Processability and Properties of Yarns Made from Polypropylene Containing Small Amounts of Polystyrene

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SYNOPSIS

The effect of the addition of 2–8% by weight of commercial atactic polystyrene to fiber-grade polypropylene on the drawability of the multifilament yarn spun from the blends and on the mechanical properties and thermal shrinkage of the drawn yarns was studied. In the as-spun state, polystyrene is present in the form of near-spherical particles and improves the drawability and plastic deformation characteristics of the yarn. In the drawn state, with higher molecular orientation and more compact structure, the intrinsic rigidity of the polystyrene molecule manifests itself in the form of enhanced stiffness and greater creep resistance. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polypropylene is known to develop considerable crystallinity during melt spinning of the fiber itself. In an effort to produce fibers with greater shrinkage or with enhanced dyeability, it has been found helpful to add a small amount of polystyrene which reduces the crystallinity of the fiber and thereby increases its shrinkage[1,2] and also improves its texturability and dyeability.[3] The presence of atactic polystyrene in polypropylene was also found to substantially reduce the shear viscosity[4,5] of the melt of the blended polymer. Similar observations have been made by Shimizu et al.[6,7] with polystyrene contents of about 10% and above in polypropylene and they also showed that the samples spun from the blends have lower birefringence. It was suggested by Han and Yu[4,5] that the weak interactive forces acting across the interface boundary of the incompatible blend system can result in the ease of slippage of the matrix phase along the interface, thereby resulting in lower shear viscosity. A similar explanation was also offered to account for the enhanced extensibility of the drawn samples[8] in the direction of drawing at elevated temperatures of about 140°C.

The present studies formed a part of an ongoing project on industrial fabrics in which attempts were made to develop a creep-resistant polypropylene fiber. One method which aims at achieving this objective was to blend polypropylene with 2–8% by weight of commercial atactic polystyrene and to produce fibers from these blends by spinning and drawing. These studies resulted in some very interesting and useful observations. These are described and discussed in this article.

EXPERIMENTAL

Sample Preparation

Commercial-grade polypropylene granules of the Shell Co. of a melt flow index (MFI) of 20 were used to prepare melt-spun yarn (PP) on a pilot-scale Fourne melt spinning plant (SST-1207) at a spinning temperature of 260°C, a throughput rate of 17.3 g min^{-1}, and a takeup velocity of 750 m min^{-1} through two spinnerets containing 26 holes, each of 0.3 mm diameter. The blended yarn samples were obtained by first dry-mixing polypropylene with 2, 5, and 8% by weight of atactic polystyrene (grade SF-1) manufactured by Polychem, Bombay, and then melt spinning the blends under identical conditions of spinning.

The spun yarns were then drawn on a two-zone laboratory-scale drawing machine to draw ratios of

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3.7 and 4.4, respectively, under the conditions listed in Table I. The sample code description and the conditions of spinning and drawing used to produce the various samples are also included in the table. Another drawn sample was obtained from the blended yarn containing 5% by weight of polystyrene by drawing the as-spun yarn to a draw ratio of 5.1 (PP5PS5.1). Equivalent polypropylene yarn of this draw ratio could not be prepared.

Spinning Stress

The spinning tension in the multifilament yarns was measured during melt spinning of the polypropylene and blended yarns by using a Schmidt tensiometer at a distance of 1.5 m from the spinneret exit and just before the first godet. The area of the cross section of the spun samples was later measured to compute the spinning stress. The data obtained are given in Table II along with the various other structural and mechanical characteristics of the samples as described below.

Birefringence

The birefringence values for the various samples were obtained with the help of a polarizing microscope fitted with a tilting compensator.

Boiling Water Shrinkage

The different spun samples and the various drawn samples were immersed in boiling water for 5 min and the percentage shrinkage was estimated from the measured change in length.

Density and Density Crystallinity

A Davenport density gradient column prepared from isopropanol and diethylene glycol was used to measure the density of the samples. The mass fraction crystallinity (β_ρ) was determined from the measured density (ρ) using the following expression[9]:

$$\beta_\rho = \frac{\rho_c}{\rho} \cdot \frac{(\rho - \rho_{am})}{(\rho_c - \rho_{am})} \qquad (1)$$

where ρ_c and ρ_{am} are the densities of the crystalline and amorphous fractions and were taken to be 0.946 and 0.854 g cm^{-3}, respectively.[9]

To estimate the density of the polypropylene portion in the blended samples, the following procedure was adopted:

(i) The rule of mixtures was first applied to compute the average density of the polypropylene fraction (ρ_{pp}) by using the following expression:

Table I   Sample Code and Conditions of Spinning and Drawing

Sample Code	Amount of Polystyrene (Wt %)	Wind-up Speed (m/min)	First-zone Draw Ratio (Draw Temperature)	Second-zone Draw Ratio (Draw Temperature)	Total Draw Ratio
As-spun yarns					
PP	—	750	—	—	—
PP2PS	2	750	—	—	—
PP5PS	5	750	—	—	—
PP8PS	8	750	—	—	—
Drawn yarns					
PP3.7	—	750	2.74 (70°C)	1.35 (130°C)	3.7
PP2PS3.7	2	750	2.74 (70°C)	1.35 (130°C)	3.7
PP5PS3.7	5	750	2.74 (70°C)	1.35 (130°C)	3.7
PP8PS3.7	8	750	2.74 (70°C)	1.35 (130°C)	3.7
PP4.4	—	750	2.74 (70°C)	1.66 (130°C)	4.4
PP2PS4.4	2	750	2.74 (70°C)	1.66 (130°C)	4.4
PP5PS4.4	5	750	2.74 (70°C)	1.66 (130°C)	4.4
PP8PS4.4	8	750	2.74 (70°C)	1.66 (130°C)	4.4
PP5PS5.1	5	750	5.1 (130°C)	—	5.1

Table II   Characteristics of the As-spun Samples

	PP	PP2PS	PP5PS	PP8PS
Density (g cm^{-3})	0.897	0.899	0.904	0.906
Density of the polypropylene part (g cm^{-3})	—	0.896	0.897	0.894
Crystallinity (%)				
Density	49.2	48.4	49.1	46.4
X-ray	41.3	38.4	36.4	33.1
Birefringence	0.007	0.004	0.003	—
Spinning stress (MPa)	5.2	4.84	4.7	4.14
Boiling water shrinkage (%)	6	4	2.7	4
Modulus (g den^{-1})	20.9	20.4	19.8	20.6
Nominal tenacity (g den^{-1})	1.47	0.7	0.45	0.53
Extension to break (%)	230	400	540	570
T_g peak (°C)				
DSC	3.7	—	−0.7	—
Torsional pendulum	3.8	—	−11.5	—

$$\frac{1}{\rho_{\text{blend}}} = \frac{W_{f_{\text{pp}}}}{\rho_{\text{pp}}} + \frac{W_{f_{\text{ps}}}}{\rho_{\text{ps}}} \qquad (2)$$

where W_f represents the weight fraction and the suffixes ps, pp, and blend refer to polystyrene, polypropylene, and the blend sample. The density of the polystyrene fraction was taken to be 1.065 g cm^{-3} for all the blended samples.[10]

(ii) Using the estimated density ρ_{pp}, the weight fraction density crystallinity (β_p) was estimated using eq. (1).

X-ray Diffraction Studies

X-ray diffraction studies were made by using the powder technique for the spun as well as the drawn samples on a Philips X-ray diffractometer using CuKα radiation. Information on crystalline form and percentage crystallinity was obtained from the I-2θ plots. For estimating X-ray crystallinity, the method suggested by Farrow[11,12] was used.

Infrared Spectroscopy

The infrared spectroscopic studies were made primarily to obtain a qualitative estimate of the orientation of the polystyrene molecules in the yarns prepared from the blends of polypropylene with 5% by weight of polystyrene of draw ratios 1 (as-spun), 3.7, 4.4, and 5.1. For this purpose, the absorption band at 699 cm^{-1}, which arises from the out-of-plane bending mode of the phenyl ring C — H bond,[13] was studied on a Jasco Fourier transform infrared (FTIR) spectrometer Model Micro FT/IR-200 using

polarized infrared radiation in the parallel and perpendicular directions with reference to the fiber axis direction. This band has been assigned as a pure mode,[13] i.e., its intensity is not coupled to any other infrared stretching, bending, or wagging mode frequency. Also, at this frequency, the polypropylene sample does not show any absorption band.

The following two estimates of orientation of the polystyrene molecules in the blended yarns were obtained from the polarized infrared spectra, using standard procedures,[14] the sample being mounted on a window and obtaining the spectra in the transmission mode: (a) the ratio of the areas (R_A) of the 699 cm^{-1} parallel and perpendicular absorption bands above the base line, viz., $R_A = (area)_{||}/(area)_{\perp}$ and (b) the ratio of peak heights (R_H) of the 699 cm^{-1} parallel and perpendicular absorption bands above the base line, viz., $R_H = (height)_{||}/(height)_{\perp}$.

Tensile Testing

Tensile tests were made on the as-spun and drawn yarns at room temperature on an Instron tensile testing machine (Model 4202). The sample length was 100 mm and the strain rate 1 min^{-1}. From the stress–strain plots, the modulus, nominal tenacity, and percentage extension at break were estimated. The as-spun polypropylene yarn was subjected to further tensile studies on another Instron tensile testing machine, Model 1112, with the provision to mount an environmental chamber to ascertain the role of strain rate and temperature on the extensibility of the sample. For this purpose, tensile tests were first carried out at room temperature at strain rates of 0.025, 0.05, 0.25, and 0.5 min^{-1}. Next, the

tensile stress–strain characteristics of the as-spun polypropylene yarn were studied at 50, 60, 70, 100, and 130°C in addition to the room-temperature test at a constant strain rate of 1 min^{-1}. The environmental chamber was preheated to the required temperature before mounting the sample between two clamps; it maintained the required temperature within an accuracy of ±1°C.

Creep and Recovery

A Stanton Redcroft thermomechanical analyzer was suitably modified to carry out isothermal creep and recovery experiments. The setup allowed temperature control up to an accuracy of ±0.1°C and the procedure for loading and unloading was very rapid but gentle. The change in length was accurately measured with the help of a transducer. The creep and recovery experiments were carried out at a temperature of 35°C. The samples were subjected to creep under a stress of 25.3 MPa for 4 h and the recovery from creep was measured for about 40 h.

Scanning Electron Microscopy

The cross sections of the following samples were prepared as described below and examined on a Cambridge scanning electron microscope (SEM Stereoscan 360): (a) The as-spun filaments prepared from polypropylene and polypropylene containing 5% by weight of polystyrene were fractured by pulling them axially in a liquid nitrogen bath, and (b) the filaments prepared by drawing the as-spun blended filament of polypropylene containing 5% by weight of polystyrene to draw ratios of 2, 3.7, 4.4, and 5.1 were fractured by cutting them transversely with a fresh razor blade. The cross sections obtained through procedures (a) and (b) were immersed in tetrahydrofuran for 2 h to etch away the polystyrene and the etched cross sections were then coated with silver before being examined on the SEM.

Glass Transition Temperature (T_g)

The glass transition temperatures of some of the samples were measured either by dynamic mechanical means or on a differential scanning calorimeter (DSC). The glass transition temperatures of the spun samples, PP and PP5PS, and the drawn sample, PP5PS5.1, were ascertained from the peaks of the tan δ curves obtained at a frequency of about 2 Hz on a torsion pendulum described in detail elsewhere.[15] The glass transition temperatures of the samples PP4.4 and PP5PS4.4 were taken as the

peaks of the tan δ curves obtained on a Rheovibron at a frequency of 3.5 Hz. A Mettler differential scanning calorimeter (DSC), Model FP85, was used to ascertain the glass transition temperature of the samples PP and PP5PS by carrying out low-temperature DSC experiments by purging the sample container with a refrigerant. In each case, two to five experiments were made to confirm that the results were reproducible. The emphasis in these studies was on a comparison of the differences between the polypropylene yarn and the blended yarn containing 5% by weight of polystyrene both in the undrawn and drawn states. The T_g studies have therefore not been made on all the samples.

RESULTS AND DISCUSSION

Spun Samples

Structural and Mechanical Characteristics of the Spun Yarns

The as-spun samples show some important differences in their structural and mechanical characteristics as is evident from the data presented in Table II. The blended samples register an increase in density with increase in polystyrene content because of the relatively higher density of polystyrene. However, the slight decrease in density of the polypropylene part (ρ_{pp}) in the blended samples is indicative of reduced compactness or packing of molecules in these samples apparently due to the presence of the dispersed polystyrene phase. The reduction in crystallinity and orientation with increase in polystyrene content is also significant.

The presence of polystyrene has been found to influence the behavior of the blended system right from the extrusion stage, wherein the polystyrene is known to reduce the shear viscosity of the blended melt due to the poor compatibility across the interface resulting in slippage of the matrix polypropylene phase along the interface.[4,5] This effect appears to be present even during extensional flow in the spinline, which is reflected in the reduced spinline stress (Table II), and since the birefringence of the sample (Δn) is related to the spinline stress (σ) through the stress optical law ($\Delta n = C_{op}\sigma$, where C_{op} is the stress optical coefficient), it is not surprising that the birefringence of the blended spun samples reduces progressively with increase in polystyrene content. It may be added that since, as shown later, polystyrene is in the isotropic state in the as-spun samples, it will not contribute to the measured birefringence. The form birefringence contribution in the present
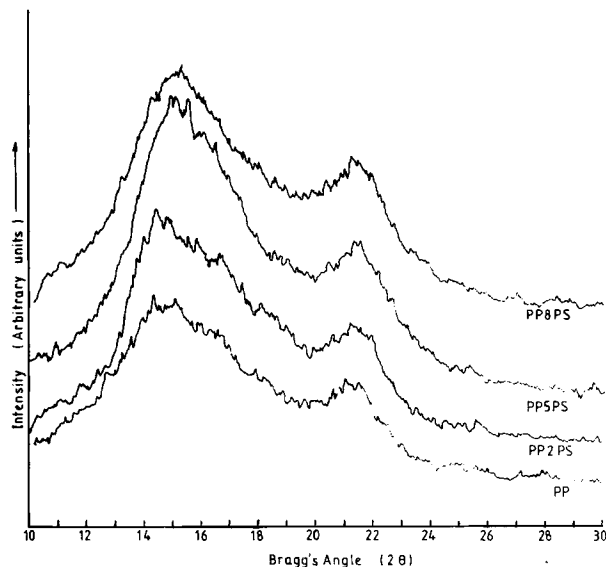
Figure 1 I-2θ plots of the as-spun polypropylene and blended samples.

case is likely to be small, as reported in the literature.[7]

The presence of polystyrene can affect the spinline stress by two routes: First, the deformation can occur at lower stresses due to the reduction in the viscosity of the system,[4-7] which, in turn, can lower the orientation and cause a shift in the temperature of onset of crystallization to lower temperatures. Second, the lower crystallization rate and lower crystallinity that follow can themselves result in a further reduction of the spinline tension since the extensional viscosity would be a strong function of crystallinity. The two effects working together can effectively reduce the spinline tension. The lower boiling water shrinkage of the as-spun blended samples compared to that of the corresponding as-spun polypropylene yarn (Table II) obviously relates to the lower residual stress in the former and provides supporting evidence for the lower spinline tension and the lower birefringence in these samples. The lower crystallinity and orientation of the as-spun blended samples would also contribute to the lower tenacity and higher extension to break of these samples. These differences in structural and mechanical characteristics between the samples with and without polystyrene can also be considered as a manifestation of the state of aggregation of polystyrene and its interaction with the polypropylene matrix in the as-spun blended samples. The lower glass transition temperature of the as-spun blended sample containing 5% by weight of polystyrene compared to that of the as-spun polypropylene sam-

ple, as observed from both the techniques used, is noteworthy. While the differences in crystallinity, crystal size, and orientation will undoubtedly be expected to affect T_g, the weak interactive forces acting across the interface boundary of the incompatible blend system[4,5] could also contribute to it. The T_g of the polystyrene around 100°C could not be located in the blended samples, apparently because the former was present in rather small quantity in these samples.

The I-2θ plots of the as-spun yarns (Fig. 1) show an interesting feature. While the as-spun polypropylene yarn shows peaks associated with the monoclinic crystalline form along with the peaks of the metastable pseudohexagonal (smectic) form, the incorporation of increasing amounts of polystyrene results in the blended samples moving toward a predominantly pseudohexagonal crystalline form. It would be expected that the lower spinline stress can lower the temperature of onset of crystallization and lead to the predominantly pseudohexagonal form. This can have important consequences on properties, as will be discussed later.

The scanning electron micrographs of the fracture surface of as-spun polypropylene sample, treated with tetrahydrofuran (THF) for 2 h [Fig. 2(a) and (b)], show some noteworthy differences when compared with the micrographs of the fracture surface of THF-treated as-spun blended sample containing 5% by weight of atactic polystyrene [Fig. 2(c) and (d)]. It is obvious that in the latter sample polystyrene is present in the form of near-spherical particles of about 0.5–1 μm size. This is consistent with the present thinking on how morphology initially develops during polymer–polymer blending.[16] These spherical particles can act like a plasticizer by keeping the molecular chains of polypropylene in the amorphous phase apart.

Drawability Characteristics of Spun Yarns

The stress–strain curves of the as-spun samples shown in Figure 3 bring out the substantial improvement in drawability of the blended samples, which show an extension to break of 400–570%, in comparison with the polypropylene sample, which shows an extension to break of 230%. The blended samples also display a more distinct yield point and enhanced plastic deformation with relatively less strain hardening prior to failure. In contrast, the polypropylene sample reveals a more prominent strain-hardening effect and the extent of plastic deformation is also much less. It has been pointed out[17] that as the degree of orientation increases the dif-
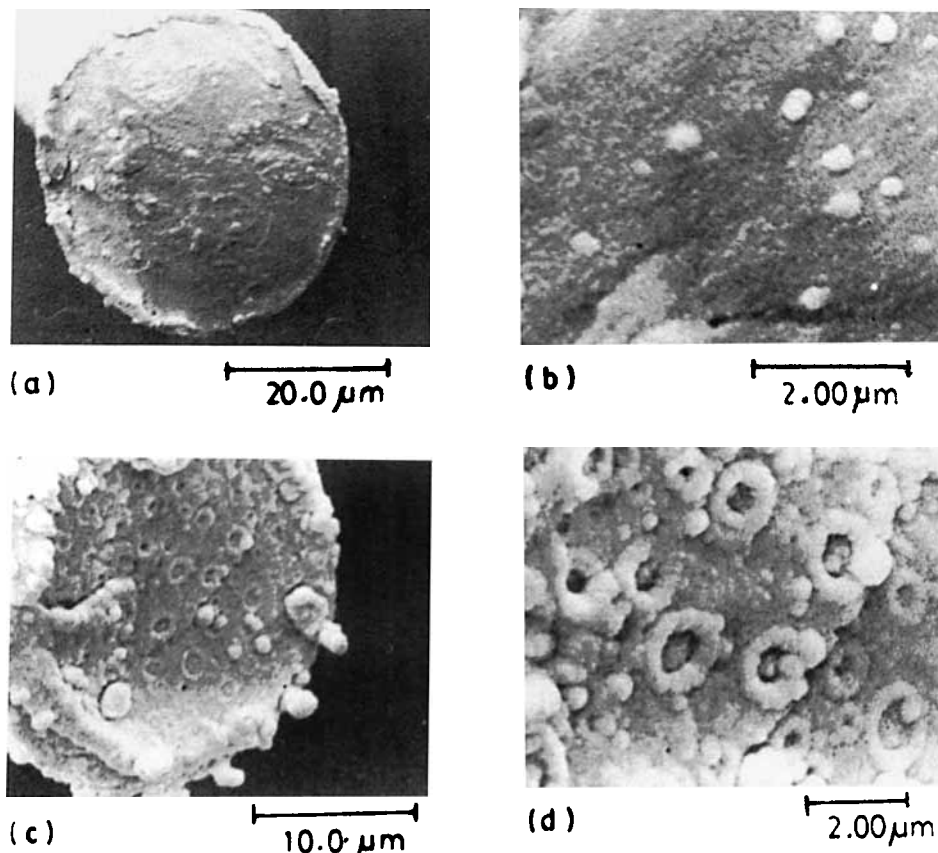
Figure 2 Scanning electron micrographs of as-spun samples fractured in liquid nitrogen and immersed in tetrahydrofuran for 2 h: (a, b) as-spun polypropylene sample (PP); (c, d) as-spun polypropylene blended with 5% polystyrene.

ferences in stiffness of the bulk material before and after subsequent yielding become less noticeable, resulting in a more indiscrete yield point, as observed. It can also be noticed from figure 3 that the natural draw ratio is higher in the samples contain-
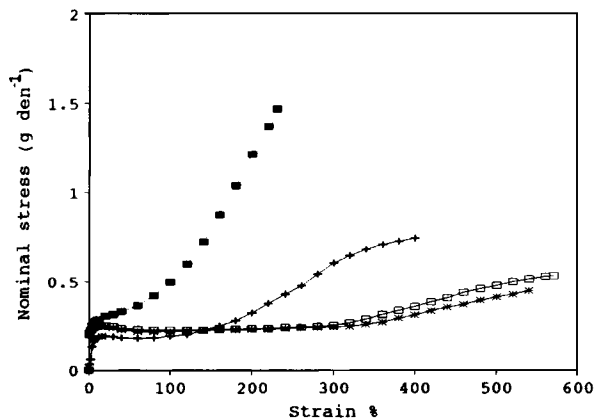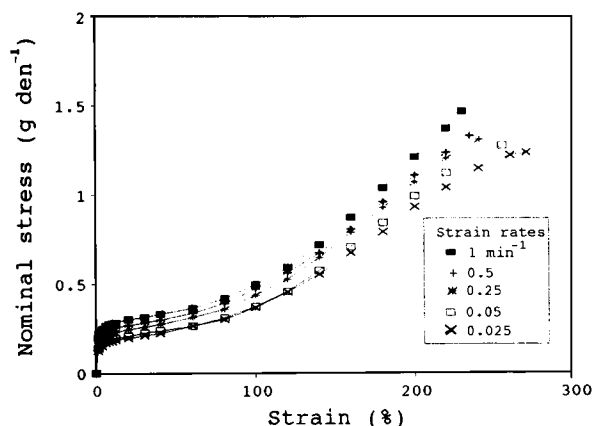

Figure 3 Nominal stress–strain curves of as-spun samples: (■) PP; (+) PP2PS; (*) PP5PS; (□) PP8PS.

ing more polystyrene. It has been suggested that the incompatible nature of the blend composition leads to weak interactions across the phase interface[4-6] which is responsible for easy slippage of the matrix polypropylene phase along the interface, thus resulting in enhanced plastic deformation at relatively lower stresses. As shown earlier (Table II), the as-spun blended sample PP5PS has a lower glass transition temperature compared to the as-spun polypropylene sample, which supports the possibility of plasticization of polypropylene by polystyrene. Further, it has also been pointed out that the nature of packing in the crystalline domains has an important role to play on the yield behavior and the extent of plastic deformation that occurs.[18-20] The presence of a predominantly pseudohexagonal crystalline order in the as-spun blended samples (Fig. 1) would be expected to facilitate the plastic deformation due to the metastable nature of the crystal form[18] and also due to the much lower density of the pseudohexagonal form (0.916 g cm^{-3}) in comparison to that of the monoclinic crystal form[9] (0.946 g cm^{-3}). Such
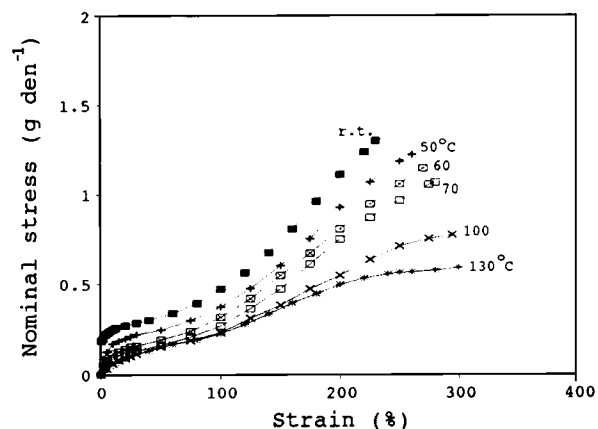
effects have also been reported in the literature with regard to the hexagonal β phase of polypropylene,[19,20] which incidentally also has a lower density[9] (0.926 g cm^{-3}) compared to the monoclinic crystal form. On the other hand, the presence of higher orientation, higher crystallinity, and the greater extent of the α-monoclinic crystal form in the as-spun polypropylene yarn could all be responsible for lower drawability and the lack of a clear yield point. In fact, the polypropylene sample displays substantial amount of strain hardening prior to failure (Fig. 3).

Strain Rate and Temperature Dependence of Tensile Behavior of As-spun Polypropylene Yarn

The stress–strain curves of the as-spun polypropylene yarn obtained under room-temperature conditions at various strain rates are shown in Figure 4. The sample displays a small, gradual increase in its extensibility and a lowering of the yield stress as the strain rate decreases. The sample also shows a decrease in tenacity (and also in modulus) with decreasing strain rate. The extension to break at the lowest strain rate studied, viz., 0.025 min^{-1}, shows an increase to about 270% from 230% obtained at a strain rate of 1 min^{-1}. The effect of temperature on the stress–strain behavior of the as-spun polypropylene yarn at a strain rate of 1 min^{-1} is shown in Figure 5. It can be observed that at higher temperatures the sample shows a reduction in modulus, yield stress, and tenacity, while increasing the extension to break to about 300% at a temperature of 130°C. It is interesting to compare the stress–strain curves of the as-spun blended yarns at room temperature (Fig. 3) with those of the as-spun polypropylene yarn between room temperature and 130°C
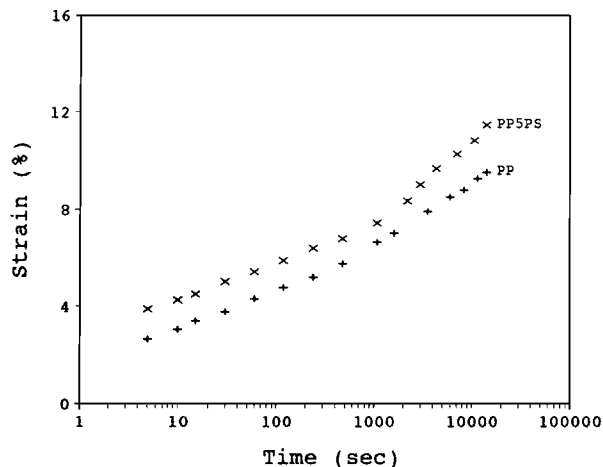

Figure 5   Nominal stress–strain curves of as-spun polypropylene yarn obtained at various temperatures at a strain rate of 1 min^{-1}.

(Fig. 5). It is interesting to note that compared to the effects of an increase in temperature the mechanical properties are more affected by the incorporation of small amounts of polystyrene. This difference may be explained as follows: Polystyrene is dispersed in the form of near-spherical particles in the amorphous phase of as-spun polypropylene yarn (Fig. 2) and the weak interactive forces acting across the interface boundary can result in ease of slippage of the matrix phase along the interface. In addition, as shown in Figure 1, the presence of polystyrene also results in the blended fibers moving toward a predominantly pseudohexagonal structure which is less dense, thus rendering the crystallites to be more drawable. Increase of temperature, on the other hand, assists in transforming the structure to the more stable α-form which shows strain-hardening characteristics.

Creep Behavior of As-spun Samples

A creep experiment carried out at a stress of 25.3 MPa at a temperature of 35°C on polypropylene and PP5PS (Fig. 6) as-spun yarns also clearly brings out the greater extent of deformation that occurs in the blended sample in comparison to that in the polypropylene spun yarn. This observation is consistent with that reported by Turner[21] regarding the enhanced creep deformation in the quenched sample which has a low density, indicating the presence of a predominantly pseudohexagonal crystal form in comparison to the annealed polypropylene sample whose density suggests the presence of the stabler α-monoclinic crystal form.
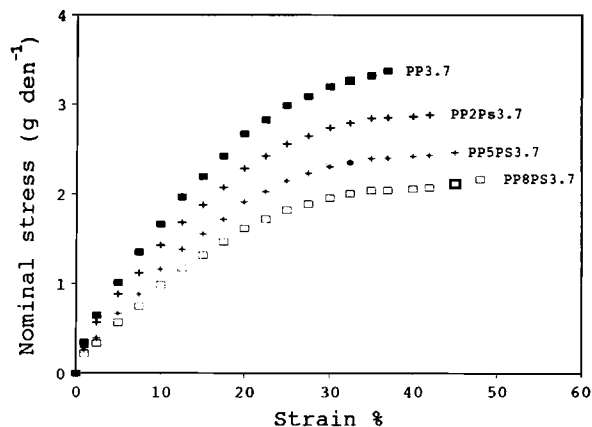

Figure 4   Nominal stress–strain curves of as-spun polypropylene yarn obtained at various strain rates at room temperature.

Figure 6 Creep of as-spun yarns made from polypropylene and polypropylene blended with 5% polystyrene at 35°C, stress of 25.3 MPa for 4 h.

Figure 7 Nominal stress–strain plots of yarns of draw ratio 3.7 made from polypropylene and its blends with various amounts of polystyrene.

Drawn Samples

Structural and Mechanical Characteristics of the Drawn Samples

As shown in Table I, the as-spun samples of polypropylene and of the three blends of polypropylene with varying amounts of polystyrene were all drawn to total draw ratios of 3.7 and 4.4, respectively. In addition, the sample containing 5% by weight of polystyrene was also drawn to a draw ratio of 5.1. The structural and mechanical characteristics of these various samples will be considered briefly in this subsection.

The structural and mechanical data on samples of draw ratio 3.7 are presented in Table III while their stress–strain curves are shown in Figure 7. As expected, the blended samples have higher density but the lower density of polypropylene portion is noteworthy. The blended samples have lower crystallinity values, as expected. The average molecular

orientation, as represented by birefringence, is also relatively lower in the blended samples. As stated earlier, the form birefringence contribution will be expected to be small. However, since the intrinsic birefringence of polystyrene[22] is −0.1, the oriented polystyrene molecules may make a small negative contribution to the measured birefringence. No attempt has been made to estimate their contribution. The boiling water shrinkage values of the blended yarns show an increase with increase in the polystyrene content. It may be recalled that in the case of as-spun samples the blended samples showed lower boiling water shrinkage compared to the as-spun polypropylene sample. The higher boiling water shrinkage of the blended samples in the present case will at least partly be related to their greater amorphous content. However, the crystallinity changes are rather small compared to the differences in shrinkage. To obtain more insight into this problem, the scanning electron micrographs of the THF-treated cross sections of the samples of draw ratio

Table III   Characteristics of 3.7 Draw Ratio Samples

	PP3.7	PP2PS3.7	PP5PS3.7	PP8PS3.7
Density (g cm⁻³)	0.904	0.905	0.907	0.909
Density of the polypropylene part (g cm⁻³)	—	0.902	0.900	0.898
Crystallinity (%)				
Density	56.9	55	52.5	49.9
X-ray	45.1	43.3	40.6	—
Birefringence	0.037	0.033	0.033	0.032
Boiling water shrinkage (%)	6.5	8	8.5	14.9
Modulus (g den⁻¹)	34.6	29.1	26.4	21.9
Nominal tenacity (g den⁻¹)	3.37	2.86	2.46	2.11
Extension to break (%)	37	42	45	50

2, 3.7, 4.4, and 5.1 were obtained and are presented in Figure 8(a), (b), (c), and (d), respectively. It is interesting to note that while in the sample of draw ratio 2 polystyrene particles are still present the micrographs of samples of higher draw ratio indicate that the structure is now typical of an oriented polymer system. As the extension ratio increases, the layered structure becomes more compact and spherical particles of polystyrene can no longer be located. The oriented polystyrene molecules will all be expected to be trapped in the amorphous regions of the fiber, and as the contracting segments exert entropic forces, there is likely to be enhancement of boiling water shrinkage, as is observed to be the case.

Before discussing the mechanical data as given in Table III of draw ratio 3.7, it will be worthwhile examining the structural and mechanical data for samples of draw ratio 4.4 given in Table IV and their stress–strain behavior shown in Fig. 9. The density, crystallinity, birefringence, and boiling water shrinkage data for these samples follow the same trends as have been discussed for samples of draw

ratio 3.7. However, the mechanical data for the two sets of samples show a very interesting feature which deserves detailed consideration. While discussing these data, it should be kept in mind that the Young's modulus of polystyrene is much higher than that of polypropylene both in the unoriented and oriented states.[7] Against this backdrop, it is noteworthy that while in the case of draw ratio 3.7 the blended samples have inferior mechanical properties compared to the polypropylene yarn of the corresponding draw ratio (Table III and Fig. 7), the blended samples of draw ratio 4.4 have superior mechanical properties compared to the polypropylene yarn of the corresponding draw ratio (Table IV and Fig. 9), except the blended sample containing 8 parts by weight of polystyrene in which case the reduction in crystallinity and orientation appear to have a predominant effect on mechanical properties. It is also noteworthy that the T_g of the blended yarn of draw ratio 4.4 is higher than the T_g of the corresponding polypropylene sample. Thus, in a sample of draw ratio 4.4, the oriented polystyrene molecules

(a)   2.00 μm   **(b)**   2.00 μm
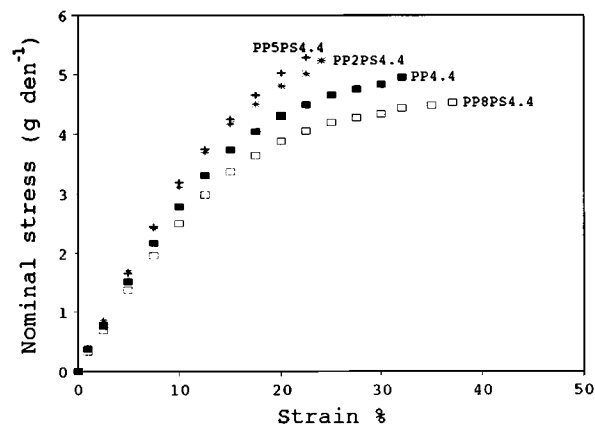
(c)   2.00 μm   **(d)**   2.00 μm
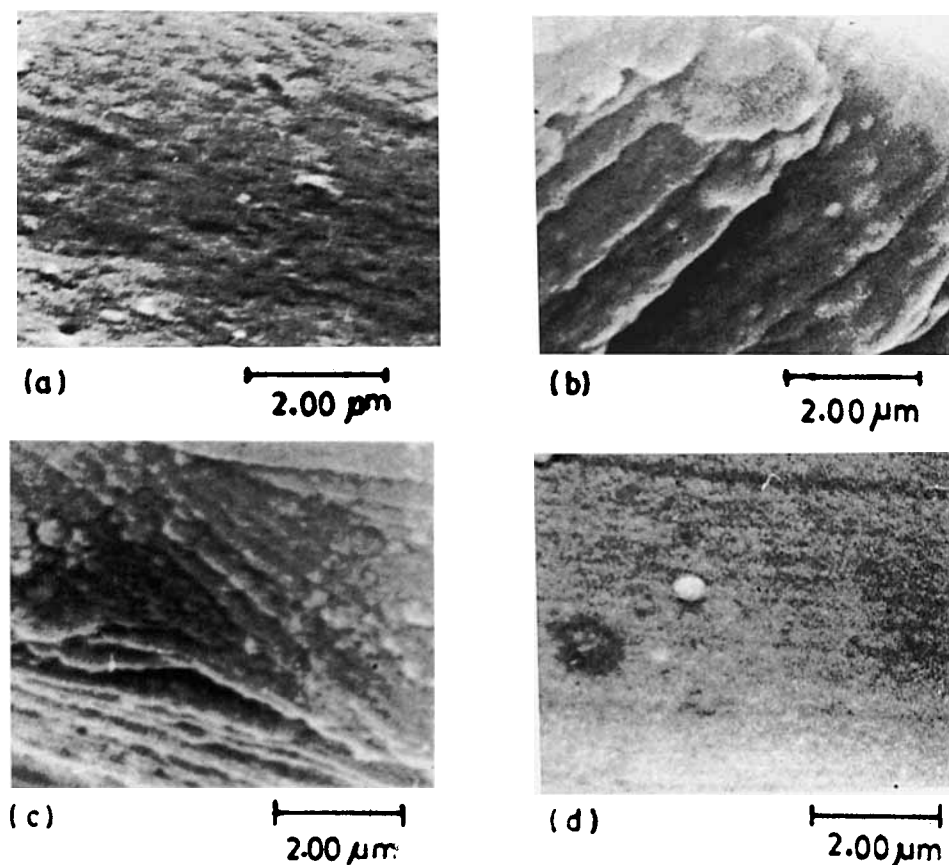
Figure 8   Scanning electron micrographs of cross sections of samples obtained by drawing yarns of polypropylene blended with 5% polystyrene to various draw ratios and then cutting them and immersing in tetrahydrofuran for 2 h. Draw ratios: (a) 2; (b) 3.7; (c) 4.4; (d) 5.1.

Table IV   **Characteristics of 4.4 Draw Ratio Samples**

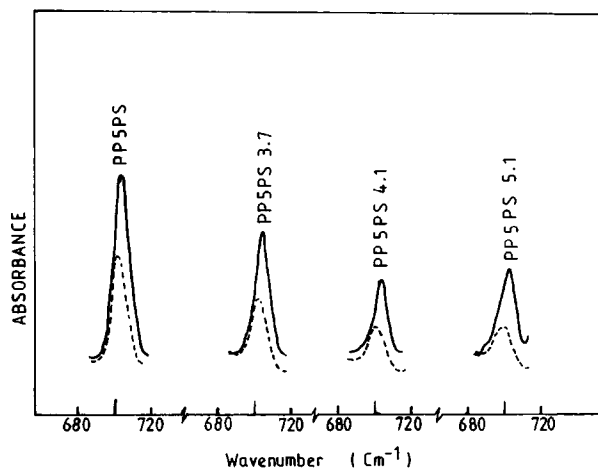|	PP4.4	PP2PS4.4	PP5PS4.4	PP8PS4.4
Density (g cm^{-3})	0.907	0.908	0.909	0.911
Density of the polypropylene part (g cm^{-3})	—	0.905	0.902	0.900
Crystallinity (%)				
Density	60.1	58.2	54.8	52.2
X-ray	52.5	47	46	43
Birefringence	0.039	0.034	0.035	0.033
Boiling water shrinkage (%)	8.5	9.5	9.7	12.3
Modulus (g den^{-1})	37.5	38.6	40.6	33.4
Nominal tenacity (g den^{-1})	4.95	5.29	5.23	4.53
Extension to break (%)	32	22	24	38
T_g peak (°C)				
Rheovibron	8.6	—	11.4	—

reinforce the structure and make it more rigid and stronger, the effect being more pronounced in the sample containing 5% by weight of polystyrene. The explanation given above receives strong support from the data obtained from the infrared studies. The absorption peak at 699 cm^{-1} arises from the out-of-plane bending mode of the phenyl ring C — H bond, and as shown in Figure 10, the absorption peak is very sharp, even though polystyrene is present only to the extent of 5% in the blended yarns. The differences in absorption in the parallel and perpendicular directions shows a very clear trend as the draw ratio increases, and as shown in Figure 11, the peak height ratio (R_H) and the absorption band area ratio (R_A), which are related to orientation of the polystyrene molecule in the blended fibers of different draw ratios, show a significant increase beyond a draw ratio of 3.7. This correlates very well with the mechanical data presented earlier.

The I-2θ plots for samples of draw ratios 3.7 and 4.4 are presented in Figure 12(a) and (b), respectively. It may also be observed from Figure 12(a) that the X-ray diffraction patterns of the 3.7 draw ratio samples show features similar to those observed with the as-spun samples in Figure 1. As the amount of polystyrene increases, the samples [Fig. 12(a)] display a gradual shift in the X-ray diffraction patterns from a monoclinic crystalline form in the polypropylene sample toward a higher content of the pseudohexagonal crystalline form. On the other hand, the samples of draw ratio 4.4 in Figure 12(b) all display an advanced shift in their X-ray diffraction patterns toward the stabler α-monoclinic crystal form in comparison to the 3.7 draw ratio samples.

The as-spun blended yarn containing 5% by weight of polystyrene was drawn to a draw ratio of

Figure 9   Nominal stress–strain plots of yarns of draw ratio 4.4 made from polypropylene and its blends with various amounts of polystyrene.

Figure 10   Infrared absorption peaks at 699 cm^{-1} for yarns of various draw ratios obtained from polypropylene blended with 5% polystyrene: (——) parallel; (-----) perpendicular.
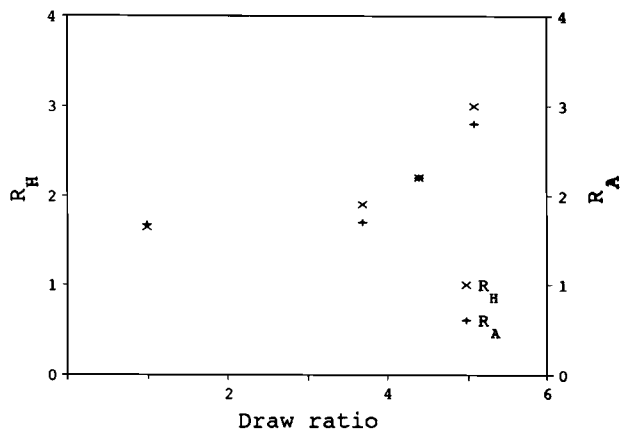
**Figure 11** Plots of infrared absorption peak (699 cm^{-1}) height ratio (R_H) and absorption band area ratio (R_A) vs. draw ratio of samples obtained from polypropylene blended with 5% polystyrene.

5.1. The as-spun polypropylene sample could not be drawn to this draw ratio. The structural and mechanical characteristics of this sample are summarized in Table V and its stress–strain curve shown in Figure 13. The density, crystallinity, and orientation of this sample are very high and its boiling water shrinkage is substantially less than those of the other samples. As far as mechanical properties are concerned (Fig. 13 and Table V), they are outstanding and its glass transition temperature is also the highest among the samples studied. The I-2θ plot for this sample (Fig. 14) shows a fully developed monoclinic crystalline form. The high crystallinity and the more stable monoclinic crystal structure lead to a significant reduction in boiling water shrinkage compared to those of earlier samples. It is noteworthy that these desirable features in this sample have been possible because of the high drawability due to the presence of 5% by weight of polystyrene.

Creep and Recovery Behavior of Drawn Samples

The observations made earlier with respect to the samples of draw ratio 4.4 and the blended sample of draw ratio 5.1 suggest that the presence of atactic polystyrene in the highly drawn samples achieves improvement in mechanical properties due to the reinforcement action of polystyrene. The PP5PS5.1 sample has much better orientation as revealed by its birefringence due to the higher draw ratio imparted to the sample (Table V). Hence, it is not surprising to see that the sample also has much better creep resistance (Fig. 15) when compared to the other drawn samples. The PP5PS4.4 sample also shows a small improvement in its creep and recovery

behavior when compared to the PP4.4 sample. However, the PP5PS5.1 sample clearly shows much less creep, almost one-half of that observed with the PP5PS4.4 sample. The rigidifying effect of the atactic polystyrene in the oriented samples not only improves its creep resistance but also the recovery be-
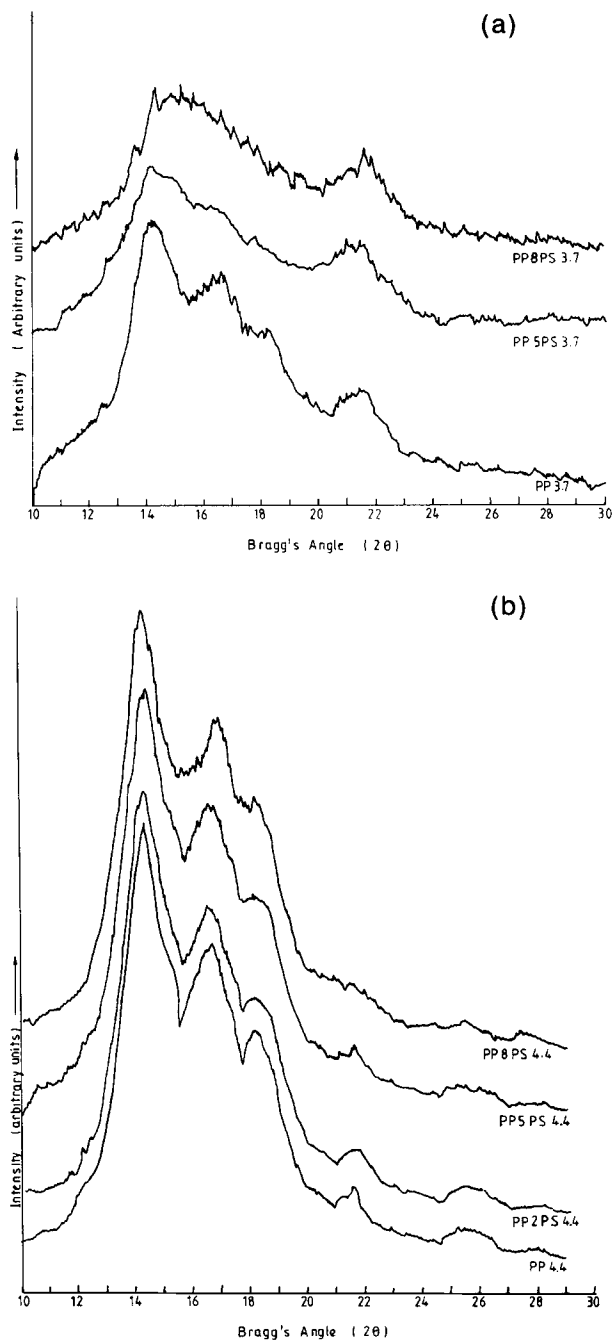
Figure 12 I-2θ plots of polypropylene sample and its blends with polystyrene drawn to a draw ratio of (a) 3.7 and (b) 4.4.
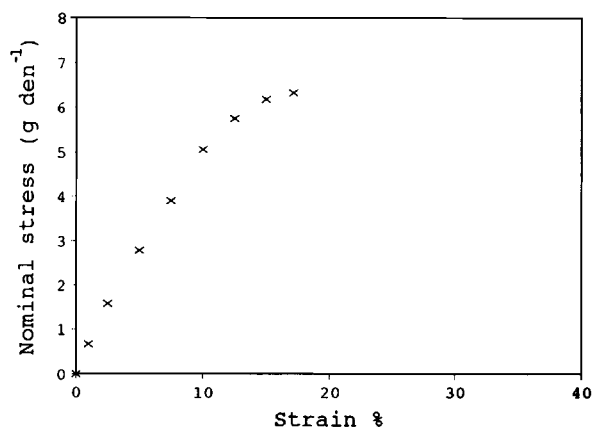
Table V   Characteristics of 5.1 Draw Ratio Sample

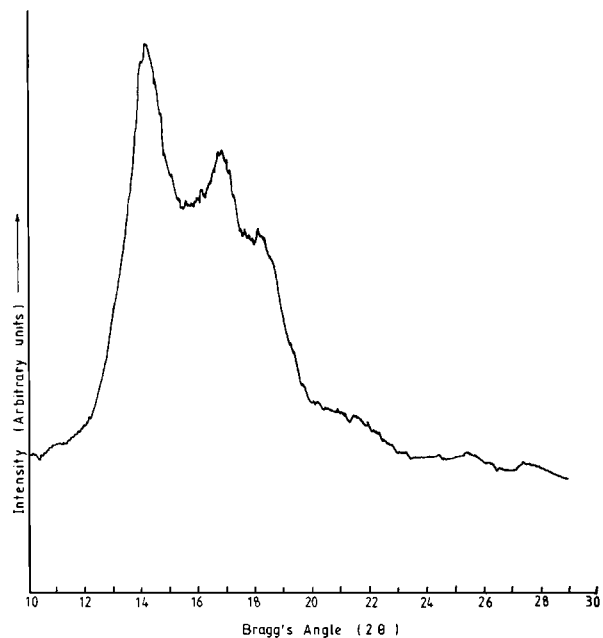|	PP5PS5.1
Density (g cm^{-3})	0.917
Density of the polypropylene part (g cm^{-3})	0.910
Crystallinity (%)	
Density	63.6
X-ray	59.8
Birefringence	0.056
Boiling water shrinkage (%)	7
Modulus (g den^{-1})	66.8
Nominal tenacity (g den^{-1})	6.32
Extension to break (%)	18
T_g peak	
Dynamic torsion apparatus	14.1

havior. The rigidifying effect may be observed from a comparison of the glass transition temperatures of the samples. The PP5PS4.4 sample has a higher glass transition and the sample PP5PS5.1 reveals an even higher glass transition temperature associated with the tan δ peak of the polypropylene phase.

CONCLUSIONS

The presence of the atactic polystyrene in the spun samples is found to substantially enhance the plastic deformation of the spun samples. The blended spun sample PP5PPS also showed a large reduction in its tan δ peak associated with the glass transition temperature of polypropylene in comparison to the


Figure 14 I-2θ plot of a yarn of draw ratio 5.1 made from polypropylene blended with 5% polystyrene.

PP sample. The blended samples also displayed lower spinline tension during melt spinning under identical conditions of spinning, which is perhaps responsible for the observation of lower orientation and crystallinity and the attainment of a disrupted structural order in terms of a shift toward a predominantly pseudohexagonal crystalline form in the blended samples in comparison to the polypropylene sample which displayed a predominantly α-monoclinic crystal form. These factors along with the possibility of slippage of the matrix polypropylene across the polystyrene phase could be responsible for the enhanced plastic deformation and improved

Figure 13   Nominal stress–strain curve of a yarn of draw ratio 5.1 made from polypropylene blended with 5% polystyrene.
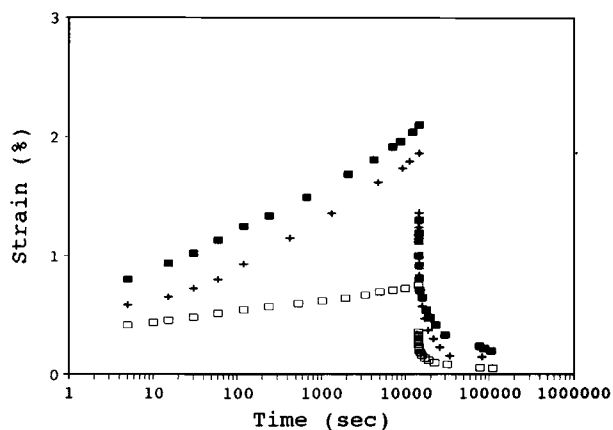
Figure 15   Creep and recovery behavior of (■) PP4.4, (+) PP5PS4.4, and (□) PP5PS5.1.

drawability of the blended spun samples. On the other hand, this improved drawability in the blended spun yarns makes it possible to impart higher draw ratios, thereby providing drawn yarns with much higher orientation. The glass transition temperature of the polypropylene phase was found to be higher in the blended samples PP5PS4.4 and PP5PS5.1 in comparison to the PP4.4 sample. The improved orientation coupled with the rigidifying effect of the oriented atactic polystyrene chains could be responsible for the substantial improvement in its mechanical properties and much better creep resistance and recovery behavior in comparison to the drawn polypropylene yarn.

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