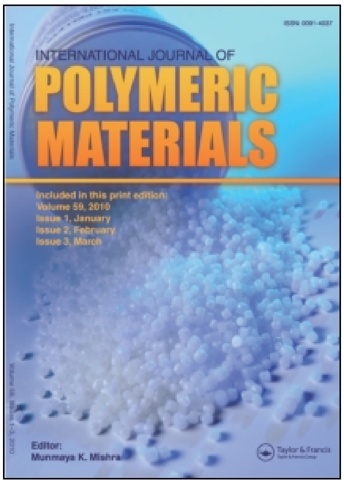

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Technical Grade Filaments from Polymer Blends of Nylon 6 and Nylon 66

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Technical Grade Filaments from Polymer Blends of Nylon 6 and Nylon 66

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Significant improvement in properties is observed for filaments produced from blending of nylon 6/nylon 66 by melt spinning process. As-spun blend filaments show higher drawability due to wider crystal size distribution and interfacial slippage at the boundary between both components. This results in improved mechanical properties with tenacity of ~1.0 GPa and initial modulus of ~7.0 GPa. The improved tensile properties are associated with increased orientation, possible reduction in fibrillar size and formation of interconnected fibrillar network.

KEY WORDS Nylon 6, Nylon 66, polymer blends, tenacity, modulus.

INTRODUCTION

Nylon 6 and nylon 66, two of the polyamides, are widely used as technical grade filaments for several applications. The technical grade commercial nylon filaments have tensile strength and modulus in the range of 0.7–0.9 GPa [7–9 gpd] and 4.5–5.0 GPa (45–50 gpd) respectively. There are continuous demands for improving these properties. Some of the unconventional methods for improving the mechanical properties of nylons are: a) to increase molecular weight of the polymer,[1] b) to modify spinning/extrusion process,[2–4] c) to modify drawing process.[5,6] Another method of producing an improved product, from existing polymer, is by polymer blending. Kitao *et al.*[7] and Verma *et al.*[8] have shown that the mechanical properties of nylon 6 and nylon 66 can be improved by blending these two polymers.

This paper presents details on the production of technical grade filaments from polymer blends of nylon 6 and nylon 66.

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EXPERIMENTAL

Materials

Nylon 6 chips, supplied by J. K. Synthetics Ltd., Kota, India, were used as the basic component throughout the present study. Two types of nylon 66 chips, one nylon 66 (Type B) supplied by Monsanto Chem. Co., USA, and another nylon 66 (Type D) supplied by Sasmira, Bombay, India, were used. Characteristics of nylon chips are given in Table I.

Production of Filament

Spinning of nylons and blend samples were carried out on a Fuji Melt Spinning unit (Type-C) by direct chips blending. Composition of samples is given in Table II.

Details of spinning condition are given in Table III. As-spun yarns were drawn

TABLE I

Characteristics of nylon 6 and nylon 66 chips

Chips	[η] m-cresol at 25°C dl/gm	Mol.[a] weight ($\bar{M}_w$)	Melting temp. °C
Nylon 6 (N6)	1.49	46000	227
Nylon 66 (N66B) Bright	1.14	24000	271
Nylon 66 (N66D) with TiO_2 (0.2%)	1.06	23000	271

[a] $[\eta]_{N6} = 5.26 \times 10^{-4} \bar{M}_w\ 0.74$ [9]
$[\eta]_{N66} = 24.0 \times 10^{-4} \bar{M}_w\ 0.61$ [10]

TABLE II

Composition of blend samples

Sample code	Weight of nylon 6 (%)	Weight of nylon 66 (%)
N6	100	0
20B	80	20
30B	70	30
50B	50	50
70B	30	70
N66B	0	100

TABLE III

Spinning conditions

Spinnerette	No. of holes 9; Hole dia. 0.5 mm; L/D 2.0
Take up-speed	55 m/min.; Spin draw ratio: 18
Spinning room temp. and R.H.	30 ± 1°C, 60%
Spinnerette Temperature	N6, N66B, 20B to 70B, 20D to 50D–295°C N66D, 70D–285°C
As-spun denier	910 ± 20

on a two-zone drawing machine at first zone draw ratio (2.8) and temperature (110°C) with maximum workable draw ratio at different temperatures (190°–225°C) in the second zone.[11]

CHARACTERIZATION

Melting and crystallization studies of nylons and blend samples both undrawn and drawn, were carried out by DSC (Perkin-Elmer DSC-7). Thermo-mechanical analyser (Perkin-Elmer TMA-7) was used for shrinkage studies.

Density and density crystallinity (x_w) measurements were done by density gradient-column method. Birefringence ($\Delta\eta$) was measured using Leitz polarizing microscope and compensator. Wide angle X-ray diffraction (Philips, PW 1710 diffractometer control, PM 8203A one line recorder, Cuk_α radiation) studies were carried out for determination of crystallinity, crystal size, crystalline orientation function. Crystallinity was measured according to a method by Bhattacharya.[12] For the blends, the peak at around $2\theta = 20°$ was considered as superimposition of two peaks due to [200] planes of nylon 6 and [100] planes of nylon 66. The crystal size was calculated from the peak of about $2\theta = 20°$, using Scherrer equation,[13] taking constant K as 0.89. The crystalline orientation function (f_c) was calculated by the method of Farrow and Bagley.[14] Method of Stepaniak et al.[15] for nylon 6 or the method of Dumbleton *et al.*[16] for nylon 66 are not suitable in case of blends. Tensile and cyclic extension (80% of breaking extension) tests were carried out by Instron tensile tester (model 1112) at 100%/min. strain rate. The dynamic mechanical properties of samples were measured by Rheovibron (Model-DDV-II-EP) at 3.5 Hz at heating rate of 3°C/min and dynamic displacement of $\pm 50 \times 10^{-6}$ m.

RESULTS AND DISCUSSION

As-Spun Filament and Drawability

The spinning temperatures were optimized for obtaining a) transparent melt and b) flow rate to keep the as-spun filament with nearly equal denier for different blend systems. The spinning temperatures are given in Table III. The density varies from 1.133 to 1.137 g/cc for N6, N66B and blends. Birefringence values of as-spun nylon 6, nylon 66B and blend samples varies between 1.7×10^{-3} to 2.4×10^{-3}.

The diffractometer plots from the meridional scanning of samples of nylon 6, 20B, 30B, 50B obtained after first zone drawing i.e. drawn at draw ratio of 2.8 and temperature of 110°C are shown in Figure 1. The peak, at about 11° of 2θ, is due to the [020] reflection of the γ-phase.[17,18] The relative normalized intensity of the [020] meridional peak indicates that after first zone drawing, the γ-phase content in blend samples is low, as compared to nylon 6 sample. Verma *et al.*[8] have observed that with incorporation of small amounts (~2–10%) of nylon 66 in nylon 6, the γ-crystal form of nylon 6 increases significantly. In our studies, as-spun nylon 6 rich blends i.e. 20–30% of nylon 66 in nylon 6, do not show any appreciable

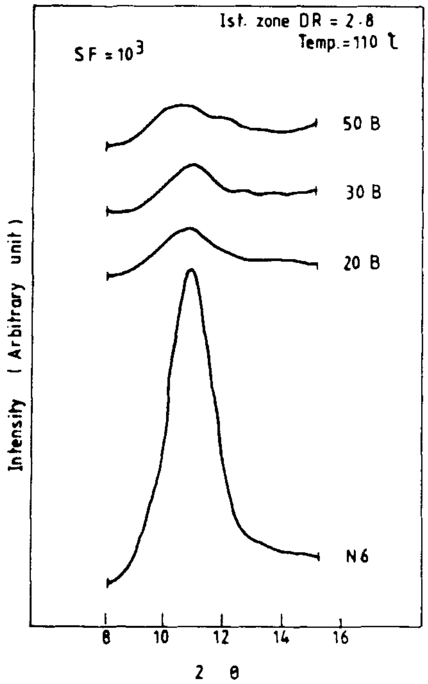


FIGURE 1 Meridional diffractometer plots of nylon 6 and blends.

difference in γ-form content. This may be due to phase segregation at these compositions.

It has been observed that the natural draw ratio (NDR) varies from 2.4–2.7. The NDR of nylon 66 is the lowest i.e. 2.4 which may be due to higher as-spun crystallinity. Maximum draw ratio (MDR) for all blends are 8–12% higher as compared to MDR of nylon 6 and nylon 66. With nearly same NDR, higher MDR of blends indicates that blends have higher drawability. The change in total draw ratio with the blend composition is shown in Figure 2. The draw ratios of blend filaments obtained after two zone drawing process are 6.1 as compared to 5.7 and 5.51 for nylon 6 and nylon 66, respectively. The similar higher draw ratio of nylon 6/nylon 66 blends as compared to parent polymers, have also been observed by Kitao *et al.*[7] and Verma *et al.*[8]

The higher drawability of the blend filament yarns is due to combined effect of: a) increased crystal size distribution (as observed in DSC studies), b) presence of metastable crystal form (as observed by wide angle X-ray studies) and c) interfacial slippage at the boundary between the components.

Melting and Crystallization Behaviour

The melting and crystallization data for nylons and blend samples, as obtained by DSC are given in Table IV.

In case of as-spun blend samples i.e. 20B, 30B and 50B, nylon 6 and nylon 66 crystallize independently as observed by two distinct peaks during melting. For

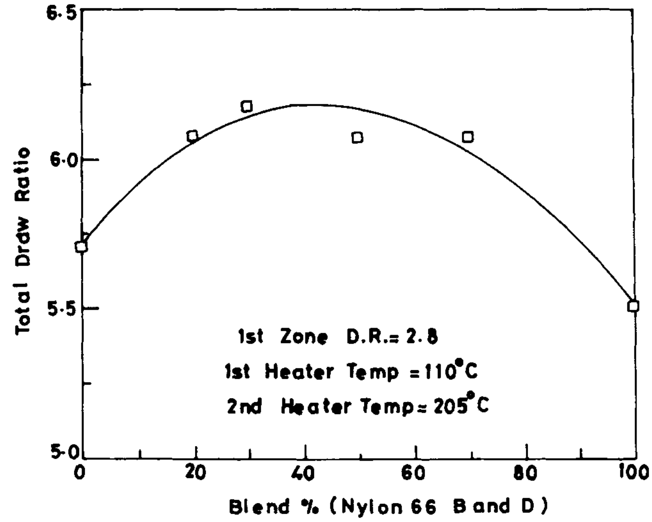


FIGURE 2 Change in total draw ratio with blend composition.

TABLE IV

Melting and crystallization of nylons and blend samples

	Undrawn				Drawn 2.8/110°C/205°C	
	Melting		Crystallization		Melting	
Sample	First melting peak temp. (°C)	Second melting peak temp. (°C)	$(T_{ic} - T_{fc})^a$ (°C)	Peak Cryst. temp. (T_c) (°C)	First melting peak temp. (°C)	Second melting peak temp. (°C)
N6	223 (227)[b]	—	26	187	222 (230)	—
20B	218	257 (263)	73	191	—	—
30B	213	253 (254)	56	213	221	255 (263)
50B	206	256 (264)	80	224	222	251 (266)
70B	—	260 (266)	32	226	195 (Broad)	261 (267)
N66B	—	267 (270)	18	236	—	267 (270)

[a] $T_{ic} - T_{fc}$ = Crystallization width
= Difference of initiation and completion of crystallization temperature.

[b] The temperatures in the bracket correspond to the respective final melting temperature.

sample 50B, only a small melting peak at 206°C is observed. 70B blend sample shows only broad single melting peak and nylon 6 crystallizes to a very small extent and has a very wide crystal size distribution. This is probably because of the much higher crystallization rate and temperature of nylon 66 which prevent diffusion and crystallization of nylon 6. This may also be related to compatibility of nylon 6 and nylon 66 in amorphous region.

All undrawn and drawn blends show a depression in melting peak temperature (Tm) as compared to the parent samples. Figure 3A shows the trend in depression of melting peaks of undrawn samples. A similar small depression has also been observed by several workers.[7,8,19,20] Sufficiently strong polymer-polymer interactions exist at the crystal amorphous interface and result in a drop in Tm.[21] Other factors leading to decrease in Tm are reduced lameller thickness, large crystal size distribution and reduced crystal perfection.

The crystallization temperature (T_c) as observed during cooling increases with increasing nylon 66 content in nylon 6. Figure 3B shows the trend of increase in

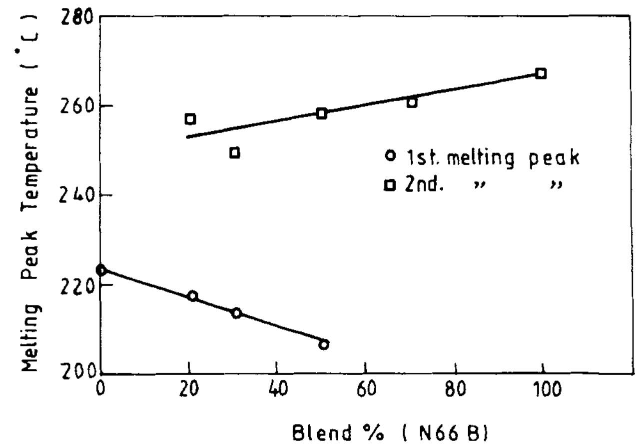


FIGURE 3A Effect of blend composition on melting peak temperature of undrawn samples.

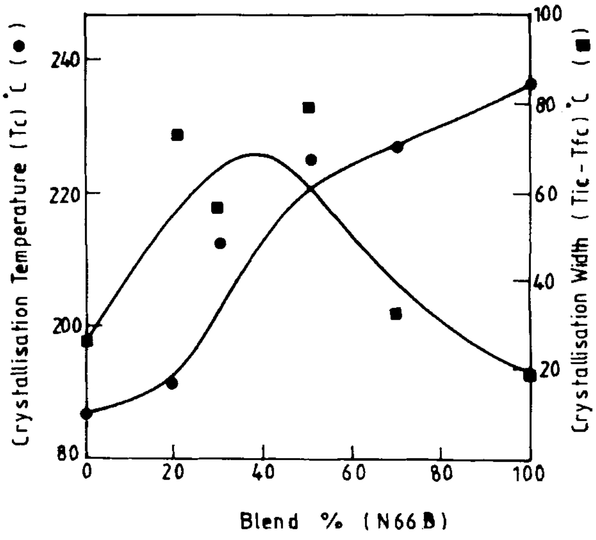


FIGURE 3B Effect of blend composition on crystallization temperature and crystallization width.

T_c. There is sharp increase in T_c in the range of 30–50% of nylon 66 in nylon 6. The rise in T_c of blend samples is due to nucleating effect of nylon 66 on nylon 6.[22] The width of the crystallization peak ΔT i.e. $(T_{ic} - T_{fc})$°C is higher for blend samples as compared to parent nylons. The ΔT is large in the range of 30–50% of nylon 66 in nylon 6 blends, as shown in Figure 3B. The large peak width indicates that the crystallization behaviour of one nylon is significantly affected by the other nylon. This may also lead to larger crystallite size distribution, for samples in the range of 30B–50B blends. Similar observations are reported for PP/PET,[23] PBT/PET[24] and HDPE/PP[25] blend systems.

Structural Characteristics of Two Zone Drawn Samples

Figure 4 shows the changes in structural characteristics i.e. X-ray crystallinity (x_c), density, $\Delta\eta$, f_c and crystal sizes for blend filaments. These samples are drawn at 2.8 as first zone DR and 110° and 205°C as first and second zone temperatures respectively.

It is seen from Figure 4 that the X-ray crystallinity, density and density crystallinity of blend samples decrease slightly up to 50% of nylon 66 in nylon 6. The lowest value of crystallinity is obtained at 70% of nylon 66 in nylon 6. This is an indication that a part of both the components is not crystallized. From the observations of density, crystallinity and DSC thermograms as shown earlier, it can be referred that at compositions up to 50B, where significant phase segregation has taken place and the crystallinity values do not decrease much. At the phase boundaries, the nylon 66 component having higher crystallizing temperature, could also act as sites for nucleation and crystallization.[22]

Figure 4 shows that the birefringence ($\Delta\eta$) values of the blends are always higher than those of parent samples. It is attributed to the higher drawability of the blends. Kitao *et al.*[7] have also observed the increased drawability of nylon 6/nylon 66 blends. As seen from Figure 4, crystalline orientation function, f_c, is nearly same for blends, the increased $\Delta\eta$ shows that the amorphous orientation functions for the blends are higher than those of parent polymers. The estimation of amorphous orientation function (f_a) for blends is not carried out, because it was not possible to determine accurately the crystalline contribution of each component in the blend, and there are differences in birefringence values of nylon 6 and nylon 66.[26]

Some of the representative X-ray diffraction photographs of oriented fibre bundles are shown in Figure 5. The larger width of the equatorial diffraction scans for blends by incorporation of one nylon in the other, indicate decrease in the average crystallite size as shown in Figure 4 and larger defects in crystals. The calculated crystallite sizes by Scherrer equation are plotted in Figure 4. Minimum crystallite size of 21A is obtained at 50/50 of nylon 6/nylon 66 blend. This supports the results from melting and crystallization behaviour of the blends.

Tensile Mechanical Properties

Effect of second zone temperature. Figure 6(a,b) shows the effect of second zone temperature on tenacity and modulus of nylons and blend filaments. Figure 6(a,b) shows that strength and modulus values of nylon 6 and blends up to 50%

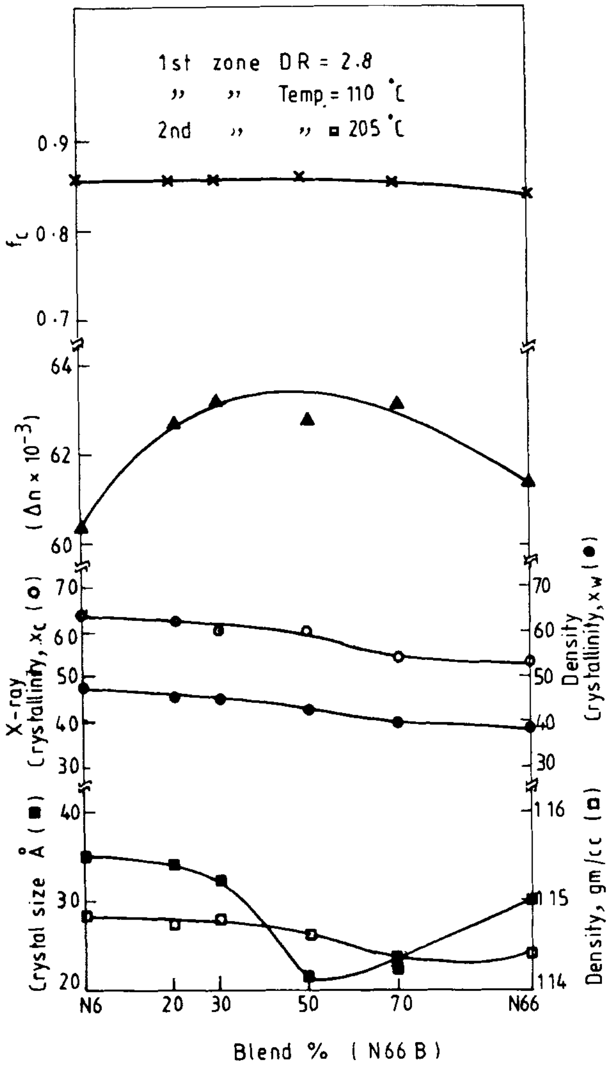
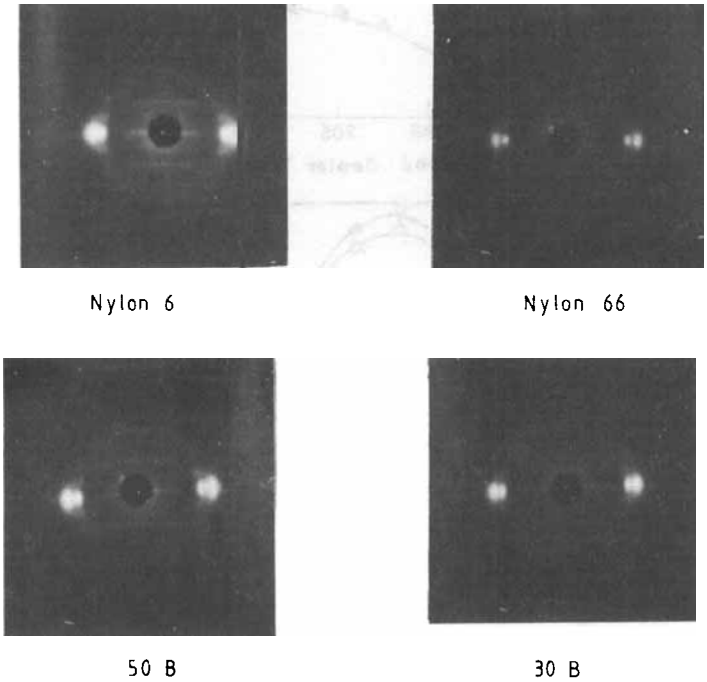


FIGURE 4 Changes in crystallinity, density, birefringence (Δη), f_c and crystal size of two zone drawn samples with blend composition.

of nylon 66B in nylon 6 increase with second zone temperature up to about 200°C and 205°C respectively. Almost similar behaviour is observed for blends of nylon 6/nylon 66D.

Increasing tensile mechanical properties with second zone temperature is related with higher drawability leading to higher orientation and crystallinity as observed earlier. For blends up to 50%, decrease in strength and modulus beyond 200°C and 205°C of second zone temperature respectively, may be due to partial melting of nylon 6 and relaxation in the amorphous region. A slightly different behaviour



Nylon 6

Nylon 66

50 B

30 B

FIGURE 5 X-ray photographs of drawn nylon 6, nylon 66, 50 B and 30 B samples.

of 70% blend and nylon 66 may be due to lower second zone drawing temperatures as compared to its crystallization temperatures.

Effect of blend composition. Figure 7(a,b) shows the tenacity values of two zone drawn filaments from nylons and blends from two types of nylon 66 (N66B, N66D).

The tenacity values for blends of nylon 66B type increases up to 50% of nylon 66B in nylon 6 and then it decreases. The blends show a synergistic effect. Similar trend is observed for total draw ratio and orientation. This is to be expected since tenacity is closely related with orientation of molecular chains, compactness and uniformity in the structure. In the case of blends from nylon 66D, the tenacity increases up to 30% of nylon 66D. This change in tenacity for nylon 66D blend samples may be due to presence of TiO_2, which acts as a defects in the filaments.

The optimum blend composition is in the range of 30–50% of nylon 66 with tenacity of ~1.01 GPa. These tenacity values are significantly higher than that of both the nylons.

Figure 7(a,b) shows the composition dependence of modulus of nylons and blends from two types (B,D) of nylon 66. The modulus of blends increases up to 70% of nylon 66B, whereas, it increases only up to 30% for nylon 66D blends. The higher modulus values of blends is attributed to similar reasons as described for tenacity. The optimum blend compositions are again in the range of 30–50% for nylon 66 with nylon 6. A modulus of 7.0 GPa is obtained, which is significantly higher as compared to either of nylons.

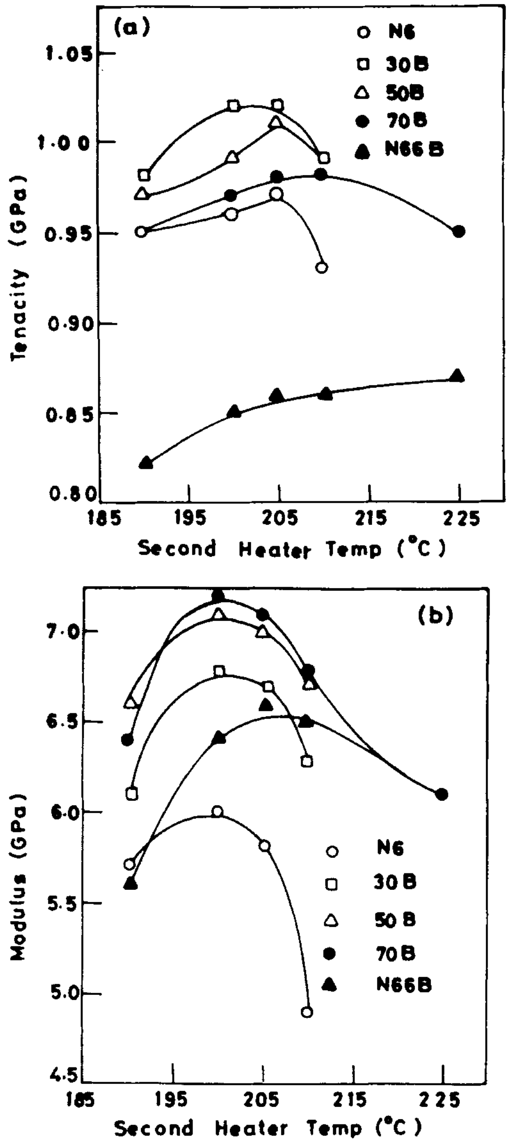


FIGURE 6A,B Change in tenacity and modulus with second zone temperature of drawn nylon and blends.

The synergistically improved tensile properties of nylon 6/nylon 66 blend filaments can be related to generation of highly interconnected inter-fibrillar network and reduction in the fibrillar size. The higher drawability of blends leading to higher amorphous orientation, as observed earlier, and improved mechanical properties provide evidence for the existence of strong interconnection at the interfacial boundary and/or formation of homogeneous microstructure in the blends. This microstructure of the blends may be similar to the structural model for polyamide proposed by Prevorsek *et al.*[27] The formation of highly interconnected inter-fibrillar network

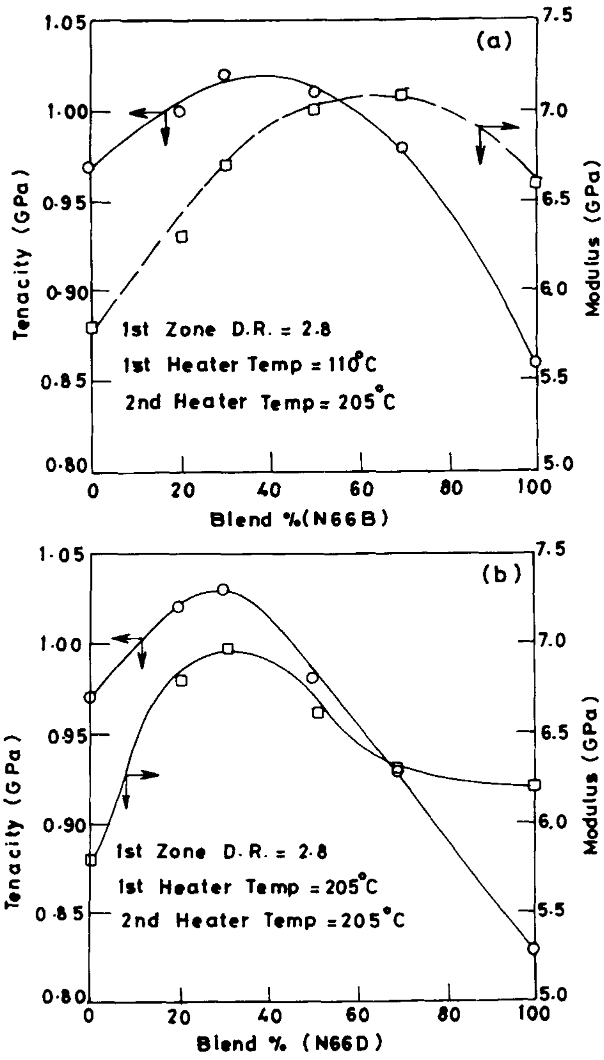


FIGURE 7A,B Change in tenacity and modulus with blend composition of drawn samples.

may also be related to a very low degree of transamidation occurring, forming block copolymer in the blends. Zimmerman *et al.*[28] reported that blends of nylon 66 and polyhexamethylene isophthalamide or poly (*m*-phenylene adipamide), have a certain degree of amide interchange with block copolymer formation. The process depends on the compatibility of the polymers, as well as, on the kinetic factors.

The breaking elongation percent for all two zone drawn samples are in the range of 12–13%. There is no clear trend in breaking elongation with blend composition.

Dynamic Mechanical Properties

Dynamic mechanical properties of two zone drawn dried nylons and blends filaments are shown in Figure 8. The tan δ peak appears at ~95°C for nylon 6 and at

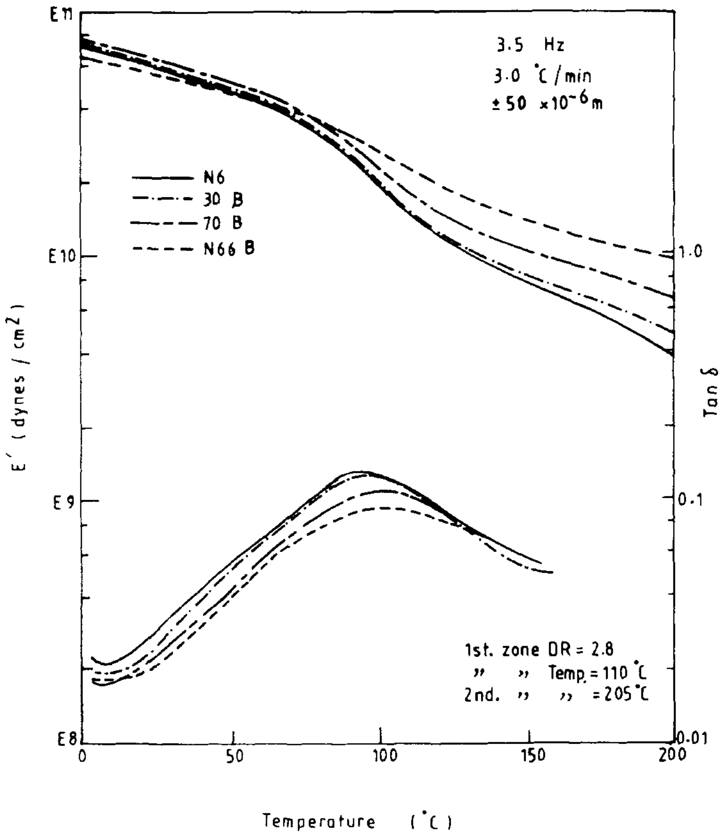


FIGURE 8 E' and tan δ of drawn nylons and blend samples.

~103°C for nylon 66. The blends show a single tan δ peak which gradually shifts from 95°C to 103°C with increase in nylon 66 content. Similar shifts have also been observed by Verma *et al.*[8] It has also been observed that the tan δ maximum decreases with blend composition. The presence of a single tan δ peak with decreased maximum value and the gradual shifts suggest a partial compatibility of nylon 6 and nylon 66.

The storage modulus data show that the blends have higher modulus as compared to nylon 6, throughout the temperature range of test (i.e. 0 to 200°C). Nylon 66 has lower modulus values below 50°C and higher values at higher temperatures as compared to the blend samples.

Higher modulus values of blends as compared to both nylons at lower temperature side (below ~50°C) is attributed to the increased orientation and number of tie chains as discussed earlier. This supports the observation of blends for tensile modulus. The higher modulus of blends as compared to nylon 6 for 50–200°C is due to the improved stability of the structure developed in presence of nylon 66 which has higher melting temperature.

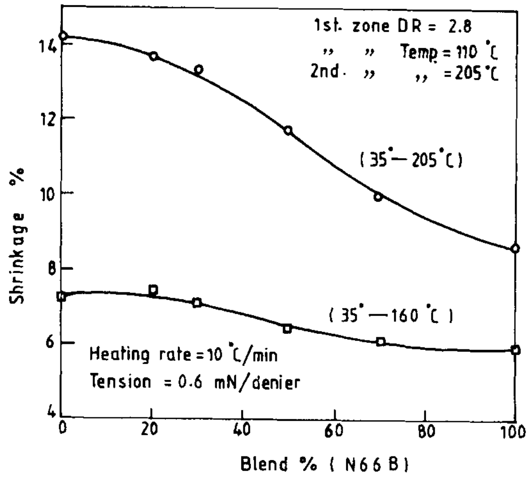


FIGURE 9 Change in shrinkage of drawn samples with blend composition.

TABLE V

Comparative values of tenacity, modulus and recovery of different samples

Sample	Tenacity (GPa)	Initial modulus (GPa)	Recovery (%)
N6	0.97	5.8	94
50B	1.01	7.0	91
Nylon 6 (SRF)	0.90	4.5	90
Nylon 66 (Monsanto)	0.88	5.8	88

Shrinkage Studies

Thermomechanical methods provide a direct means for studying the time-temperature-tension relationship which govern the fibre's production, subsequent processing and use.[29]

Figure 9 shows the shrinkage behaviour by Thermo-mechanical analysis for two zone drawn nylon and blend filaments. Shrinkage decreases with increased nylon 66 content in nylon 6. The effect is much more pronounced in the higher temperature range. It can also be seen that blends, though having higher draw ratio, show lower shrinkage.

Generally shrinkage increases with draw ratio.[30,31] Drawn filament contain a distribution of structures ranging through poorly oriented, non-crystalline regions of low order to highly oriented, highly crystalline and well-ordered regions. The relative proportions of these structures and the nature of the amorphous crystalline energy continuum, determine the shrinkage behaviour of the filament. Blending of nylon 66 with nylon 6 improves the stability of the structure developed as blends show lower TMA shrinkage. This also supports the dynamic mechanical behaviour of the blends.

A Comparative Study

A comparative study of filaments produced in this work and commercially available nylon 6 and nylon 66 filament was carried out in terms of tensile, cyclic and dynamic mechanical testing. Commercial nylon 6 filament yarn of 1260/210 denier was supplied by M/s. Shriram Fibres (SRF), India and nylon 66 yarn of 200/34 denier was supplied by Monsanto Chemical Co., USA. These samples are compared with nylon 6 (N6) and blend of 50% nylon 66B in nylon 6 i.e. 50B, filament. Table V shows the comparative tenacity, modulus and recovery % data.

The comparative study shows that the increase in tenacity and modulus of blend samples are ~10% and ~20–55% respectively. The percent recovery, in cyclic test, for blend shows value comparable to that of parent samples (~90%). The fibrillation tendencies for blend filaments are expected to be comparable to the parent systems due to high degree of compatibility of the components in amorphous regions and interconnected fibrillar network structure. Prevorsek et al.[32] have discussed the relative advantages and disadvantages of nylon 6 and nylon 66 cords. These observations indicate that blend sample may give better performance in use due to combined effect of both components.

Thus, blends of nylon 6/nylon 66 as filaments having higher strength, modulus and reasonable loss, may provide a superior balance of properties for technical applications such as, tyres, V- and conveyor belt cords, ropes, cables, nets, coated fabrics and geotextiles etc.

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