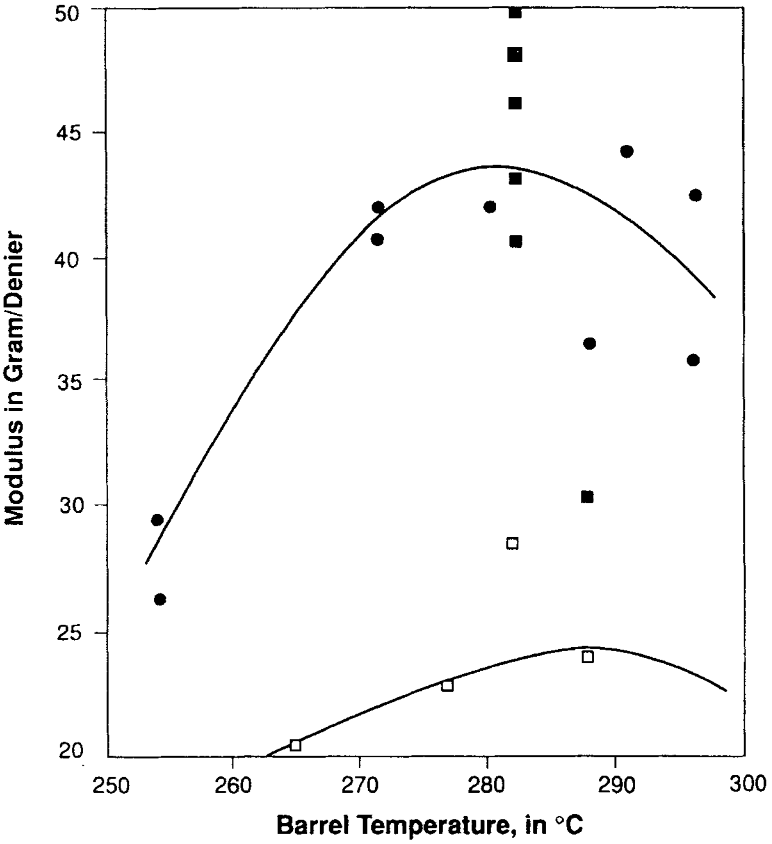


FIGURE 4 Effects of spin/interfacial bonding temperature on modulus of microfibrillar-reinforced fibers. ● - LSB + 30% PET masterbatched with 1.5% TPP. □ - LSB + 15% PET, no TPP. ■ - LSB + 15% PET masterbatched with 1.5% TPP.

temperature to fall essentially on the same lines as for our MRF's equilibrated at about 50% R.H. In considering the changes in T_g with DR, one should keep in mind that part of the increases in T_g may be associated with increases in the crystallinity index (% crystallinity) of the nylon in the MRF's, an index that grows with increasing draw ratio. Because the volume fraction of PET in the MRF's was usually small, our ability to clearly resolve the T_g of the PET minor phase was rather limited. In the few instances the T_g was nicely resolvable, it showed a dependence on draw ratio comparable with that of the nylon-6 matrix.

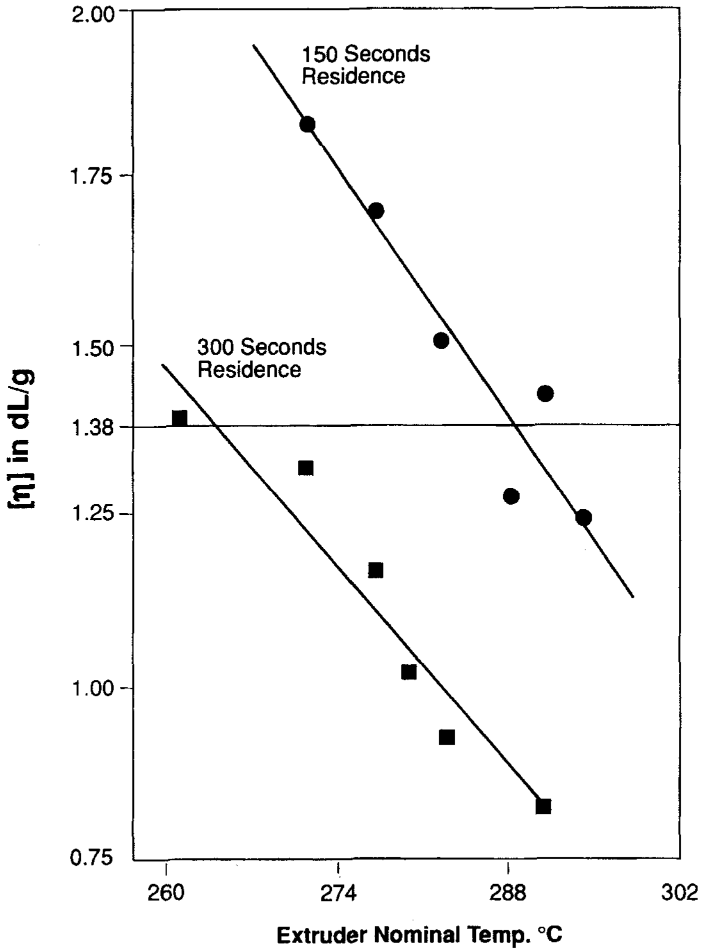


FIGURE 5 Viscosity as function of extrusion temperature of nylon-6 BHS grade + 15% PET MB at 150 and 300 seconds residence time.

The crystallinity index of nylon-6 in the MRF's is substantially affected by factors such as the draw ratio and whether the fibers were time-lagged or not, but almost completely unaffected by the amount of PET in the MRF's, at least up to 15% PET. This is clearly evident from the results in Figure 8. Within the crystalline fraction of the nylon-6, the ratio of the α-modification to γ-modification appears to remain high and rather constant for time-lagged fibers. The α/γ ratio

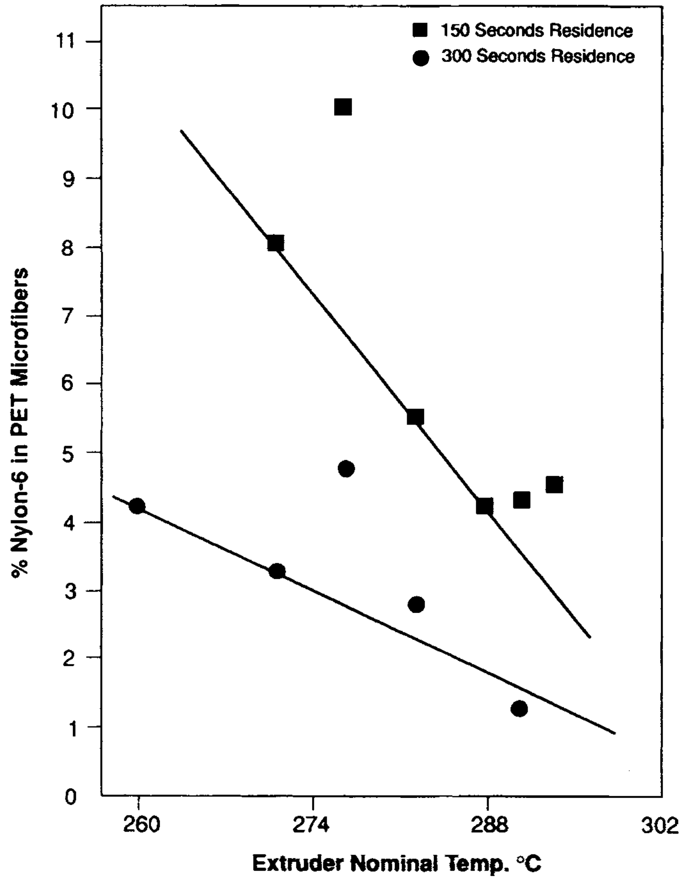


FIGURE 6 Percent nylon-6 grafted onto surfaces of PET microfibrils as function of extrusion temperature. Nylon-6 BHS grade + 15% PET MB at 150 and 300 seconds residence time.

shows, however, a dramatic increase with composition in fibers drawn immediately after spinning. The change in the α/γ ratio is by about an order of magnitude and occurs in the composition interval between 5 and 10% PET. The reasons for the change in the α/γ ratio at this particular concentration and its dependence on whether the fibers were time-lagged or not are not clear to us at present. We may hypothesize, however, that whenever the nylon-6 chains experience high local stresses during their elongation in the process of drawing they

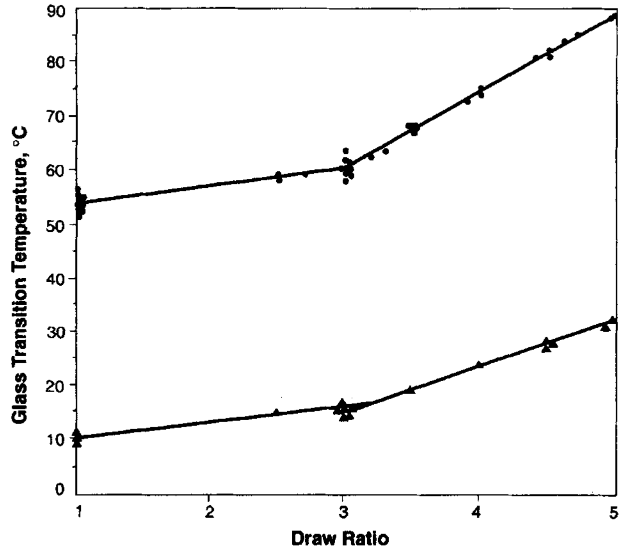


FIGURE 7 Glass transition temperature of nylon-6 in MRF's and fibers of neat nylon-6 as function of draw ratio. ● – Data obtained at about 0% R.H. on fibers equilibrated at 0% R.H. ▲ – Data obtained at 45% R.H. on nylon-6 fibers equilibrated at 45% R.H. (19), and at 50% R.H. on MRF's equilibrated at 50% R.H.

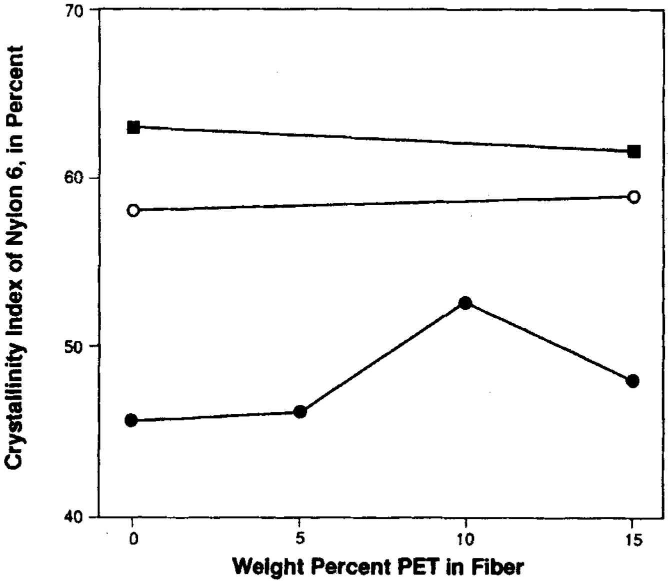


FIGURE 8 Total nylon-6 crystallinity in drawn MRF's. ● – Spun and immediately drawn to 3:1 draw ratio. ○ – Spun, time-lagged, then drawn to 3:1 draw ratio. ■ – Spun, time-lagged, then drawn to 4.5:1 draw ratio.

will settle into a thermodynamic energy minimum consistent with the α-modification of nylon-6, and when they encounter no or very low local stresses during the drawing process they may settle into a higher, thermodynamically unstable, energy minimum consistent with the γ-crystal modification. High local stresses are expected to be encountered when the nylon crystallinity is substantially and slowly developed as in time-lagged MRF's and when the existing PET crystals or second phase are present at such high concentration that their mere presence hinders the mobility of a sufficient number fraction of the nylon chains to create local stresses of magnitudes sufficient to force the straining nylon chains into a thermodynamic energy minimum consistent with the α-crystal modification. When MRF's with low levels of PET are spun and immediately drawn, there is insufficient interference by the PET phase on one hand and on the other hand the crystallinity index of the nylon-6 phase is still in the process of growing, and the amorphous phase of the nylon-6 is not yet fully relaxed to descend through the glass transition or approach it from above to such an extent that the viscosity of the amorphous phase will reach such high levels to cause the creation of the very high local stresses we believe are associated with the crystallization of the nylon preferentially into the α-modification. Under such conditions, we believe, the γ-modification appears.

Scanning and transmission electron microscopy proved to be powerful tools in elucidating the morphology of the MRF systems. For scanning electron microscopy (SEM), the nylon-6 matrix was carefully washed away as described in the Experimental section, and the PET component separately observed. For transmission electron microscopy (TEM), cryogenic microtomy was conducted on MRF's embedded in epoxy matrix, and then the nylon-6 was selectively stained. In Figure 10, PET particles are shown, coming from bicomponent pellets prior to the melt spinning process. They are mostly spherical but some are slightly elongated. The diameters of the spherical particles fall in the range of $150 < d < 300$ nm. After melt spinning and removing the nylon-6 matrix, we find that the spherical or slightly elongated particles were transformed in the MRF's into extremely long microfibrils with thickness in the range of 20 to 200 nm, and axial ratios routinely transcending 100. In Figure 11 are shown the PET microfibrils from systems where no PET/nylon-6 bonding took

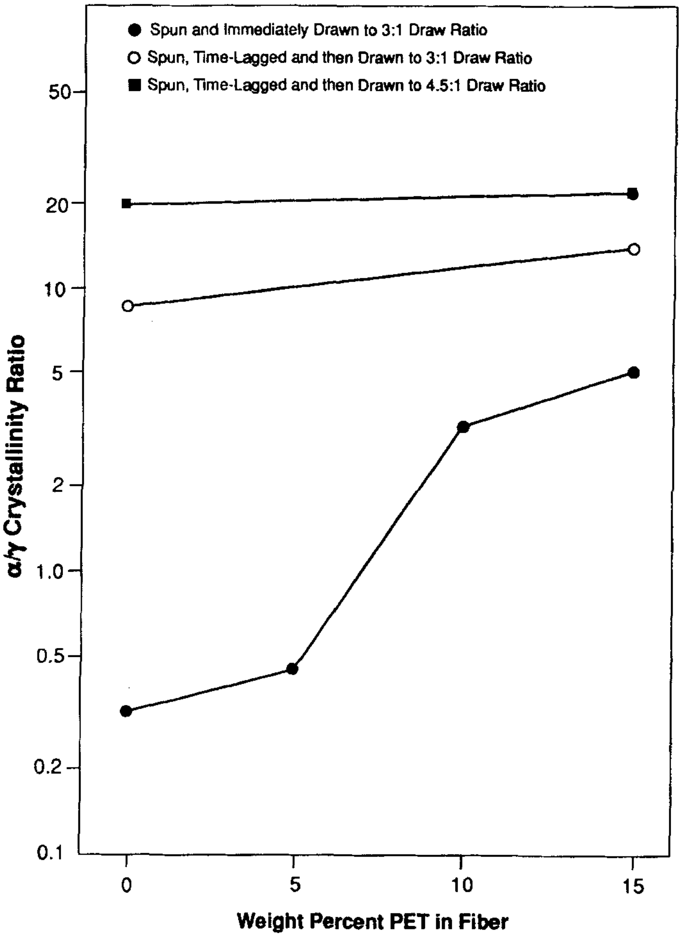
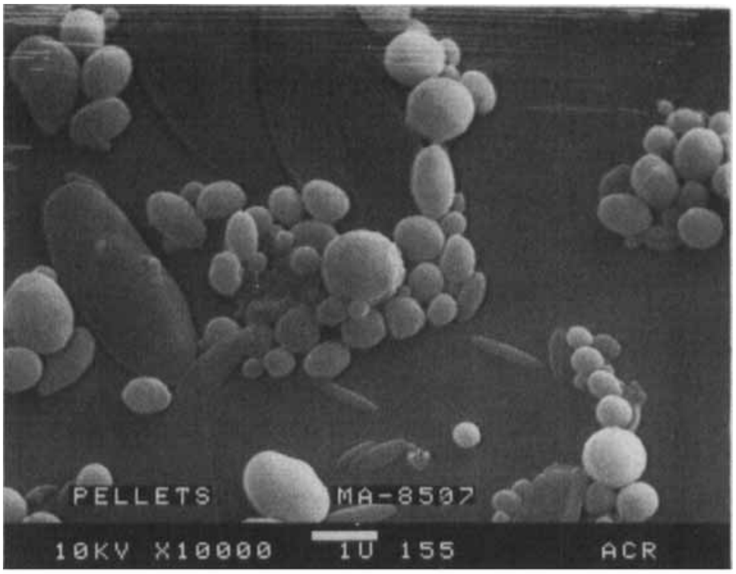


FIGURE 9 α/γ Crystallinity ratio of nylon-6 in drawn MRF's.

place. These microfibrils are smooth and clean with no attached debris. In Figure 12 are shown the PET microfibrils from systems were bonding did occur: many clumps of nylon-6 are visible attached to the PET microfibrils, which could not be removed by repeated treatments with very effective solvents selective for nylon-6.

In Figure 13, a cross-section of an MRF of nylon-6 containing 30% PET MB is shown at high magnification. This view is typical of hundreds others which were obtained from MRF's containing less



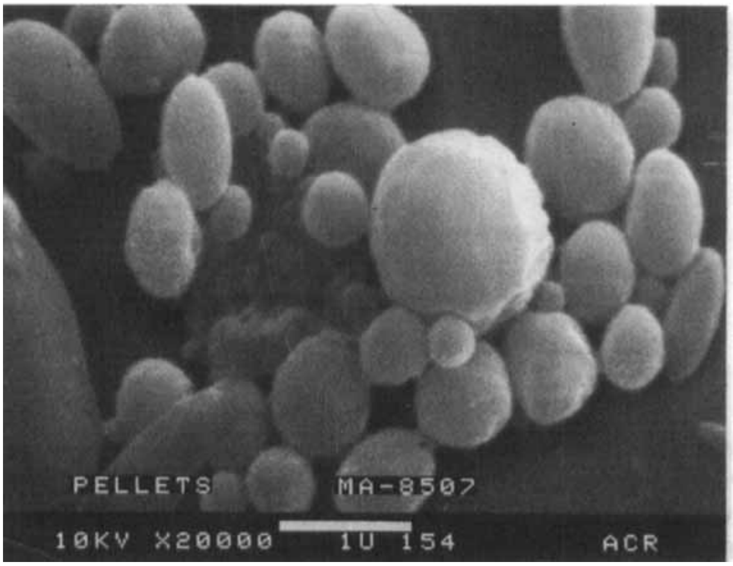


FIGURE 10 PET particles in melt-blended pellets prior to melt spinning. Original magnification by SEM: 10,000x (top) and 20,000x (bottom).

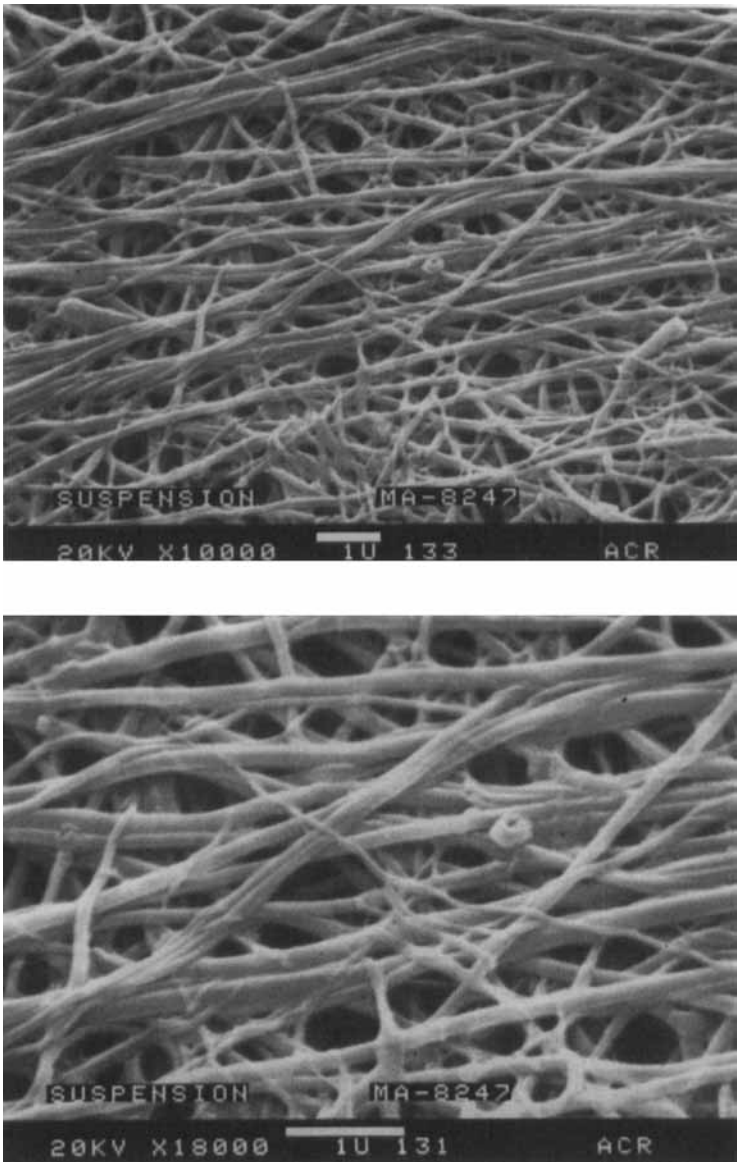


FIGURE 11 PET microfibrils with no nylon-6 attached, from MRF's containing no TPP in PET. Original magnification be SEM: 10,000x (top) and 20,000x (bottom).

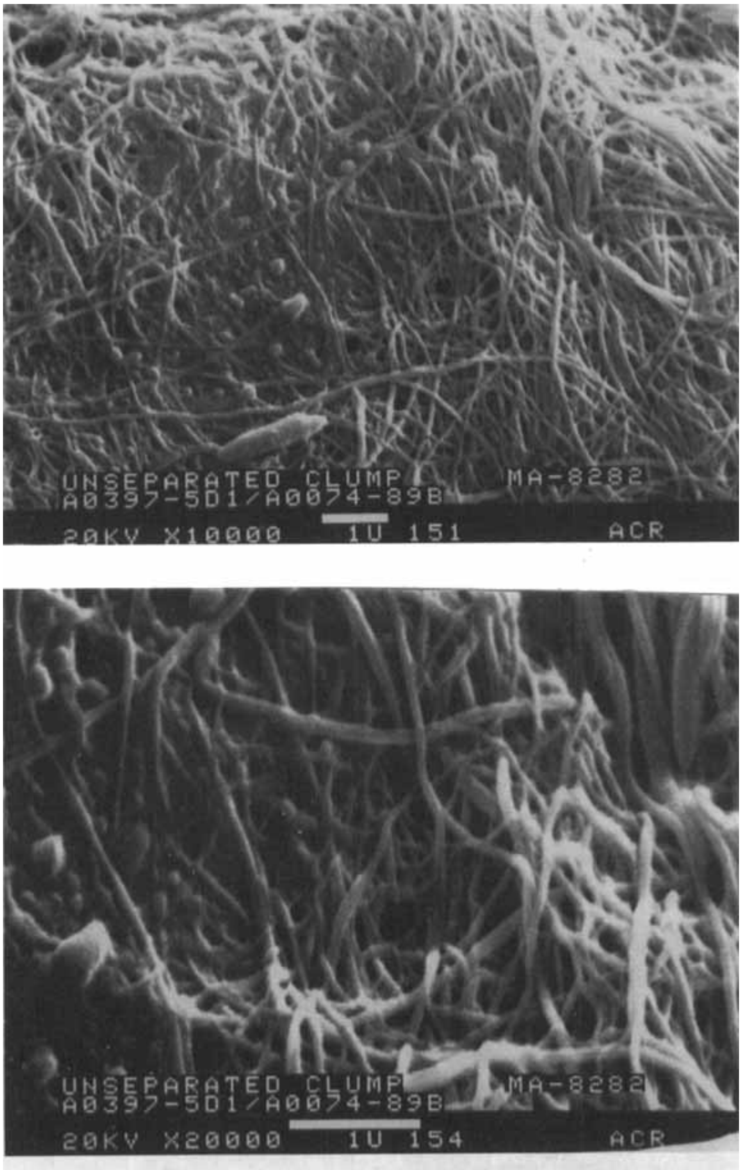


FIGURE 12 PET microfibrils with nylon-6 bonded onto their surfaces, from MRF's containing PET MB with TPP. Original magnification by SEM: 10,000x (top) and 20,000x (bottom).

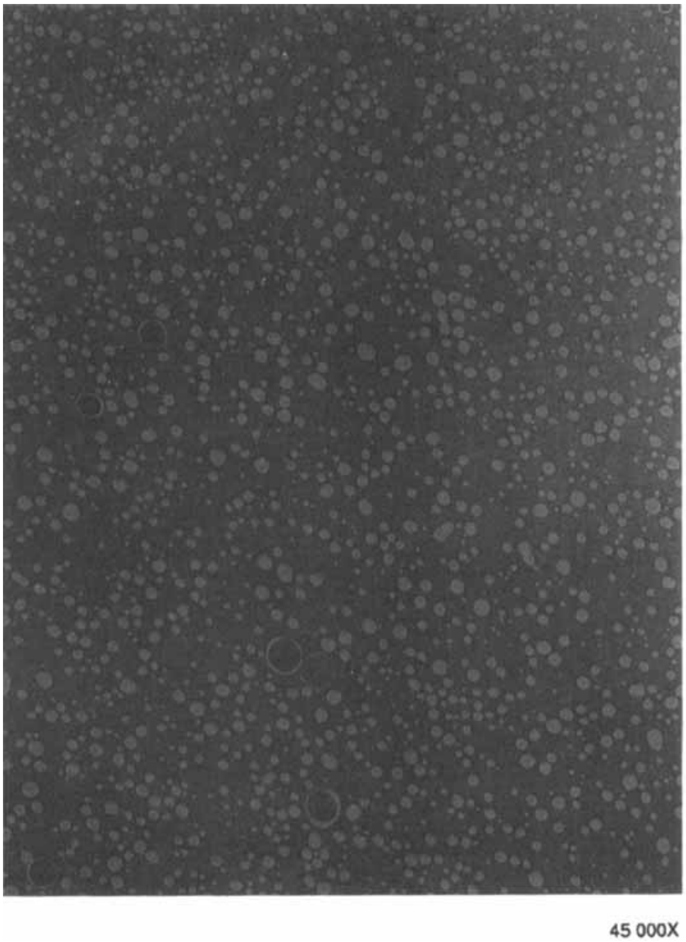


FIGURE 13 Typical cross-section of 3:1 drawn MRF containing nylon-6 (dark) and 30% PET MB (light). Original magnification by TEM: 45,000x.

that 45% PET. In practically all micrographs obtained by TEM from MRF's with less than 45% PET, the diameters of the PET microfibrils were about the same, spanning the range of $20 < d < 200$ nm. When the amount of PET MB in the MRF's reached 45% by weight, phase inversions appeared at random in various sections of the fibers, as may be seen from the characteristic Figure 14. The phase inversions took place both in the interior of individual microfibrils and in changes in the nature of the fiber matrix as a whole, from a nylon-6

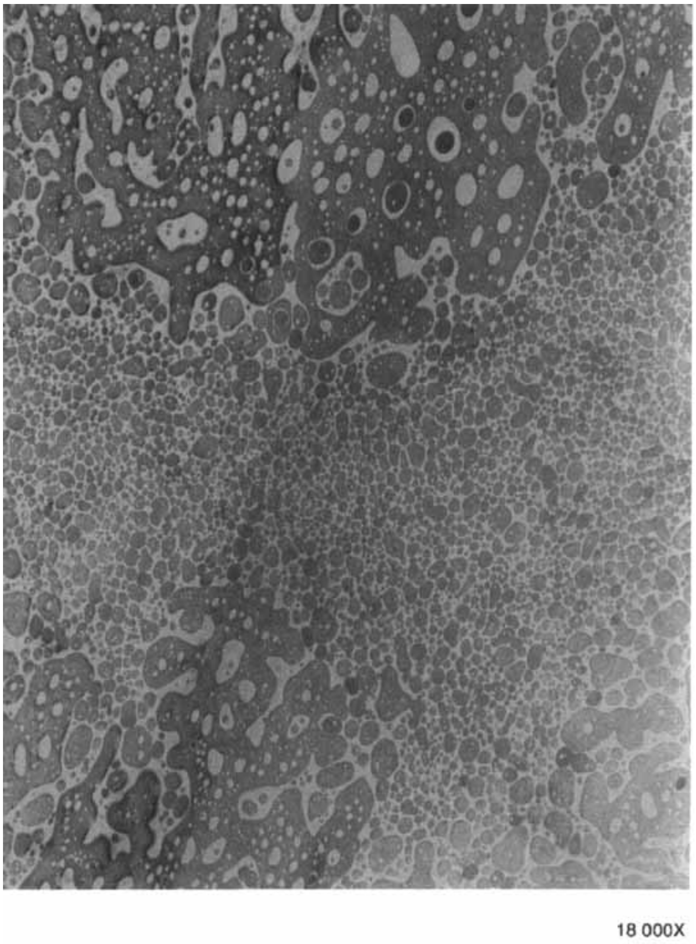


FIGURE 14 Cross section of 3:1 drawn MRF containing 55% nylon-6 (dark) and 45% PET MB (light). Original TEM magnification: 18,000x.

matrix at the top and bottom of Figure 14, to a PET matrix in its center. The complexity of the system explains the wide fluctuations and erratic inconsistencies in the mechanical properties of MRF's containing 45% PET MB.

Two important clues to the efficiency of the nylon-6 bonding to the PET. MB microfibrillar surfaces were noted during the present study. One is the fact that during sectioning and preparation of samples for

TEM studies, the cross-sectioned microfibrils remained attached to the nylon-6 matrix and never fell out. In cases where no TPP was present and/or no chemical bonding took place, the cut PET microfibrils showed a very pronounced tendency to fall out of the nylon matrix, leaving behind many voids. Such bond failures were even more dramatic in instances where, instead of cross-sectioning, longitudinal sectioning were performed in the axis direction of MRF's where no TPP was present. The second clue deals with the appearance of the MRF's. In the absence of TPP, the MRF's occasionally showed a "pearly" coloration, which never appeared when TPP and good interfacial bonding between the nylon matrix and PET microfibrils were present. We believe that the "pearly" coloration is due to the presence of thin layers of low refractive index air in between the nylon matrix and the PET microfibrils. The interfacial failure and appearance of thin air layers between the nylon and PET reflect a very poor bonding between the two polymers. The interfacial failure is eliminated to a large extent by the interfacial bonding caused by the formation of nylon-6/PET block copolymers, as a result of the presence of TPP in the PET MB.

The breaking strength of the 3:1 drawn MRF's fell in the interval of 2.5 to 4.0 g/denier. This is similar to the breaking strength of fibers of pure nylon-6. The breaking strength results and unlike the modulus result of MRF's *vs.* nylon: The tensile modulus of 3:1 drawn MRF's was about twice as high as the modulus of pure nylon drawn to the same ratio. At a draw ratio of 5:1, the breaking strength of MRF's made from BHS nylon-6 and 15% PET MB fell in the interval of 7.4 to 8.4 g/denier. As can be seen from Figure 1, the tensile modulus of MRF's are strongly influenced by both the draw ratio and the amount of PET present in the system. Comparison of our results with the literature indicates that the strength and modulus values of MRF's containing 15% PET MB and drawn to 5:1 draw ratio are comparable with the 70/30 bicomponent fibers reported by Papero *et al.* for ungrafted PET in nylon-6 [2], and are substantially higher than the values of Varma and Dhar [3] for similar compositions in the absence of interfacial chemical bonding.

During dyeing, texturizing, and heat setting, nylon-6 fibers and MRF's substantially shrinks and exhibit a large loss of tensile modulus. The ultimate strength of the fibers does not change substantially. These results are demonstrated in Table III. Here, 3:1 drawn

TABLE III Modulus and Breaking Strength (g/den) of Nylon-6 LSB MRF's, 3:1 Draw Ratio, as Function of % PET MB and 1 Hour Boiling Water Treatment

Sample Code	*% PETMB*	*Before boiling*		*After boiling*		*After boiling*	
		Modulus *g/denier*	*Strength*	*Modulus* *g/actual denier*	*Strength*	*Modulus* *g/initial denier*	*Strength*
Nylon-6 control	0	21.8	2.6	13.9	2.5	16.7	2.7
A0074-100D	15	49.8	4.0	20.2	3.3	26.8	4.2
A0593-15-2 288°C	30	36.5	2.6	22.8	2.0	35.8	3.1
A0593-15-1 282°C	30	42.0	2.6	21.9	2.4	29.5	3.1
A0593-19J1	45	52.7	2.5	32.3	2.1	54.1	3.5
A0593-19J2	45	59.3	2.6	31.3	2.2	51.0	3.2

fibers were tested as prepared and after being immersed for one full hour in boiling water. Shrinkage measurements indicated that both BHS and LSB nylon-6, drawn to 3:1 and 5:1 draw ratio, shrank about the same, namely 14.5% to 15% of their initial length. Pure PET shrinks between 3.5 and 4.4%. In the interval of zero to 45% PET, the total fiber shrinkage is more or less inversely linear with PET concentration, dropping from 15% for pure nylon-6 to 5.5–6.0% for MRF's with 45% PET. The large drop in modulus of MRF's as a consequence of exposure to boiling water is, hence, not due to shrinkage of the PET microfibrils but due to the shrinkage of the nylon-6 matrix. Since the crystallinity index of the nylon-6 generally increased somewhat [19] but never decreased by the exposure to boiling water, and because the modulus of the crystals far exceeds that of the amorphous phase, we conclude that the large drop in modulus must be due to relaxation processes taking place in the amorphous phase of the nylon-6 matrix in the MRF's. These processes are made more facile by the introduction of water into the amorphous fraction of the nylon in the fibers, and by the large reduction in the T_g of this amorphous phase. In this, and in several other respects, there is consistency between our observations and conclusions and those of Murthy and co-workers in reference [19]. Their work, however, was conducted on fibers of pure nylon-6 while our work was performed on MRF's with pure nylon-6 fibers serving as mere benchmarks for the evaluation of the effects of the reinforcement on the properties of the resulting fibers. The morphology of the PET microfibrils in our MRF's appears to be substantially different from the morphology of the oriented PET filaments in the composites created by Fakirov and associates [4–7], making it impossible to directly compare the two.

Finally, it is important to recognize that the huge change in shape of the PET inclusions during melt spinning and drawing, evident from comparison of Figures 10, 11 and 12, is largely caused by the presence of the static mixer in the extruder, by the screenpacks atop of the spinnerettes, and by the drawing process of the MRF's, and may not be attributed directly to droplet deformation during uniaxial elongational flow of the polymer melt. When the latter is the case, the system may be evaluated by methods such as Delaby's *et al.* [20], having their roots in Taylor's pioneering work on the behavior of fluid drops present in another fluid undergoing flow [21, 22].

CONCLUSIONS

1) Microfibrillar-reinforced fibers containing 15%, 20%, 25%, 30% and 45% PET MB were spun and drawn. These and other combinations were described in U.S. Patent 4,963,311 [8].
2) During the melt spinning time/temperature dependence is flexible; e.g. with barrel temperatures of 271–288°C, residence time of 150 seconds and spinnerette temperature of 260–266°C, MRF's with high interfacial bonding, constant I.V., and good filament uniformity were achieved.
3) They nylon-6 must contain at least one amine end group per chain. The PET must be masterbatched with ca. 1.5% TPP, increasing its I.V. from 0.69 to not higher than 0.80 dL/g.
4) Up to and including 30% PET MB MRF's may be easily spun and drawn to 3:1 and 5:1 draw ratio immediately or after time-lagging. At 45% PET MB massive phase inversions take place with commensurate erratic performance during processing and large fluctuations in fiber properties.
5) Chemical bonds at the interface between the PET MB microfibrils and the nylon-6 matrix were established. Spinning runs were accomplished in the presence of PET MB containing TPP. In the absence of TPP, melt dripping was a problem.
6) MRF's containing PET have higher modulus than the corresponding nylon-6 blanks. MRF's containing bonded PET MB have a modulus much higher than those containing unbonded PET.
7) At 3:1 draw ratio, the highest tensile modulus approached 60 g/denier and the highest strength was about 4.0 g/den. At 5:1 draw ratio, a tensile modulus of over 80 g/denier was achieved.
8) 3:1 drawn MRF's containing PET MB show substantial dimensional stability and retention of modulus over pure nylon-6 fibers.
9) The glass transition temperature of the nylon-6 matrix in MRF's and of pure nylon-6 fibers increases as a function of draw ratio.

Acknowledgement

It is my pleasure to acknowledge the work of A. C. Reimschuessel in performing the cryomicrotomy and obtaining the SEM and TEM photographs, the help of R. C. Morgan in the spinning and drawing of the MRF's, and that of J. T. Dunn and M. F. Martin in parts of the PET masterbatching and the DSC studies.

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