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Uniaxial deformation behaviour of ternary blends of poly(ethylene naphthalate), poly(ether imide) and poly(ether ether ketone) films

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Ternary blends of PEN with PEI and PEEK were investigated in order (i) to eliminate the neck formation that occurs during deformation in the rubbery state while maintaining the strain induced crystallizability, (ii) to increase the glass transition temperature. For this purpose, we investigated the uniaxial deformation behaviour of miscible and immiscible PEN rich ternary blend films stretched above their glass transition temperatures. The increase of PEI concentration increased glass transition temperature and eliminated the neck formation while decreasing crystallizability. In order to compensate for the latter, the concentration of PEEK was increased which recovered the strain hardening (crystallization) and associated self levelling behaviour while boosting the glass transition temperatures of the final films. PEN crystallization is hindered in blends containing 40% PEI. In these blends, although PEEK can be crystallized at concentrations as low as 10%, PEN remains amorphous. Upon annealing both PEEK and PEN separate from PEI and crystallize into their own domains. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: ternary blends; uniaxial deformation)

INTRODUCTION

In a series of publications[1–3] from our group, poly(ethylene naphthalate) (PEN), which is currently being scaled up to full commercial production, was shown to exhibit a potentially serious processing problem when it is manufactured by uni- and biaxial stretching from amorphous precursors. Upon stretching in the rubbery regions (between T_g and T_{cc} (cold crystallization temperature)) amorphous PEN exhibits a neck. A detailed analysis undertaken by Cakmak and Lee[3] revealed that the origin of this neck formation in these precursors with poor structural definition resides in the molecular architecture of the polymer. It is a result of highly localized cooperative reorientation of the naphthalene planes macroscopically manifesting itself as a neck during deformation. This behaviour is akin to a collapse of ‘deck of cards’ nucleated by the local stress concentrations that occurs as a result of local thickness fluctuations. In order to alleviate this problem, PEN rich binary blends with PEI were investigated[1] and it was found that in these melt miscible blends, the addition of PEI chains to PEN matrix causes an increase of interchain friction, thereby increasing the macroscopic stresses during deformation and resulting in rapid onset of stress hardening during deformation. The added benefit of blending is the complete elimination of neck formation in films containing approximately 15% PEI. It was also found that one could not increase the proportion of non-crystallizable PEI in the blends and maintain the processability. The thermal as well as stress induced crystallizability greatly suffers beyond 20% PEI concentration as a result of dilution effect as well as increased viscosity of the environment brought about by the increases in the glass transition temperature.

In order to counteract this dilution effect and decrease the strains at which the first onset of stress hardening occurs during deformation, we have decided to blend PEEK with the PEN/PEI mixture. PEEK and PEI are also known to be melt miscible in all compositions[4] and when stretched from amorphous precursors, PEEK exhibits small strains at which substantial stress hardening occurs[5]. It was expected that the reduction in crystallizability by the addition of PEI into PEN would reverse with the addition of PEEK.

The objective of this paper is to investigate the influence of PEEK on the uniaxial stress–strain behaviour of the PEN/PEI/PEEK ternary blends from their amorphous precursors and resulting orientation and properties. For this purpose, our studies are focused on the uniaxial deformation behaviour of the compositions containing substantial amount of PEN as shown graphically in the ternary diagram (*Figure 1*) as our intention is to improve the deformation behaviour and the glass transition temperature of PEN by this blending strategy.

EXPERIMENTAL

Preparation of the blends

First, PEI/PEEK binary blends were prepared by melt mixing using a JSW co-rotating, intermeshing twin 30 mm screw extruder with L/D 32.5. The barrel temperatures were set at 265°C in zone 1, 360°C in zone 2 and 370°C in zones 3, 4, 5, 6 and 7 (zone number increases while going from the hopper to the die). The die temperature was kept at 370°C. Prior to processing, the homopolymers were mechanically mixed and dried in the vacuum oven at 140°C. The extrudates were quenched in a water bath and pelletized. Then, the dried PEI/PEEK blend pellets were dry mixed with PEN pellets. PEN/PEI/PEEK blends were prepared by the same procedure as the binary blends. In order to

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minimize the degradation of PEN, extruder vents were closed and the feeder and hopper were blanketed with argon gas. The melt temperature was set between 320°C and 355°C depending on the composition of the blend. The compositions of the blends prepared for this study are shown in the ternary diagram (*Figure 1*).

Film preparation

The ternary blends were melt cast using a Prodex 1″ single screw extruder equipped with a 8″ wide sheet casting die and a take up system equipped with a temperature controlled quench roll. The melt temperature at the die was kept between 335°C and 355°C depending on the composition. The blends containing higher proportions of PEEK required higher temperatures. The quench roll temperature was maintained at 70–80°C with the help of water circulating temperature control unit. The thickness of the film was controlled between 400 and 500 μm.

Tensile tests above the glass transition temperature

An Instron 4204 Tensile Tester equipped with an oven was used to obtain stress–strain curves of the blend films. The cast films were cut into strips of 2″ by 0.5″. The oven was preheated for one hour at each processing temperature. After the sample was mounted between the grips, it was kept at the stretching temperature for 5 minutes to let the sample reach thermal equilibrium. In order to see the effect of temperature and draw rate on the uniaxial deformation behaviour of these films three temperatures ($T_g + 10$, $T_g + 20$, $T_g + 30$°C) and three draw rates (100, 250, 500 mm/min) were used.

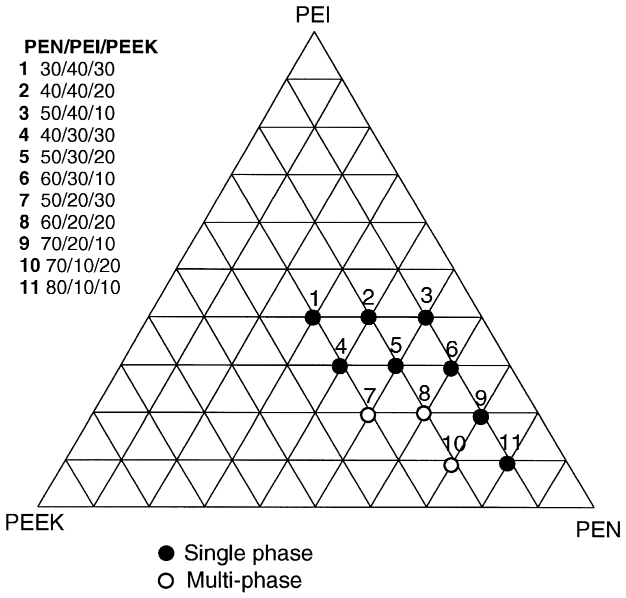

Figure 1 Ternary blend compositions investigated in this research

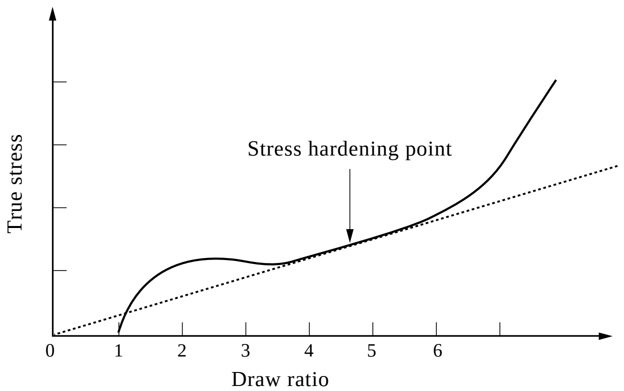

Figure 2 Schematic representation of the determination of the stress hardening point

True stress was calculated from the measured tensile force using the affine deformation assumption ($A \times L = A' \times L'$; A = cross-sectional area, L = length). The stress hardening point was taken as the point where the tangent is drawn from the origin of the true stress *versus* draw ratio curve. This is shown schematically in *Figure 2*.

Thermal analysis

Thermal analysis of both the pellets and the films was performed with DuPont 9900 d.s.c. instrument using a heating rate of 10°C/min and a sample weight of 10 ± 1 mg. The machine was first calibrated with an indium standard.

Crystallinity of unstretched films was calculated using d.s.c. thermograms. Crystallinities of PEN and PEEK were calculated separately for the compositions that showed two distinct cold crystallization and two distinct melting peaks. The following equation was used: Crystallinity (%) = $(\Delta H_{\mathrm{exp}}/\Delta H^{\circ}) \times 100$ where $\Delta H_{\mathrm{exp}} = \Delta H_{\mathrm{melting}} - \Delta H_{\mathrm{cold\ crystallization}}$ and ΔH° is the heat of fusion for 100% crystalline polymer. Heat of fusion for 100% crystalline PEN was taken as 103.4 J/g[6] and 130 J/g[7] for PEEK.

Wide angle X-ray diffraction

In order to study the orientation and the crystallinity development of the films with stretching, samples stretched at different stretch ratios were prepared. The optimum conditions for stretching were chosen as $T_g + 20$°C and a 250 mm/min stretch rate. Then, WAXS film patterns were obtained with GE XRD-6 X-ray generator equipped with a Furnas WAXS-SAXS combination camera. The machine was operated at 30 kV, 30 mA. Cu Kα radiation (λ = 1.542 Å) was obtained using a Nickel foil filter. Also, WAXS film patterns of annealed samples were taken. Annealing was done at 200°C for 30 min. The exposure times were 1.5–2 h for annealed samples and 3 h for unannealed samples.

Determination of orientation

To obtain the orientation factors, scattered intensities were measured from WAXS film patterns as follows. Transmission optical images of WAXS patterns were captured with a Photometrics 16-Bit CCD camera. With the use of a series of calibration exposures, the non-linear response of the X-ray films was corrected. The symmetry axis and the main beam position were located, then radial optical slices were obtained along a series of constant azimuthal angles (see *Figure 3*). The azimuthal angle interval between each consecutive radial slice was kept constant at 2°. The intensity profiles at $\chi = 0°$ (MD direction) to 90° (TD direction) of individual crystalline and amorphous peaks were resolved using Pearson VII function after background subtraction (see *Figure 3*).

To quantify the uniaxial orientation of a given reference direction, Herman's orientation factors[8,9] as generalized by Stein[10] are used:

$$f_{j,Z} = \frac{3\langle\cos^2(\phi_{j,Z})\rangle - 1}{2} \qquad (1)$$

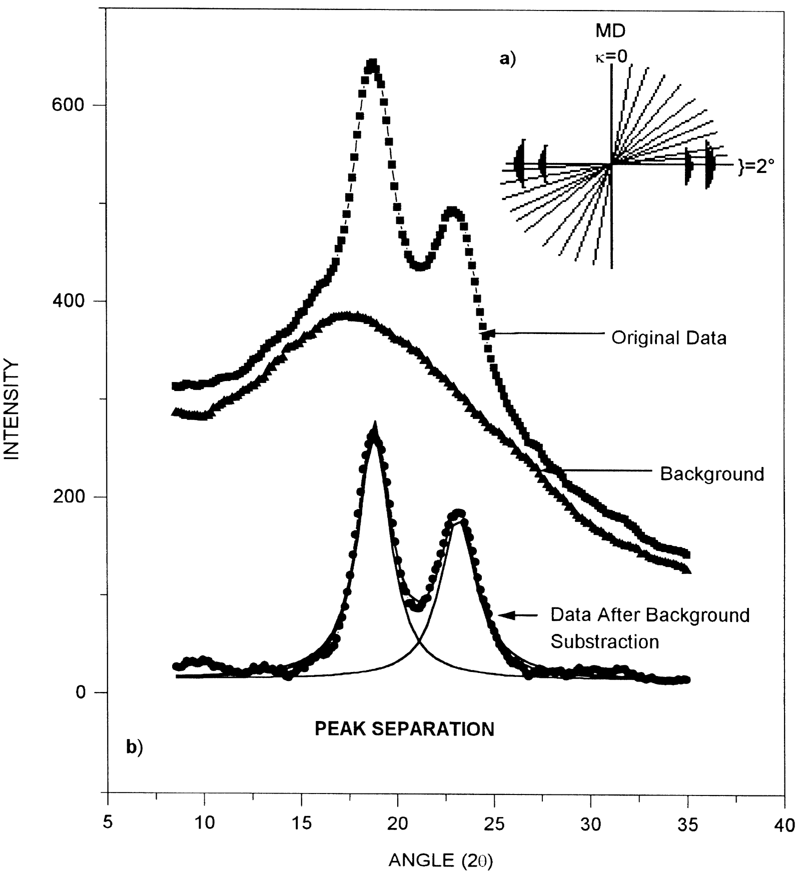

Figure 3 Schematic representation of (a) how to obtain optical slices representing intensity profiles with constant azimuthal angle on WAXD patterns and (b) peak separation procedure

where ϕ_j is the angle between the j crystallographic axis and the machine direction Z ($j = a, b, c$). The mean square cosine values of the angle between the crystallographic plane and the reference direction Z can be calculated using:

$$\langle \cos^2\phi_{hkl,Z}\rangle = \frac{\int_0^{\pi/2} I(\phi)\sin\phi\cos^2\phi\,\mathrm{d}\phi}{\int_0^{\pi/2} I(\phi)\sin\phi\,\mathrm{d}\phi} \qquad (2)$$

where $I(\phi)$ is the diffracted intensity.

In the determination of $\langle\cos^2(\phi_{c,Z})\rangle$ for PEEK, Fratini *et al.*'s unit cell parameters were used. The final equation is as follows:

$$\langle\cos^2\phi_Z, c\rangle = 1 - 0.4207\langle\cos^2\phi_Z, 200\rangle - 1.579\langle\cos^2\phi_Z, 110\rangle \qquad (3)$$

Mechanical properties of stretched films

Mechanical properties of three selected compositions #1 (30/40/30), #3 (50/40/10) and #6 (60/30/10) were studied. Strips 2 cm long (MD) and 0.5 cm (TD) wide were cut from the uniaxially drawn films. They were then tested at room temperature using Instron 4204 tensile tester with a load cell of 1 kN. The testing speed was 80%/min. Five samples were tested for each condition and the results averaged.

RESULTS AND DISCUSSION

Thermal behaviour of the blends and as-cast films

Figures 4 and *5* show d.s.c. thermograms of the blends prepared by twin screw extruder. Compositions 7, 8 and 10 (see *Figure 1*) exhibit two T_g's and the remaining compositions exhibit a single T_g. Above the glass transition temperature region, cold crystallization behaviour of the blends is typical of vitrified crystallizable polymers and this crystallization occurs at two distinct temperature ranges in

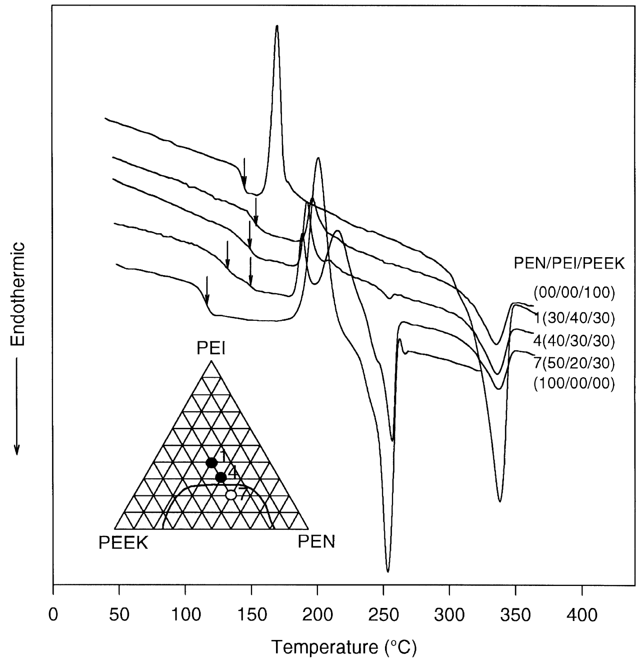

Figure 4 d.s.c. scans of PEN/PEI/PEEK blends containing 30% PEEK. Heating rate is 10°C/min. The vertical arrows indicate location of T_g

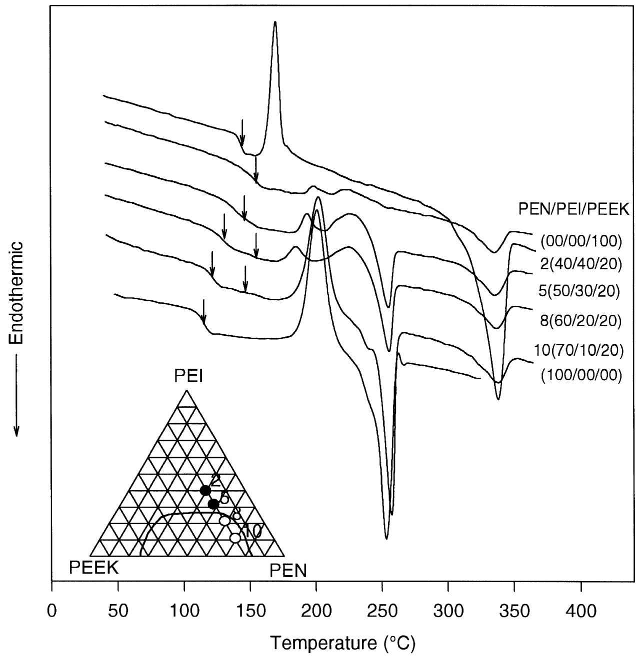

Figure 5 d.s.c. scans of PEN/PEI/PEEK blends containing 20% PEEK. Heating rate is 10°C/min. The vertical arrows indicate location of T_g

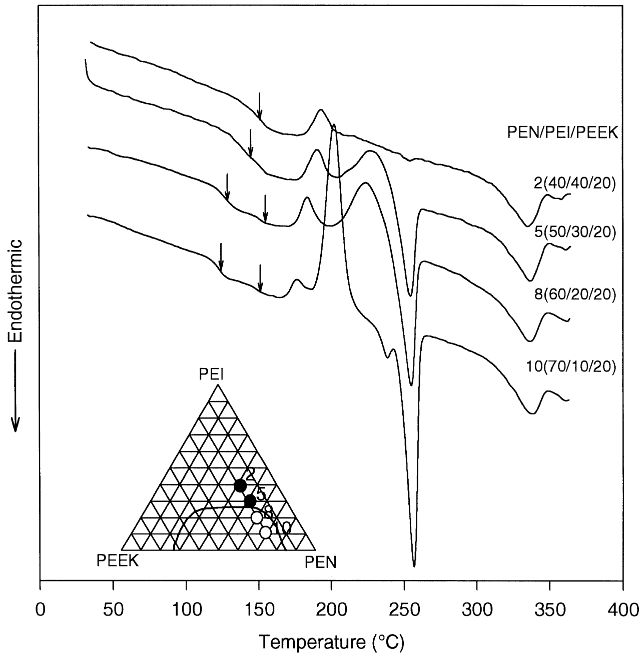

Figure 6 d.s.c. scans of PEN/PEI/PEEK films containing 20% PEEK before stretching. Heating rate is 10°C/min. The arrows indicate the location of T_g(s)

blends containing less than 40% PEI. This suggests that the crystallizable components PEN and PEEK separate into their own domains during crystallization, leaving some of their chains mixed with PEI. This is further confirmed by the observation of two distinct melting peaks at temperatures where the unmixed PEN (250–270°C) and PEEK (330–350°C) crystallites melt.

In composition 1 (30/40/30), only PEEK is able to crystallize and PEN remains amorphous throughout the d.s.c. scan. This result is very similar to that observed in the vitrified binary PEN/PEI blends where PEN is not able to crystallize in blends containing more than 30% PEI when a heating rate of 10°C/min is used during the d.s.c. scan. Presumably this is as a result of two processes: one being the dilution effect which spatially separates the crystallizable chains and the second is the reduction of the movement of the chains by the decrease of diffusion of the chains past one another as characterized by self and cross diffusion coefficients. For crystallization to take place through nucleation and growth process, the nucleus has to form and subsequent growth process is accomplished through the diffusion of crystallizable polymer chains through a sea of non-crystallizable matrix. If the crystallizable polymer chains are well separated from one another, their chances of reptating to the growing crystal boundary is limited by the cross diffusion coefficient (diffusion coefficient of the PEN chains in the PEI matrix) which itself is influenced by the viscosity of the matrix. The data further indicate that the cold crystallization region of both PEN and PEEK crystals move to higher temperatures with the addition of PEI. This is a direct result of the dilution effect and the diffusion limitation as compounded by the increase of the environment 'viscosity' by the presence of the stiffer (high T_g) PEI chains. In order to overcome these difficulties in crystallization, higher thermal energies are needed. This is the reason for the increase of cold crystallization temperature with the increase of PEI fraction.

It is well known in the PET (poly ethylene terephthalate) film literature[11] that in order to obtain films with uniform thickness and transparency one needs to quench the crystallizable polymers (those that possess slow enough crystallization to allow complete vitrification) into the glassy state. In a subsequent step, these films are brought to temperatures between T_g and T_{cc} where they exhibit rubbery consistency. Then stretching these films results in stress induced crystallization which helps in self levelling of the films. This is as a direct result of stress hardening that accompanies the deformation.

In order to determine the processing temperature window

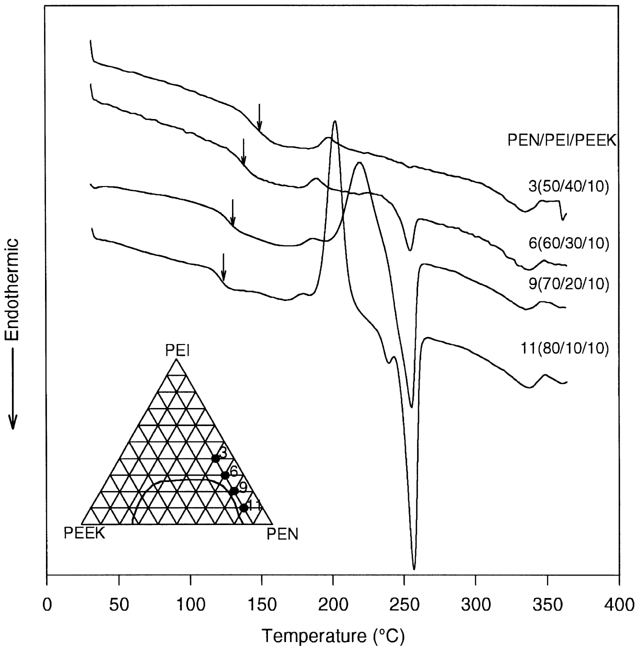

Figure 7 d.s.c. scans of PEN/PEI/PEEK films containing 10% PEEK before stretching. Heating rate is 10°C/min. The arrows indicate the location of T_g

for the blend films, the d.s.c. scans of the quenched ternary blend films were obtained at a heating rate of 10°C/min (*Figures 6 and 7*). As shown in *Table 1*, the difference between T_{cc} and T_g varies between 35 and 62°C depending on the blend composition. Keeping the PEEK proportion constant, this window becomes larger with the increase of PEN concentration in the blend.

Also, the percent crystallinities of unstretched films were calculated using the areas under the cold crystallization and the melting peaks corresponding to PEN and PEEK separately. It was found that the original films were essentially amorphous.

Influence of temperature on the deformation

Since the glass transition temperature of the blends varies with composition, for a meaningful comparison of the deformation behaviour between various compositions it was decided to investigate the deformation behaviour at temperatures a constant value above the glass transition temperature of each individual blend. Based on the experiences with the stretching behaviour of the homopolymers PEEK and PEN, we decided to investigate the stretching behaviour of ternary blends at $T_g + 10$°C, $T_g +$ 20°C and $T_g + 30$°C using three different stretch rates: 100, 250 and 500 mm/min.

The influence of stretching temperature on the stress strain behaviour of selected PEN rich ternary blends is shown in *Figures 8 and 9*.

The 80/10/10 PEN/PEI/PEEK melt miscible ternary blend contains the largest proportion of PEN in the ternary blends we investigated. At $T_g + 10$°C the stress–strain curve exhibits distinct yielding followed by stress drop which accompanies the neck formation. At the later stages of deformation the rapid rise in the stress signifies rapid stress hardening which occurs as a result of stress induced crystallization. When the temperature is raised to $T_g +$ 20°C, yielding followed by stress drop is essentially eliminated and the whole stress–strain curve resembles affinely deforming cross-linked rubber. The observations on the samples also indicated the elimination of necking which was previously observed in the stress–strain curves of PEN and PEN/PEI blends under these processing conditions. The critical strain at which the substantial stress hardening occurs is indicated by arrows on each figure. At $T_g + 30$°C this increase occurs around 3.5–4.0 stretch ratio. In order for these blends to succeed in the biaxially stretched film market commercially, they need to be processed in the machines already developed and optimized for PET which exhibit low critical strains beyond which rapid rise in stress is observed at its respected optimum processing temperature range (~85–95°C). The substantial presence of this stress hardening is essential for thickness uniformity in the final products. This effect is called ‘self levelling’. We increased the proportion of PEI at the expense of PEN while keeping the proportion of PEEK the same (*Figure 8*). The result indicates that there are distinct changes in the deformation behaviour. One is that the stress drop after the yield point that was observed in PEN and 80/10/10 PEN/PEI/PEEK films at $T_g + 10$°C is eliminated but the elongation at break is also reduced. However, at $T_g + 20$°C and $T_g + 30$°C ideal stress–strain curves are observed. The increased proportion of PEI has essentially two effects. One is that at low deformations the level of stresses experienced becomes higher as a result of increased friction between the polymer chains by the presence of the stiffer and bulkier PEI chains (anti-plasticizer effect!). But this comes at the expense of

Table 1 Cold crystallization and glass transition temperature difference of unstretched films

No.	PEN/PEI/PEEK	$\Delta(T_{cc} - T_g)$
1	30/40/30	35
2	40/40/20	40
3	50/40/10	54
4	40/30/30	38
5	50/30/20	58
6	60/30/10	53
9	70/20/10	58
11	80/10/10	62

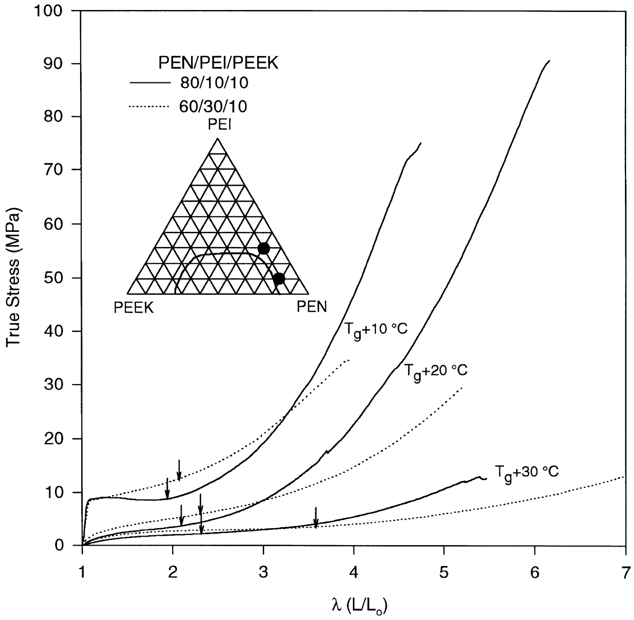

Figure 8 Effect of temperature on the uniaxial deformation behaviour of PEN/PEI/PEEK (80/0/10), (60/30/10) films stretched at 250 mm/min. The arrows indicate the onset of stress hardening

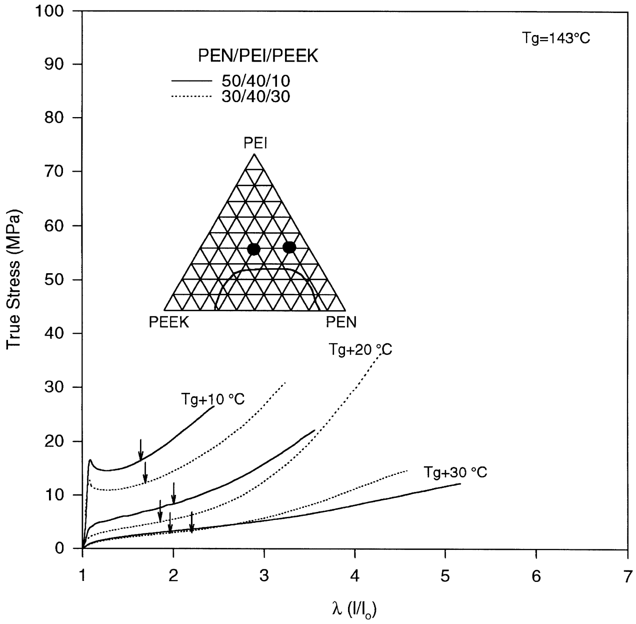

Figure 9 Effect of temperature on the uniaxial deformation behavior of PEN/PEI/PEEK (50/40/10), (30/40/30) films stretched at 250 mm/min. The arrows indicate the onset of stress hardening

reduced stresses at higher strains since the stress induced crystallization process is detrimentally influenced by the increased proportion of non-crystallizable PEI chains. This is clearly shown in *Figure 8* where the stress–strain curves of 80/10/10 and 60/30/10 blends are shown for $T_g + 20°C$ processing temperature.

In order to counteract this reduction of stress at high strains we increased the proportion of PEEK to 30%. The results indicate that this is in fact what occurs at the optimum processing temperature of $T_g + 20°C$ and even at $T_g + 30°C$, as shown in *Figure 9* where stress–strain curves for 30/40/30 and 50/40/10 at $T_g + 20°C$ are compared.

The overall goal of increasing the glass transition temperature while reducing the critical strain beyond which substantial stress hardening occurs is thus accomplished.

Influence of stretch rate on the deformation

The rates of stretching utilized in this research are about an order of magnitude smaller than those typically used in commercial machines such as tentering frame. Therefore, the results we report below give the general trends with the change of stretching rate and do not necessarily represent the quantitative effects one would see in a commercial process. At commercial rates some of the physical

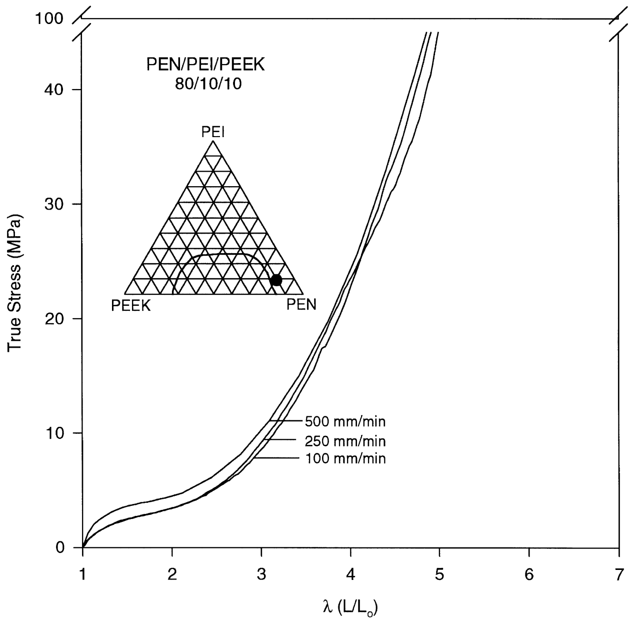

Figure 10 Effect of stretch rate on the uniaxial deformation behaviour of PEN/PEI/PEEK (80/10/10) films stretched at $T_g + 20°C$ ($T_g = 122°C$)

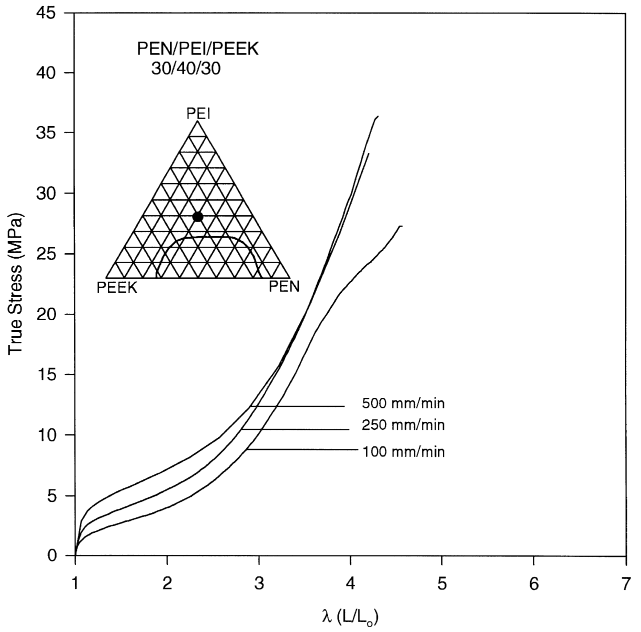

Figure 11 Effect of stretch rate on the uniaxial deformation behaviour of PEN/PEI/PEEK (30/40/30) films stretched at $T_g + 20°C$ ($T_g = 154°C$)

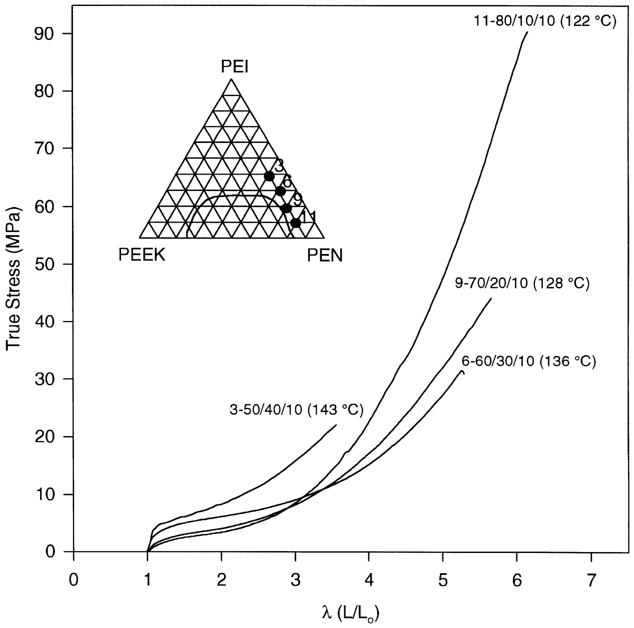

Figure 12 Effect of composition on the uniaxial deformation behaviour of PEN/PEI/PEEK films containing 10% PEEK and stretched at $T_g + 20°C$ with 250 mm/min stretch rate

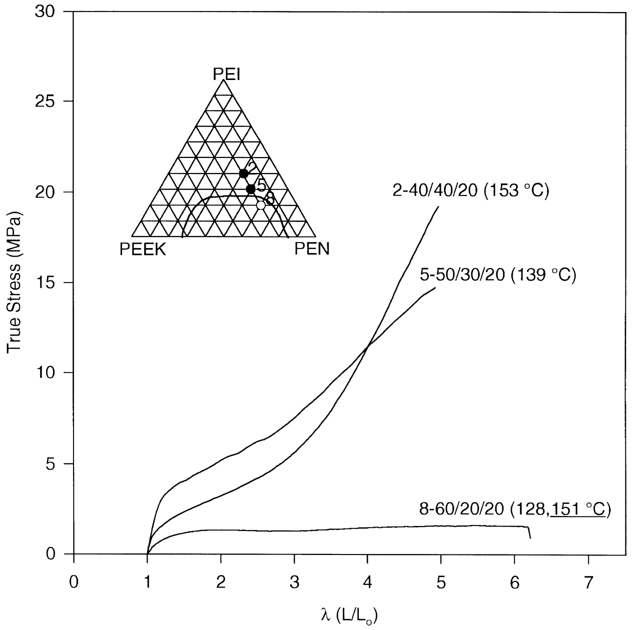

Figure 13 Effect of composition on the uniaxial deformation behaviour of PEN/PEI/PEEK films containing 20% PEEK and stretched at $T_g + 20°C$ with 250 mm/min stretch rate

phenomena such as strain hardening etc. would be accelerated.

In the PEN rich blend, the increase of stretching rate from 100 mm/min to 500 mm/min does not have a significant influence on the stress–strain behaviour as shown in *Figure 10*. As the proportions of PEI and PEEK increase in the blends, the influence of the stretching rate becomes more evident (see *Figure 11*). In general, the level of stress increases with the increase of stretching rate. This occurs partly due to the increases in stress induced crystallization at higher rates.

Influence of composition on the deformation

The influence of composition on the deformation behaviour of the films are shown in *Figures 12–14* at increasing levels of PEEK concentration respectively. All the precursor samples shown in *Figure 12* exhibit a single T_g. As the PEI concentration increases, the stress levels at low deformation levels increase and those in the high strain region where stress hardening is observed decrease, indicating the increased presence of non-crystallizable PEI which provides increased resistance to deformation at low deformations but detrimentally affects the stress induced crystallization which is primarily responsible for the observed stress hardening. This occurs despite the fact that all the films are processed at a constant 20°C above their respective glass transition temperatures. This deformation behaviour changes when the PEI concentration reaches 40% in #3 sample where rapid rise of stress comes at the expense of lower elongation at break.

As we have seen earlier, when the PEEK concentration is increased to 20% and 30% those blends containing the lowest fraction of PEI exhibit two glass transition temperatures which indicates that although they are essentially amorphous they contain at least two distinct phases: PEN and PEEK rich phases. These compositions (#7 and #8) are indicated by the unfilled circles on the ternary diagrams shown in the inset. The blends containing more that 20% PEI are amorphous and one phase.

As shown in *Figure 13*, at higher strains, stress levels are decreased with a decrease of PEI concentration. But in *Figure 14*, at all strains, stress levels are increased with the increase of PEI concentration. *Figures 13 and 14* indicate that immiscible blend films stretched at 20°C higher than their high T_g exhibit very low stress levels compared with miscible compositions, stress-hardening essentially disappears and the deformations resemble a 'taffy pull' until failure. This behaviour is typical deformation behaviour of amorphous 100% PEN when it is processed at these temperatures. This change in stress–strain behaviour occurs with only a 10% change in concentration from #2 to #8 and from #4 to #7. The stress–strain curves obtained for the two phase blends were processed at $T_{g(high)} + 20°C$ so both phases are in the rubbery state. The higher T_g (149°C) represents the phase containing mostly PEEK mixed with a small amount of PEI. Since this phase constitutes a smaller phase compared with the PEN rich phase ($T_g = 128°C$), the absence of stress hardening from the stress–strain curves suggests that in #7 and #8 compositions, the PEEK rich phase most likely constitutes discontinuous domains. If they were to form some sort of continuous network they would have exhibited stress induced crystallization and the resulting stress hardening—however small—would have been observed in the stress–strain curves.

In order to elucidate the influence of processing temperature on the stress–strain curves of the phase separated amorphous blends, we obtained the deformation behaviour of blends 7 and 8 exhibiting two glass transition temperatures at $T_{g(low)} + 10, 20, 30°C$ and $T_{g(high)} + 20°C$. The results are shown in *Figures 15 and 16*. At stretching temperatures above $T_{g(low)}$, phase separated blend films exhibit stress hardening which is a result of stress-induced crystallization of only PEN since PEEK at this temperatures is in the glassy state. Above $T_{g(high)}$ at which both PEN and PEEK are in the rubbery region, the film exhibits very low stresses, indicating that PEEK regions are the unconnected dispersed phase and they do not contribute to stress–strain curves and these curves are typical of 100% PEN at these temperatures. Obviously, in these partially phase separated

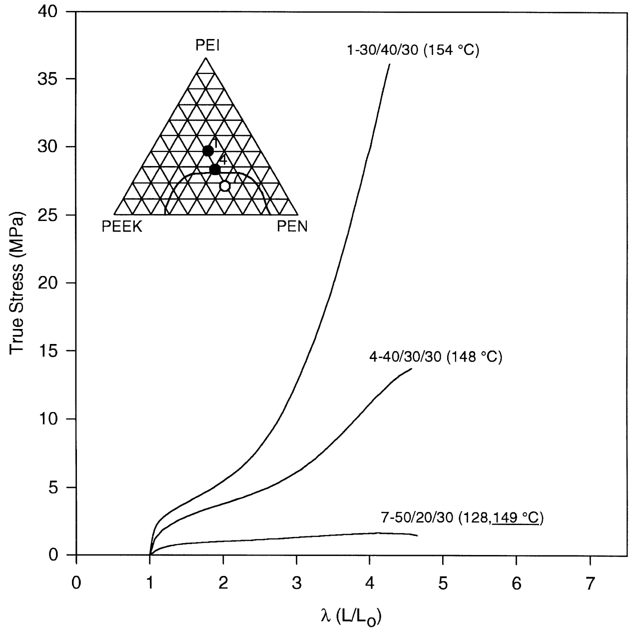

Figure 14 Effect of composition on the uniaxial deformation behaviour of PEN/PEI/PEEK films containing 30% PEEK and stretched at $T_g + 20°C$ and with 250 mm/min

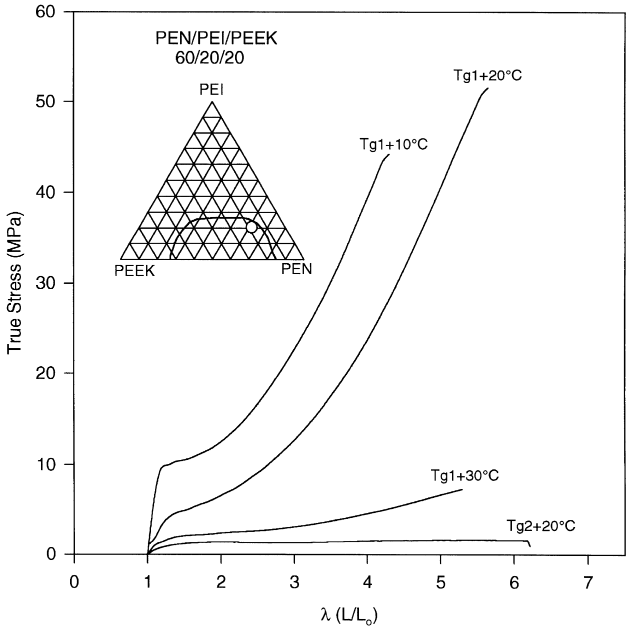

Figure 15 Stress–strain behaviour of phase separated blend film 8 (60/20/20) at $T_{g1(128)} + 10, 20, 30°C$ and $T_{g2(151)} + 20°C$

blends the overall mechanical response is governed by the phase forming the matrix.

Thermal behaviour of stretched films

As shown in *Figures 17–19*, when the stretch ratio increases, the area under the cold crystallization peaks becomes smaller and moves to lower temperatures approaching the glass transition. This is a typical behaviour observed in crystallizable polymers stretched from the amorphous precursors at temperatures between their glass transition and cold crystallization temperatures. With the increase of stretch ratio, the orientation of the chains increases and some of these chains crystallize in the oriented state as will be shown later by WAXS analysis and some orient but do not crystallize. During the d.s.c. scan these oriented amorphous regions require much less thermal energy as a result of reduction of conformational entropy, consequently they crystallize at lower temperatures. This is the reason why the cold crystallization peak shifts to lower temperatures and the area under the peak decreases with deformation. In addition, at intermediate stretch ratios the breadth of this peak increases, suggesting that the orientation distribution in the amorphous regions becomes broad, resulting in broad crystallization range during d.s.c. scan. Although PEEK is present in small proportion in 80/10/10 blend, we can still discern its cold crystallization

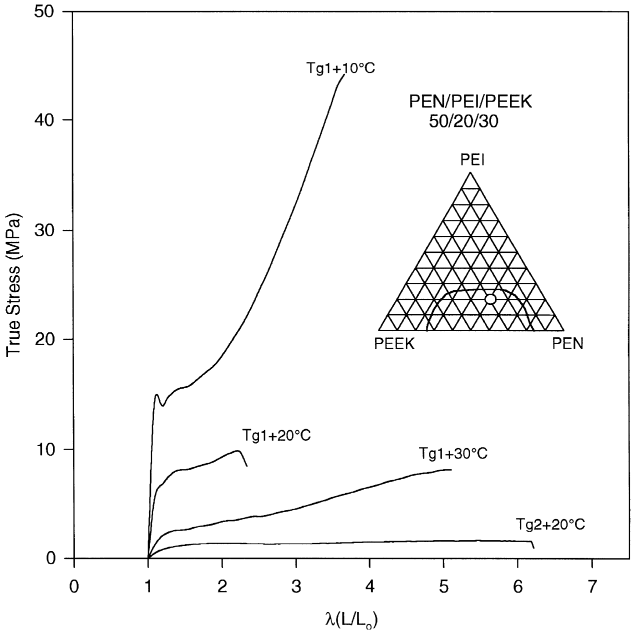

Figure 16 Stress–strain behaviour of phase separated blend film 7 (50/20/30) at $T_{g1(128)}$ + 10, 20, 30°C and $T_{g2(149)}$ + 20°C

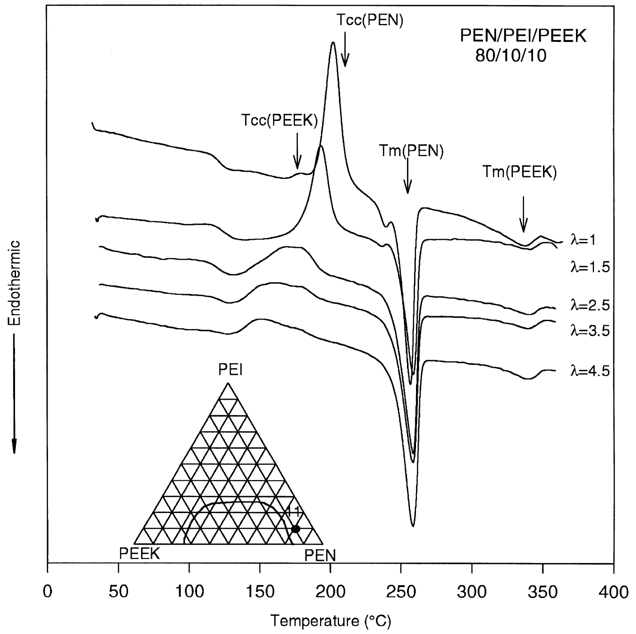

Figure 17 d.s.c. scans of PEN/PEI/PEEK (80/10/10) films stretched at T_g + 20°C and at different stretch ratios. T_g = 122°C. Heating rate = 10°C/min

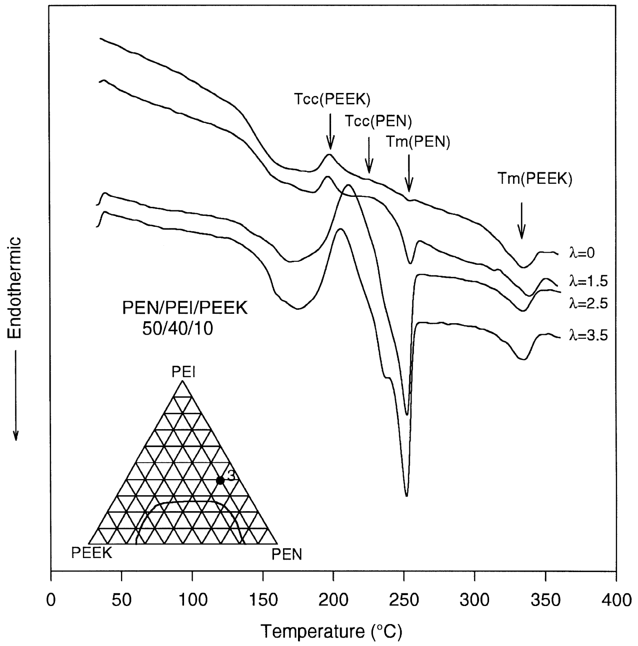

Figure 18 d.s.c. scans of PEN/PEI/PEEK (50/40/10) films stretched at T_g + 20°C and at different stretch ratios. T_g = 143°C. Heating rate = 10°C/min

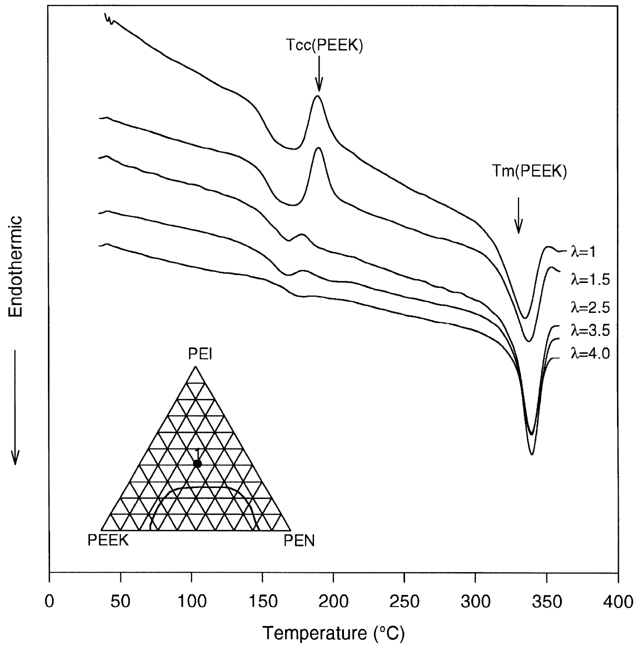

Figure 19 d.s.c. scans of PEN/PEI/PEEK (30/40/30) films stretched at T_g + 20°C and at different stretch ratios. T_g = 154°C. Heating rate = 10°C/min

temperature around 170°C, indicated by an arrow in the curve for the unstretched sample (*Figure 17*). This also suggests that the PEEK chains form distinct and separate domains with the PEI even at these low concentrations and they phase separate into their own crystalline domains upon heating in the d.s.c. These regions subsequently melt around 340°C.

The exact crystallinities of the stretched films could not be calculated because although there are two melting peaks only one cold crystallization peak is present as a result of the overlap of the separate peaks of PEN and PEEK. But with the experimental evidence obtained we can still state that the crystallinity of the films is increased with stretch ratio since the area under the cold crystallization peaks becomes smaller, the area under the melting peaks becomes larger and their difference increases. Also, crystallinity is increased with stretch ratio, since it is proportional to this difference.

When the proportion of PEI is increased at the expense of PEN in sample 6 (60/30/10), the crystallizability during the heating scan is detrimentally affected. The areas under the cold crystallization peaks for PEEK and PEN are rather small and consequently so are those under the melting peaks. Upon imposing even the smallest amount of stretch the crystallizability in PEN phase significantly increases at this 10°C/min heating rate as evidenced by the increase in the area under the cold crystallization peak. This occurs as a result of increased orientation in the crystallizable phases. Further increase in stretching results in decrease of cold crystallization peak position and increases its breadth. In fact, at high stretch ratios the temperature gap between the glass transition region and cold crystallization temperature essentially disappears. In these samples, as soon as the chains attain sufficient mobility, they rapidly crystallize with those chains in the amorphous state having highest orientation crystallizing first. These data also indicate that even at high stretch ratios, a significant portion of the material remains in the amorphous state as they crystallize during the d.s.c. scan. Further increase of PEI to 40% in 50/40/10 films further reduces the crystallizability, particularly in the PEN phase (*Figure 18*). We still observe cold crystallization and melting peaks of PEEK but not PEN in the as-cast films. Crystallization and melting peaks do not emerge until a sufficient amount of stretching has been applied to the films. Here also we see that a large portion of crystallizable material remains amorphous even at high stretch ratios. The behaviour changes when the PEEK proportion is increased to 30% in the blend with 30/40/30 PEN/PEI/PEEK composition (*Figure 19*). In this blend we see no evidence of crystallization or melting of PEN and only the transition peaks associated with PEEK. As the stretch ratio increases the cold crystallization peak for PEEK located around 170°C shifts to lower temperatures and reduces in size and eventually disappears at a draw ratio of about 4.0. As we will see in the next section, these films exhibit only PEEK crystalline peaks which are very highly oriented and no evidence of PEN crystallites is observed, indicating that PEN chains are held firmly in the mixture with noncrystallizable PEI during stretching.

Influence of deformation on the development of crystalline lattice and orientation

At least four films of differing stretch ratios were prepared for each selected composition. In order to determine the structural evolution during stretching, WAXS film patterns were obtained with the X-ray beam

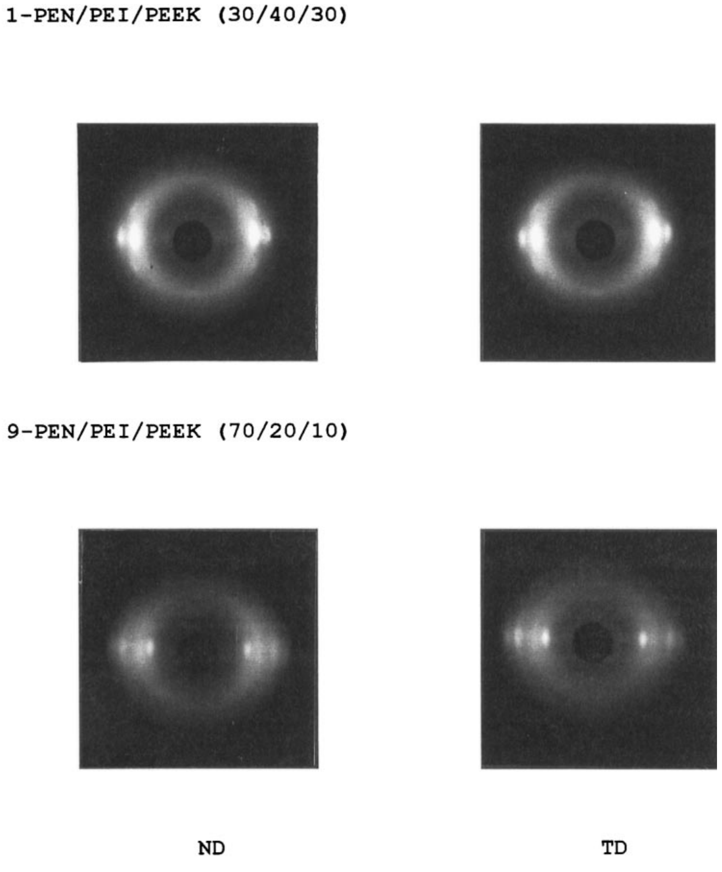

Figure 20 Comparison of WAXS patterns of 3.5 × stretched films in normal direction and in transverse direction

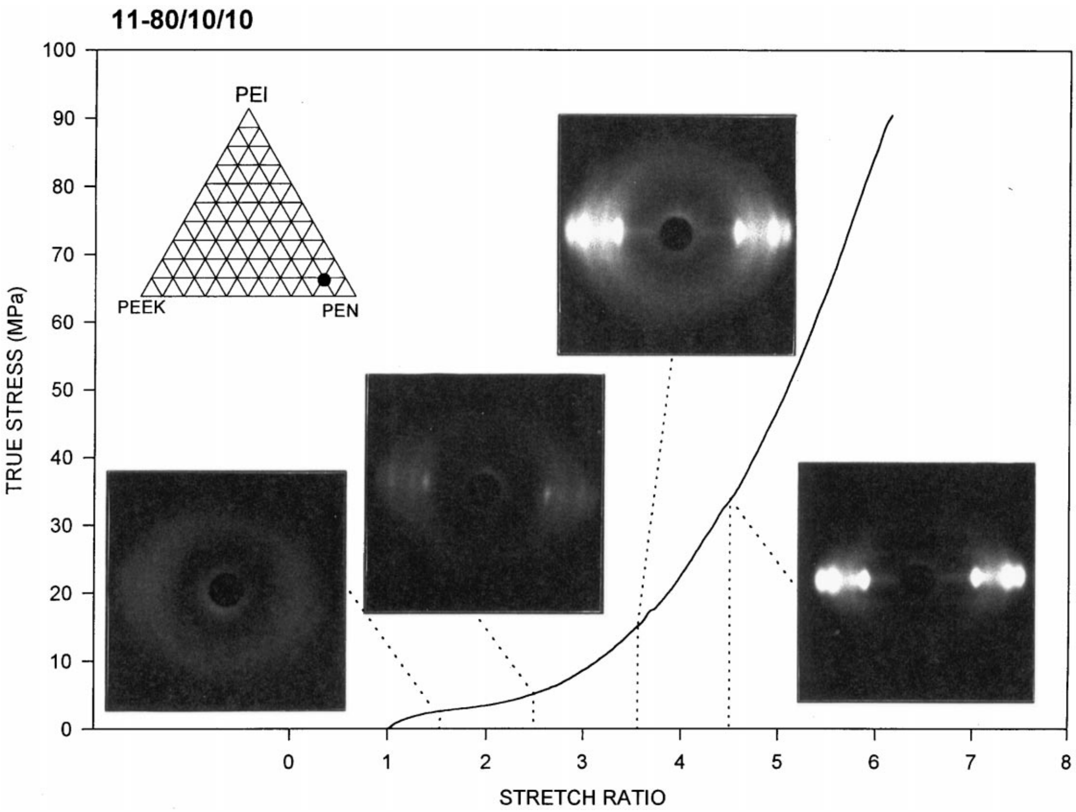

Figure 21 WAXS patterns of the stretched films of composition 11 (80/10/10)

normal to the broad surface of the films. In order to confirm the transverse isotropy in these films we obtained flat film WAXS patterns on films 1 and 9 stretched to 3.5 stretch ratio with X-ray beam both in ND and in TD. These are shown in *Figure 20*. The results indicate that compositions 1(30/40/30) and 9(70/20/10) show transverse isotropy.

As indicated in the thermal analysis section, the starting films are all essentially amorphous regardless of the number of phases present based on the number of T_gs observed. In these blends there are a number of questions one can ask. Some of these are as follows.

(1) When does the crystalline lattice form during deformation if it forms at all?
(2) Which one of the two crystallizable polymers crystallizes during deformation and what is the level of orientation exhibited by the crystalline regions?
(3) Do the polymers co-crystallize? Does the presence of noncrystallizable PEI influence the lattice structure of the crystalline regions or are they excluded from these regions?

In the following, we will address these questions. As shown in *Figure 21*, at the early stages of deformation the blend 80/10/10 (PEN/PEI/PEEK) remains amorphous. In this figure, WAXS patterns are shown at their corresponding strain levels on the true stress–strain curve. When the stretch ratio reaches 2.5 × sharp equatorial diffraction spots with very small azimuthal spread are observed. These planes correspond to those of the α-phase of PEN. PEN crystal planes were identified by comparing d-spacing values with the literature[12]. *Figure 22* shows the indices of the planes existing in blend film 11 stretched to a stretch ratio of 3.5. The absence of azimuthal spread in these peaks clearly indicates that the PEN crystalline regions are formed by very highly extended chains. These regions are most possibly formed in needle like crystallites distributed throughout the matrix.

As the stretch ratio increases into regions where stress rise is accelerated, additional PEEK peaks appear but they become broader. These results indicate that at these high deformation levels the crystallinity increases but the level of perfection of crystalline lattice suffers, as indicated by the large breadth of the equatorial peaks. In addition, the absence of off-equatorial peaks indicates a lack of full three-dimensional order in the crystalline regions.. These WAXS patterns also indicate that even though it is present in small quantities, PEEK regions also crystallize and give rise to the equatorial peaks.

When the PEI proportion is increased at the expense of

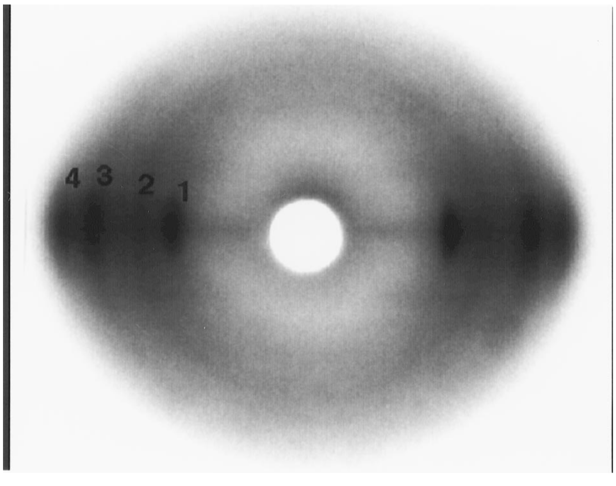

Figure 22 The indices of the crystal planes in 3.5 × stretched film 11 (80/10/10) 1-(010) PEN 2-(110) PEEK 3-(100) PEN 4-($\bar{1}$10) PEN

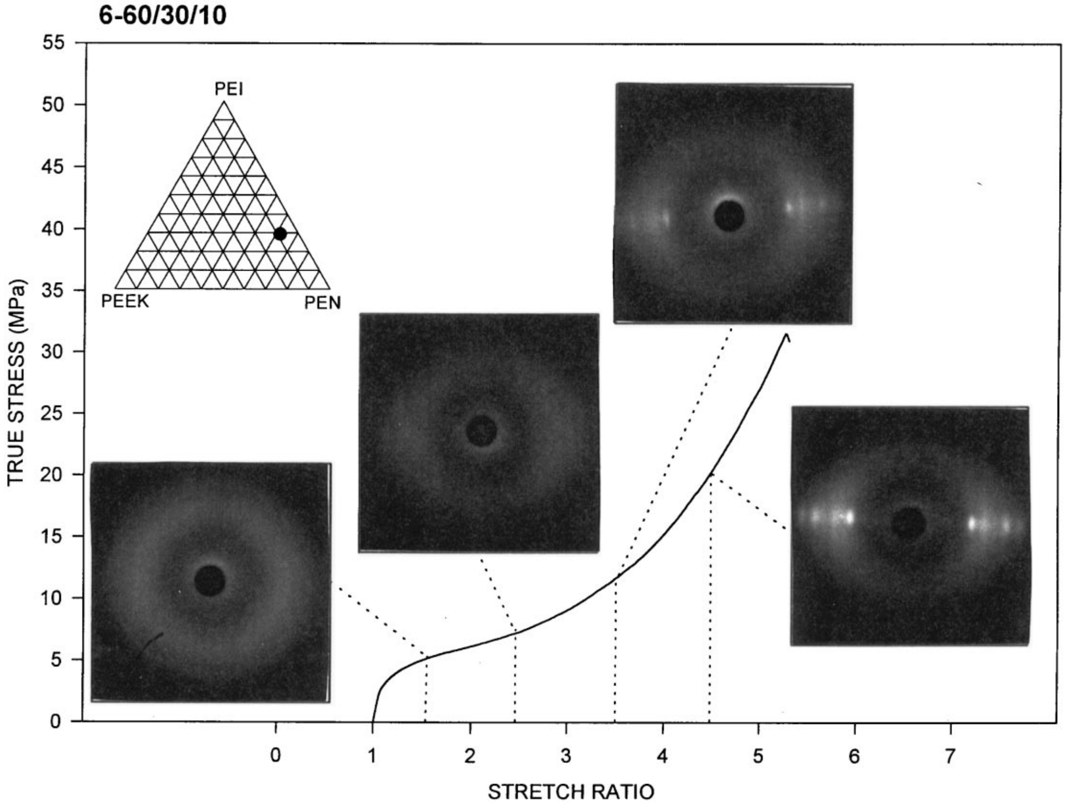

Figure 23 WAXS patterns of the stretched films of composition 6 (60/30/10)

PEN, the formation of crystalline lattice is retarded to larger stretch ratios. *Figure 23* indicates that the first signs of crystallinity are observed around a stretch ratio of 3.5. With further increase of strain this structural conversion is enhanced. This behaviour is quite understandable as the proportion of non-crystallizable PEI phase is increased, the dilution effect spatially separates the crystallizable chains from one another, rendering crystallization more difficult.

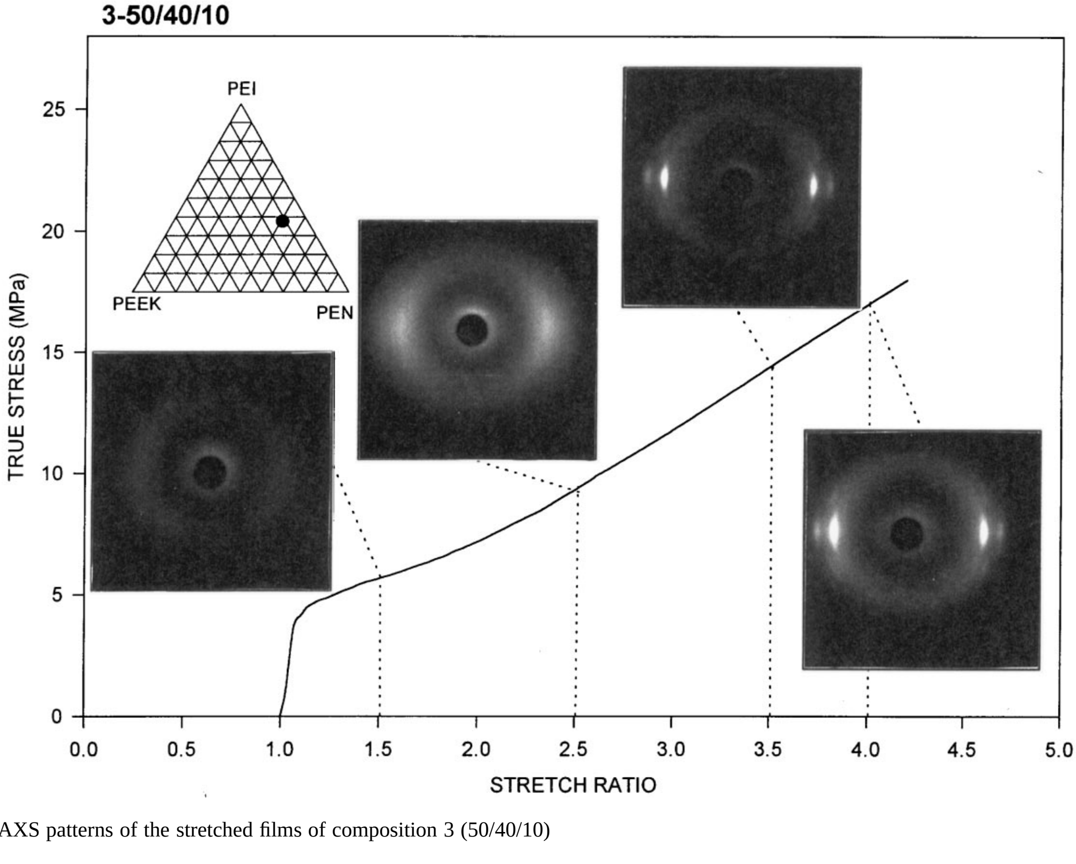

Figure 24 WAXS patterns of the stretched films of composition 3 (50/40/10)

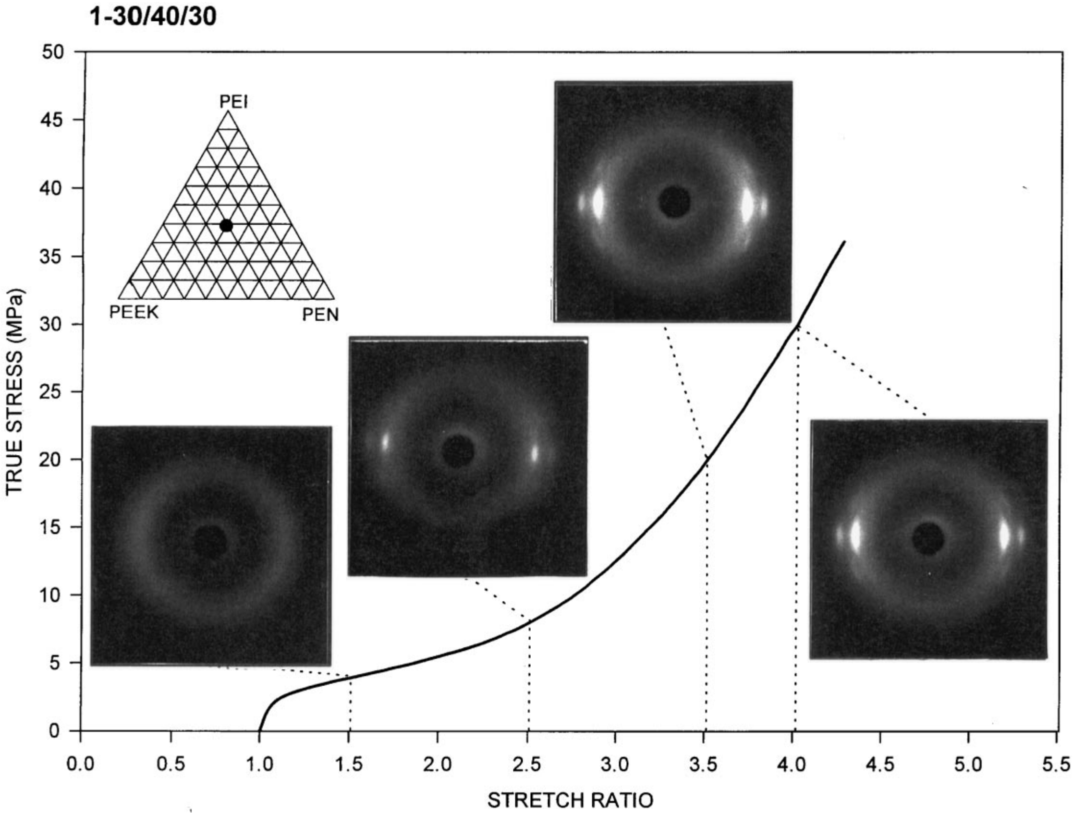

Figure 25 WAXS patterns of the stretched films of composition 1 (30/40/30)

Again at this composition the dominant crystalline phase is PEN and faint equatorial peaks of PEEK are also observable.

With a further increase of PEI proportion to 40% in 50/40/10 PEN/PEI/PEEK blend a remarkable transformation in the structural formation is observed in *Figure 24*. In this blend containing substantial amount of PEN (50%) and PEI (40%), the crystalline peaks observed in the WAXS patterns at high stretch ratios all belong to PEEK which only occupies 10% of the mass.

When the proportion of PEEK was increased from 10% to 30% at the expense of PEN the minimum stretch ratio at which the first crystalline peaks are observed decreases, indicating a positive influence of the presence of PEEK on the stress induced crystallization. We saw no signs of crystalline peaks of PEN in these compositions, indicating that PEEK chains are readily oriented upon deformation and PEN chains are not (see *Figure 25*). The indices of the crystal planes corresponding to PEEK are shown in *Figure 26*.

Effect of annealing

The stretched films were annealed with fixed length at 200°C and the effect of annealing on their crystal structure was observed through the X-ray film patterns (*Figure 27*). As in the case of unannealed samples, compositions 6 and 11 have a combination of PEN and PEEK crystals. PEN forms the dominant crystal structure in these blends. PEN chains which were oriented but not packed into a crystal lattice in as-stretched films rearrange and subsequently crystallize during the annealing process where they gain the necessary energy. The identification of the crystalline planes is shown in *Figure 28*.

The films containing 40% PEI and 50% PEN have PEEK crystals in their stretched forms and annealed WAXS patterns of these stretched films reveal that unoriented PEN crystals are formed during annealing. Although PEN chains are also oriented during deformation they relax during the annealing process and form isotropic diffraction rings. When the PEEK concentration is increased to 30%, only PEEK crystals are present but PEN is not able to crystallize even with annealing process. It is known that pure PEN can be crystallized at this annealing temperature. This suggests that the presence of bulky PEI molecules hinders the crystallization of PEN by penetrating in between the PEN chains. It has already been shown that in the case of PEI/PEEK blends, upon crystallization of PEEK, so-called phase

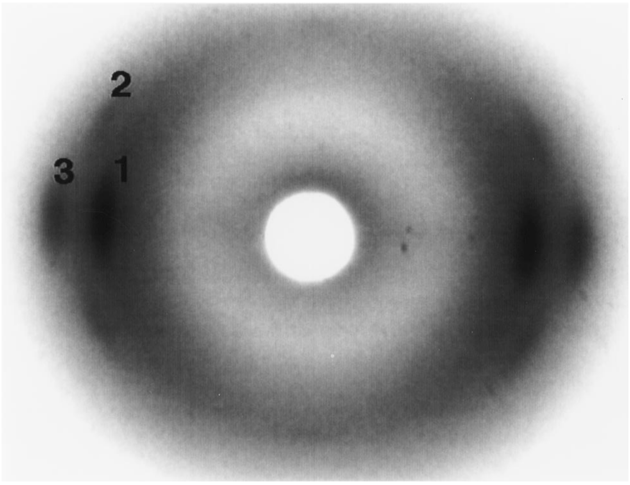

Figure 26 Indices of the crystal planes in 3.0 × stretched film 1 (30/40/30) 1-(110) PEEK 2-(113) PEEK 3-(200) PEEK

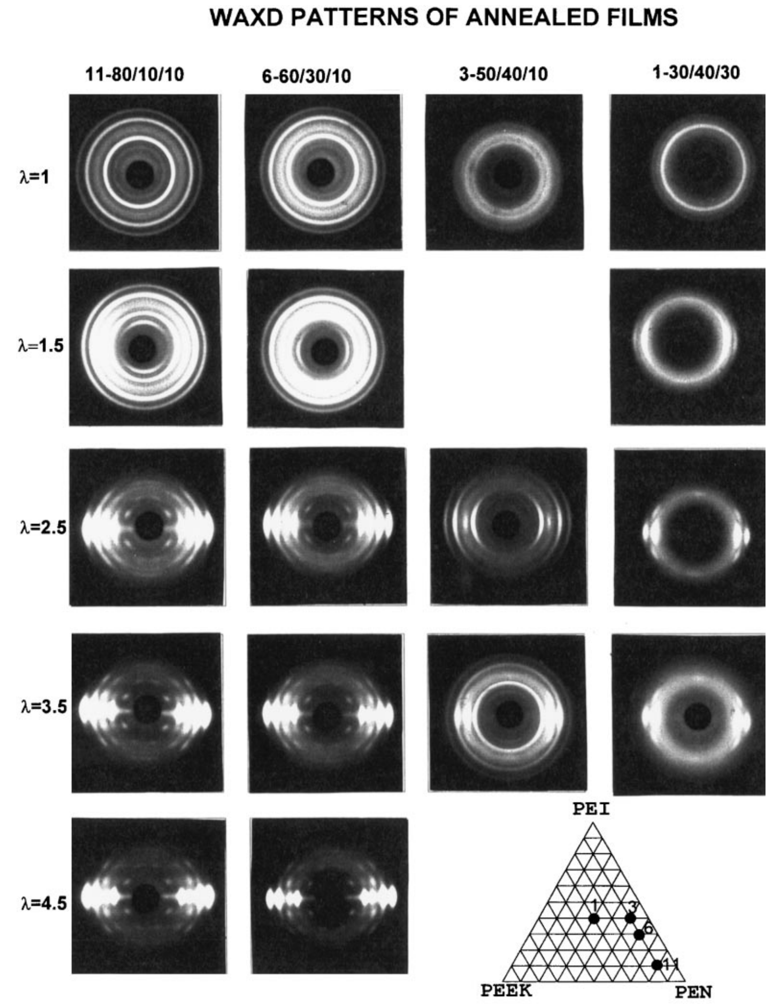

Figure 27 WAXS patterns of the stretched films annealed at 200°C with fixed ends

segregation (interlamellar[13], interfibrillar[14] or interspherulitic[15]) takes place, in other words PEI molecules are rejected from the crystal lattice of PEEK, the amorphous phase consists of mostly PEI and PEEK crystallizes independently of PEI. So, PEI mostly affects the crystallization of PEN but not PEEK.

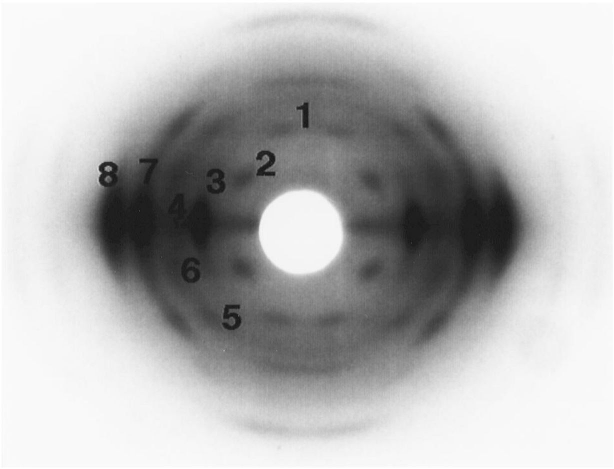

Figure 28 Identification of the crystal planes in 3.5 × stretched and fixed length annealed film 11 (80/10/10) 1-(001) PEN 2-$(\bar{1}02)$ PEN 3-(010) PEN 4-(110) PEEK 5-$(\bar{1}12)$ PEN 6-$(\bar{1}11)$ PEN 7-(100) PEN 8-$(\bar{1}10)$ PEN

We also calculated the orientation factors of PEEK crystal axes for the compositions containing 40% PEI where only PEEK crystallizes in films stretched 3.5 times. The orientation factor of the *c*-axis is very close to 1 and the orientation factors of *a* and *b* axes are very close to −0.5. These findings suggest that the chains are almost parallel to the stretching direction. *Figure 29* shows that with the decrease of PEEK concentration the degree of orientation of the *c*-axis decreases.

It was also observed that when the stretched films are annealed with fixed ends, the degree of orientation of the chain axis (*c*-axis) is slightly decreased. This is a result of crystallization of the additional PEEK chains which were oriented to a lower degree before annealing. Upon crystallization of the latter population, the overall orientation levels are reduced.

Mechanical properties of uniaxially stretched films

Figures 30–32 show the variation of some of the mechanical properties of the uniaxially stretched ternary blend film with stretch ratio. The compositions tested are 1 (30/40/30), 3 (50/40/10) and 6 (60/30/10). For all the compositions tensile strength and elastic modulus increase with stretch ratio. This can be explained by considering the orientation and crystallinity development in stretched films. We have already shown that these initially amorphous films crystallize during deformation as a result of stress induced

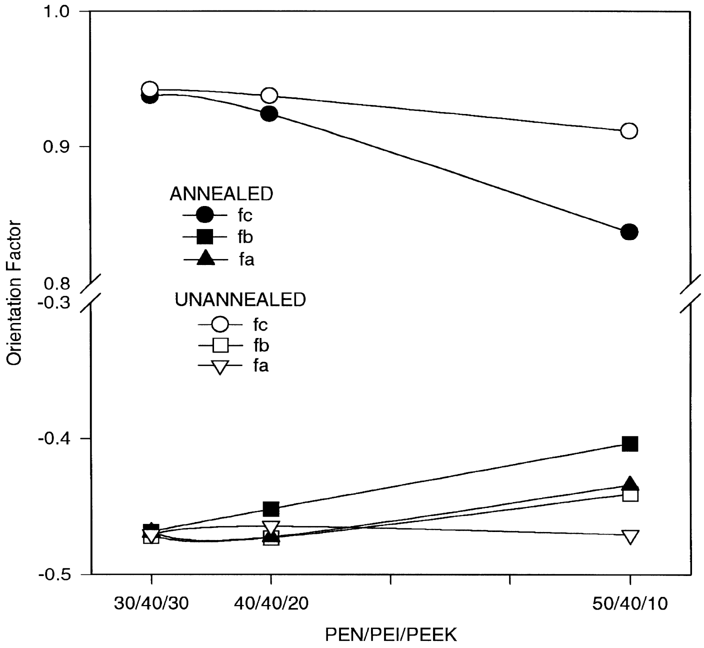

Figure 29 The degree of orientation of PEEK crystal axes in the annealed and unnealed films containing 40% PEI and stretched 3.5 ×

crystallization. In addition, these crystalline domains show high resistance to drawing forces and consequently the strength of the material is improved by deformation. The elongation at break, on the other hand, decreases with the increase of strain for compositions 6 and 3. This is a combined consequence of the increase of orientation and crystallinity which makes the material more brittle and already elongated chains tend to break at lower strains. For the composition containing 30% PEN and 30% PEEK, elongation at break slightly increases with stretch ratio. This may be related to a higher percentage of amorphous concentration present in this composition which will give rise to higher elongations. We note that the elongation of unstretched film containing 60% PEN

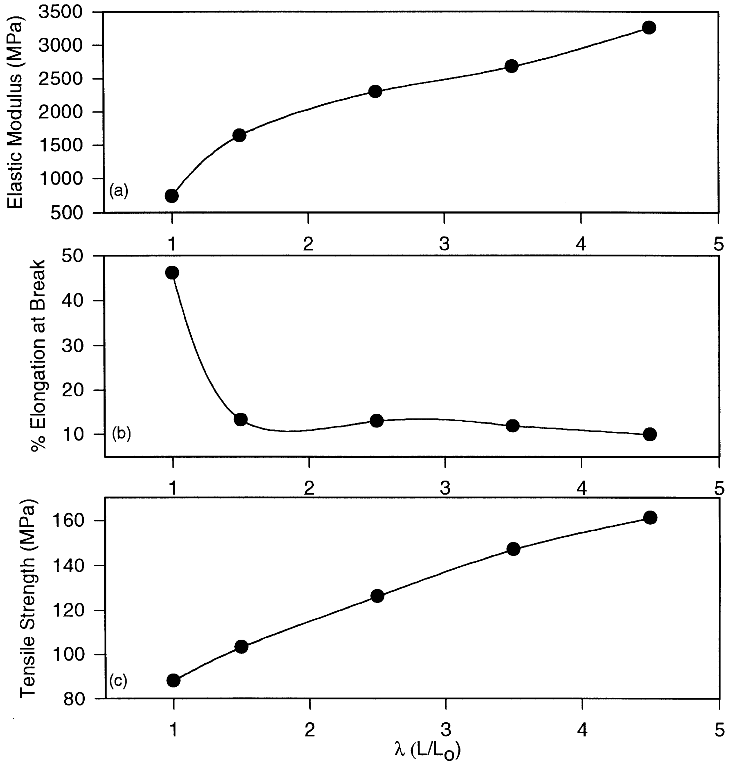

Figure 30 Mechanical properties of uniaxially drawn PEN/PEI/PEEK (60/30/10) stretched at RT and at 80%/min stretch rate: (a) elastic modulus; (b) percent elongation at break; (c) tensile strength *versus* stretch ratio

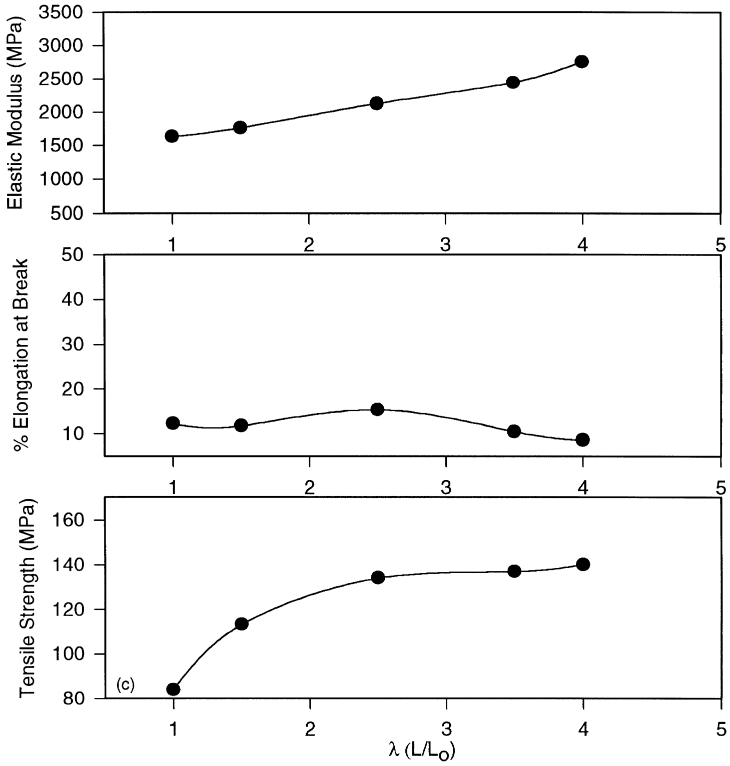

Figure 31 Mechanical properties of uniaxially drawn PEN/PEI/PEEK (50/40/10) stretched at RT and at 80%/min stretch rate: (a) elastic modulus; (b) percent elongation at break; (c) tensile strength *versus* stretch ratio

is significantly higher than the stretched films. This is explained by the formation of cold drawing following the neck. All the other specimens exhibited brittle failure, i.e. the specimen broke before reaching yield stress.

SUMMARY

The deformation behaviour of miscible and partially phase separated PEN rich ternary blends of PEN/PEI/PEEK was studied. The addition of bulky non-crystallizable polyether

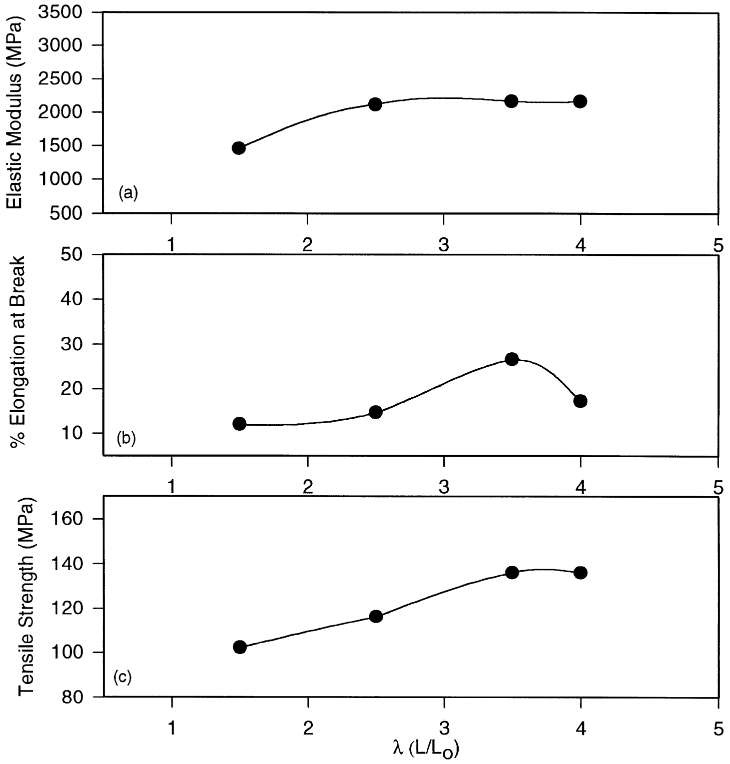

Figure 32 Mechanical properties of uniaxially drawn PEN/PEI/PEEK (30/40/30) stretched at RT and at 80%/min stretch rate: (a) elastic modulus; (b) percent elongation at break; (c) tensile strength *versus* stretch ratio

imide increases the overall stresses experienced during the uniaxial deformation at optimum $T_g + 20°C$ while it reduces the thermal and strain crystallizabilities as a result of the dilution of crystallizable chains and increasing the viscosity of the overall environment in the rubbery state. Thus the increase of PEI in the blends causes the retardation of the formation of crystalline lattice to larger stretch ratios. However, in these blends the necking behaviour observed in the rubbery region of PEN (T_g + 20–40°C) is essentially eliminated as the bulky chains disrupt the formation of local cooperative orientation of the naphthalene planes leading to a neck formation.

The addition of PEEK helps recover some of the stress hardenability in the ternary blends containing a large amount of poly ether imide. This allows one to produce films of uniform thickness as they exhibit strain hardening which is essential for self levelling of the films.

In blends diluted with a large fraction of noncrystallizable PEI, the deformation of the samples results in very high crystalline orientation levels ($fc \sim 0.95 - 1$, $fa = fb \sim -0.5$) in PEEK regions while the PEN regions remain uncrystallized. Subsequent constrained annealing of these films results in further crystallization of PEEK which reduces the overall orientation levels in the PEEK crystalline domains while PEN crystallizes into the unoriented state. This observation of very high crystalline orientation in PEEK regions was attributed to the disentaglement effect caused by the presence of PEI which results in more efficient orientation and lateral packing of the chains in PEEK crystalline domains.

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