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Relationship between stress and orientation induced structures during uniaxial drawing of poly(ethylene 2,6-naphthalate)

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Abstract

Amorphous films of poly(ethylene 2,6-naphthalate) (PEN) were drawn isothermally at temperatures between 130°C and 160°C, more specially at 145°C up to the desired draw ratios, mainly to study structure formation during uniaxial drawing by differential scanning calorimetry. During drawing, a rigid phase structure was induced and the results were analyzed in comparison with stress–strain curves in order to relate the amount of induced rigid phase structure at the earlier-mentioned temperatures with the observed stretching behaviour. During the uniaxial drawing of PEN at temperatures between 130°C and 160°C, the amount of amorphous phase was linearly related to the square root of the extra first strain invariant. The stress–strain curves were characterized by a necking behaviour and the end of the yielding or necking was reached when the amount of induced rigid phase attained 50%. The rigid phase then acted as the continuous phase and the stress increased very strongly. The stretching behaviour of PEN was characterized more by the strain induced rigid phase formation than by the stress or strain induced crystallization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene naphthalate); Stress–strain curve; Differential scanning calorimetry

1. Introduction

Poly(ethylene 2,6-naphthalate) (PEN) is a polyester whose preparation was first reported as early as 1948 [1]. PEN is produced by condensation polymerization of 2,6-naphthalenedicarboxylic acid and ethylene glycol [2–4]. There has, however, been increasing interest in its commercial use since recent indications [5,6], that the dicarboxylic acid monomer may become available in large-scale quantities. PEN molecules contain naphthalene rings, which are stiffer than those of poly(ethylene terephthalate) (PET). The important aspect of PEN is the influence of increased chain stiffness on the mechanical and thermal properties of the polymer. This polymer, like PET, can be formed into an amorphous form by quenching from the melt or it can be crystallized either by slow cooling from the melt or by stretching between the glass transition temperature and the cold crystallization temperature. PEN exhibits a glass transition temperature of about 120°C, which makes it quite attractive as a high-temperature polymer for film, tape and molding applications. PEN possess oxygen barrier properties four to five times higher than those of PET and makes PEN attractive for packaging applications.

One of the unusual characteristics of PEN is that it shows necking behaviour upon stretching from the amorphous state above the glass transition temperature [7,8]. Some authors reported that this neck formation is a result of a highly co-operative orientation of the naphthalene planes parallel to the surface of the film. This behaviour resembles an isotropic to nematic structural transition that occurs at highly localized regions of the sample.

It was reported that PEN has also two crystal forms (α and β) and both are triclinic depending on the crystallization temperature [9]. Crystallizing at 180°C yields the α form as reported by Mencik [2] while crystallizing at 240°C yields the β form. Recent X-ray work [10] has suggested the presence of a mesophase in addition to the crystal form. In this mesophase structure, the molecular chains are in registry with each other in the meridional direction but not fully crystallized in the equatorial direction. The emergence of this structure is caused by drawing of PEN at temperatures between 120°C and 150°C [11]. This structure persisted upon annealing at 180°C or 200°C which leads to the conclusion that this mesophase structure is stable at high temperature.

In this article, we will present our results on the

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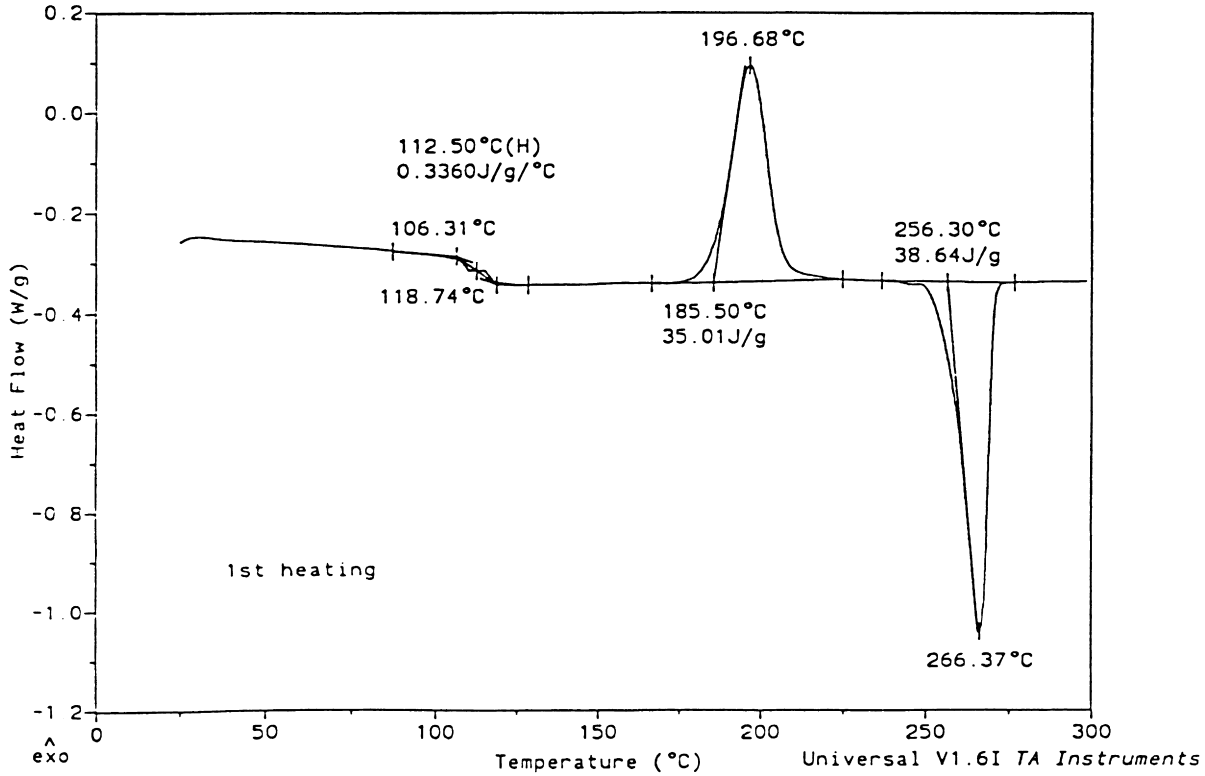

Fig. 1. D.s.c. scan for unoriented PEN film.

development of structure in PEN films as influenced by the uniaxial drawing at different draw ratios by using differential scanning calorimetry (d.s.c.) measurements in addition to the stress–strain curves to perform a structural analysis.

2. Experimental

2.1. Materials

The PEN with an intrinsic viscosity of 0.65 dl/g used in this study was provided in both the film and pellet form by the ICI Co. The thickness of the film was 0.65 mm.

2.2. Thermal analysis

The thermal properties of unoriented and oriented PEN-films were determined with a Universal V1.6I TA Instrument at a heating rate of 10°C/min in a dry nitrogen atmosphere. Typical d.s.c. scan of as-received films is shown in Fig. 1. The T_g for this sample is observed around 112°C, the cold crystallization peak temperature around 197°C and the melting temperature at 271°C. The heat of cold crystallization is around 35 J/g, the heat of fusion equals 38.64 J/g with a heat capacity increase at T_g of 0.3360 J/(g °K) or 84 J/(°K mol).

2.3. Crystallinity

The crystallinity of the films before and after orientation was determined by using d.s.c. thermograms. The crystallization exothermic enthalpy, $\Delta H_{\text{cold crystallization}}$ or ΔH_c, was subtracted from that of the melting endotherm, $\Delta H_{\text{melting}}$ or ΔH_m, to determine the amount of apparent crystallinity initially present in the samples. Crystallinity of the films was calculated according to the equation:

$$\text{Crystallinity}(\%) = \Delta H_{\text{exp}} \times 100/\Delta H_f$$

where $\Delta H_{\text{exp}} = \Delta H_{\text{melting}} - \Delta H_{\text{cold crystallization}}$ and ΔH_f is the heat of fusion for 100% crystalline PEN, 103.4 J/g [12].

2.4. Stress–strain behaviour

To determine the uniaxial stress–strain behaviour, an Instron tensile tester (Model 4202) equipped with a high-temperature chamber was used. A dumbbell-shaped test strip (total length: 30 mm) with a narrow mid-section of 5 mm width and 12.5 mm length was stretched at a drawing rate of 50 mm/min. Before drawing, the sample was equilibrated at the desired temperature for 10 min in the preheated convection oven and drawn to selected draw ratios at selected rates.

The drawing rate of 50 mm/min, which is smaller than the industrially used drawing rates, was chosen to ensure a constant temperature during drawing and to eliminate the heating effect caused by drawing of the samples. A heating time of 10 min was sufficient to attain the desired temperature of the sample, between 130°C and 160°C, and low enough to avoid crystallization of the samples before

Table 1
The uniaxially drawn PEN samples

Sample	Drawing ratio (λ)	Drawing temperature (°C)	Drawing speed (mm/min)
PEN0	1	—	—
PEN1	1.4	145	50
PEN2	1.7	145	50
PEN3	2	145	50
PEN4	4	145	50
PEN5	4.4	145	50
PEN6	5	145	50
PEN7	5.6	145	50

drawing. The d.s.c. curves of the samples, with a heating-up time of 10 min at 130°C and 160°C and which quickly cooled to room temperature, are the same as those of the starting material and show no sign of extra crystallinity.

PEN samples were drawn at 130°C, 140°C, 145°C, 150°C and 160°C at a drawing speed of 50 mm/min. Three samples were drawn at each condition. After drawing, the oriented samples are cooled quickly by clamping them between two thick metal strips, which are at room temperature. The temperature of the oriented samples is lower than 100°C after a contact time of about 5 s.

2.5. Crystallinity and rigid amorphous phase

PEN provides a new example of a polymer that may possess a crystalline and rigid amorphous fraction in the oriented state [12,13], which may be a nematic and/or mesophase structure. The rigid amorphous fraction does not contribute to the increase in the heat capacity at T_g and devitrifies only at temperature [12] (430°K) well above T_g. Similar behaviour was observed in several high-melting temperature polymers with phenylene groups in the main chain. The overall rigid fraction f_r, comprising of the rigid amorphous phase and the crystalline phase, is computed from the heat capacity C_p by setting

$$f_r = 1 - [\Delta C_p(m)/\Delta C_p(a)]$$

where $\Delta C_p(m)$ and $\Delta C_p(a)$ represent the measured and total amorphous heat capacity increase at T_g, respectively. The amount of crystallinity, in turn, is determined by d.s.c.:

$$w^c = \Delta H_{exp}/\Delta H_f$$

where ΔH_{exp} and ΔH_f are the measured and 100% crystalline heat of fusion, respectively.

In the non-oriented state, where the two-phase model of an amorphous and crystalline phase is valid, the fraction f_r is

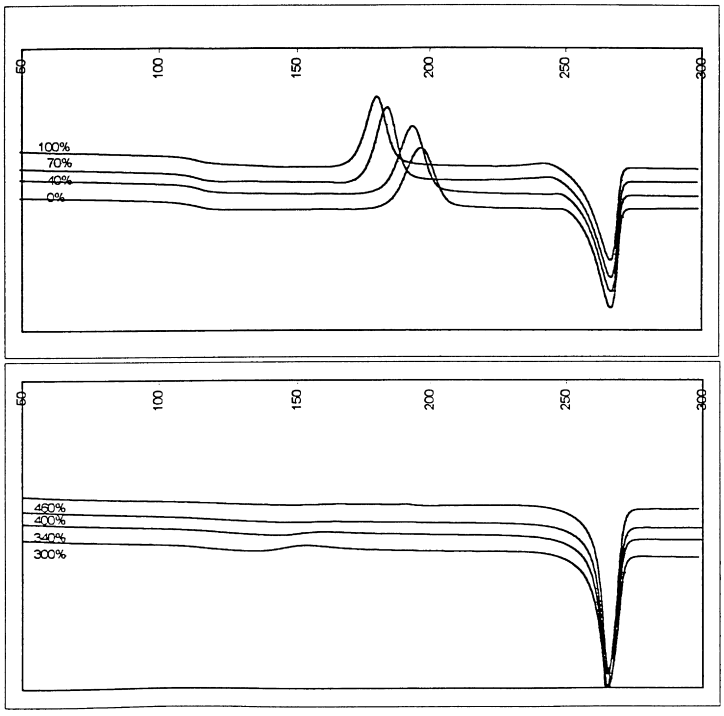

Fig. 2. D.s.c. scans for oriented PEN samples PEN 1–7. The above figures are d.s.c. scans for uniaxially oriented films below the necking behaviour, the second scans are for oriented PEN films after necking behaviour. The values on the curves are the strains measured after drawing.

Table 2
Thermal properties of uniaxially drawn PEN samples

Sample	T_g (°C)	ΔC_p (J/(Kg))	ΔH_c (J/g)	ΔH_f (J/g)	w^c	f_r	$f_r - w^c$
PEN0	112.5	0.3360	35.01	38.64	0.035	0.04	≈ 0
PEN1	114.2	0.3455	35.06	38.36	0.032	0.03	≈ 0
PEN2	112.9	0.2827	31.16	38.50	0.07	0.195	0.125
PEN3	112.8	0.2743	30.78	38.22	0.072	0.210	0.138
PEN4	115.8	0.1598	3.95	45.7	0.404	0.545	0.141
PEN5	119.0	0.1515	2.14	46.73	0.432	0.572	0.14
PEN6	117.5	0.1206	0.354	48.96	0.490	0.660	0.17
PEN7	119.8	0.0586	0	51.29	0.496	0.830	0.334
Sample crystallized at 200°C for 45 min	119.83	0.1900	0	2.37 (208°C) 39.68 (257°C)	0.42	0.42	0

equal to w^c. If f_r is greater than w^c, a rigid amorphous phase exists above T_g and can be quantified.

The amorphous PEN films were uniaxially drawn at 145°C, with a drawing speed of 50 mm/min with the drawing ratios listed in Table 1. The draw ratio, λ is the ratio of the extended length to the original length determined from the displacement of ink marks on the narrow mid-section of the dumbbell-shaped test strip.

All the samples were measured with an updated computer-interfaced Universal V1.6I TA Instruments. The heat capacity measurements were performed in the temperature range of 20°C–300 °C. The d.s.c. was calibrated using the standard procedures.

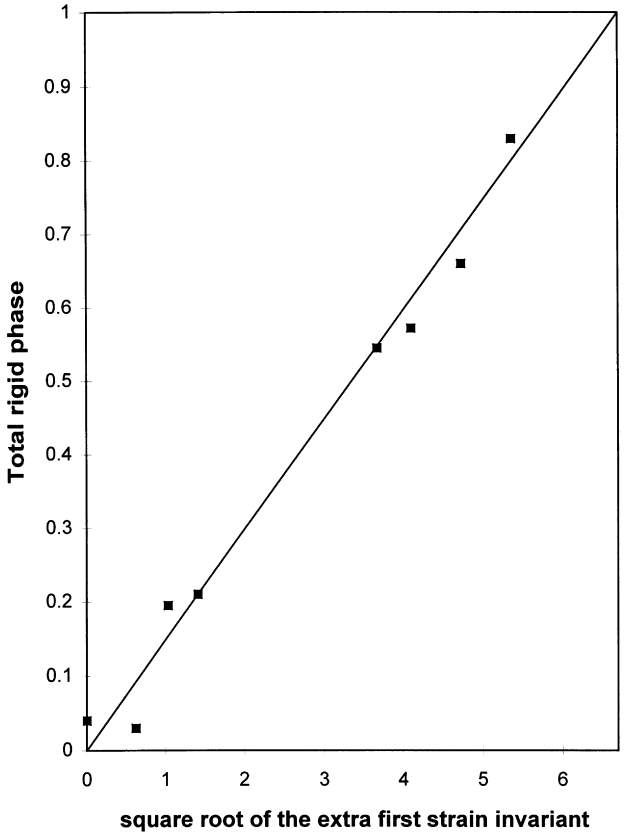

Fig. 3. Total rigid phase in relation with the extra first strain invariant I_{1e}.

Fig. 2 shows the d.s.c. melting traces for PEN 1–7, as an example, and the results of all the samples are listed in Table 2. The lowest temperatures of the glass transition zone, T_{gl}, and the melting temperature, T_m, are almost independent of the mechanical histories of these samples.

3. Results and discussion

The most important result of the d.s.c. measurements, as reproduced in Table 2, is the measured variation of ΔC_p with the draw ratio and the corresponding calculated amount of rigid phase structure f_r in the samples after uniaxial drawing.

Following Abe and Flory [14], if we assume an affine deformation of the chain end-to-end vectors within a network, the variation in the concentration of *gauche* or *trans* conformers depends on the macroscopic draw ratio expressed as the first strain invariant. For uniaxial deformation, the variation of the concentration of *trans* conformers is given by:

$$\Delta m_{trans} = \nu D_2[\lambda^2 + 2/\lambda - 3]/3$$

where ν is the total number of chains in the network, D_2 a constant of proportionality and λ the draw ratio. The expression between brackets is the first strain invariant I_1 minus 3. The structure variation is related to the values of $I_1 - 3$. For simplicity, we put $I_1 - 3$ equal to I_{1e}, the extra first strain invariant.

It seems logical to try, in view of the derived theoretical conformer variation with the first strain invariant, to relate the amount of rigid phase structure f_r to the values of I_{1e}. If we represent the amount of rigid phase structure f_r as a function of I_{1e}, a correlation between these two is experimentally obtained and the fraction f_r varies between 0 and 1 with the square root of I_{1e}. This relationship is represented in Fig. 3 and is expressed by the following equation:

$$f_r = I_{1e}^{0.5}/6.7$$

Table 3
The temperatures of the glass transition zone as a function of the orientation

Sample	T_{gl} (°C)	T_g (°C)	T_{gh} (°C)	$\Delta T = T_{gh} - T_{gl}$ (°C)
PEN0	106.3	112.5	118.7	12.4
PEN1	109.1	114.2	119.2	10.1
PEN2	108.7	112.9	117.1	8.4
PEN3	108.3	112.8	117.3	9
PEN4	109.1	115.8	122.1	13
PEN5	111.5	119.0	126.6	15.1
PEN6	109.3	117.5	125.8	16.5
PEN7	111.4	119.8	125.5	14.1
Sample crystallized at 200°C	111.4	119.8	127.9	16.5

The value of 6.7 corresponds to the value of the square root of the extra first strain invariant I_{1e} at 145°C and at the maximum attainable draw ratio. The maximum attainable draw ratio at 145°C that corresponds with this maximum value of $I_{1e}^{0.5}$ equals 6.9.

Several other experimental parameters, together with the variation of ΔC_p as a function of the draw ratio, give indications of the behaviour of the amorphous part of the material as characterized by the glass transition temperature T_g which is linked to the stiffness of the amorphous phase and the width $\Delta T_g = T_{gh} - T_{gl}$ of the glass transition zone characteristic of the heterogeneity of the amorphous phase. The starting temperatures of the glass transition T_{gl}, the glass transition temperatures T_g and the end temperatures of the glass transition zone T_{gh} for the oriented or unoriented samples of Table 1 are represented in Table 3.

The increase of T_g and ΔT_g after necking shows the influence of the mesomorphic or crystalline regions on the amorphous phase. The presence of these strongly oriented and ordered regions leads to a rather small increase in the

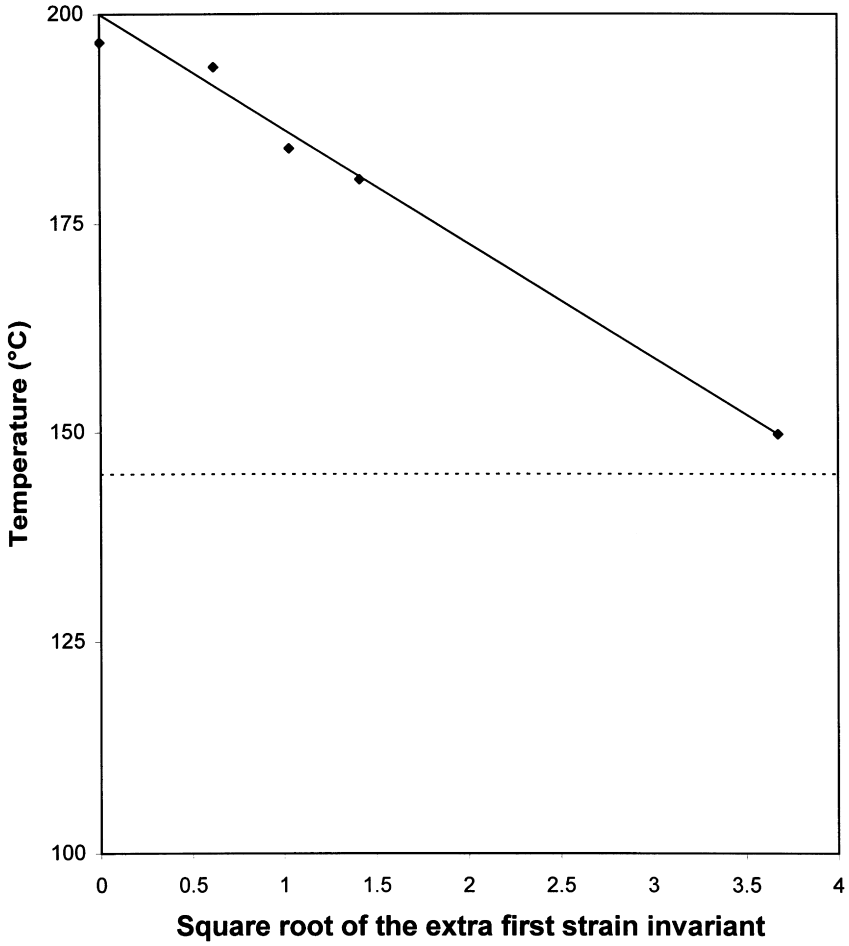

Fig. 4. The cold crystallization temperature T_c as function of the extra first strain invariant I_{1e}.

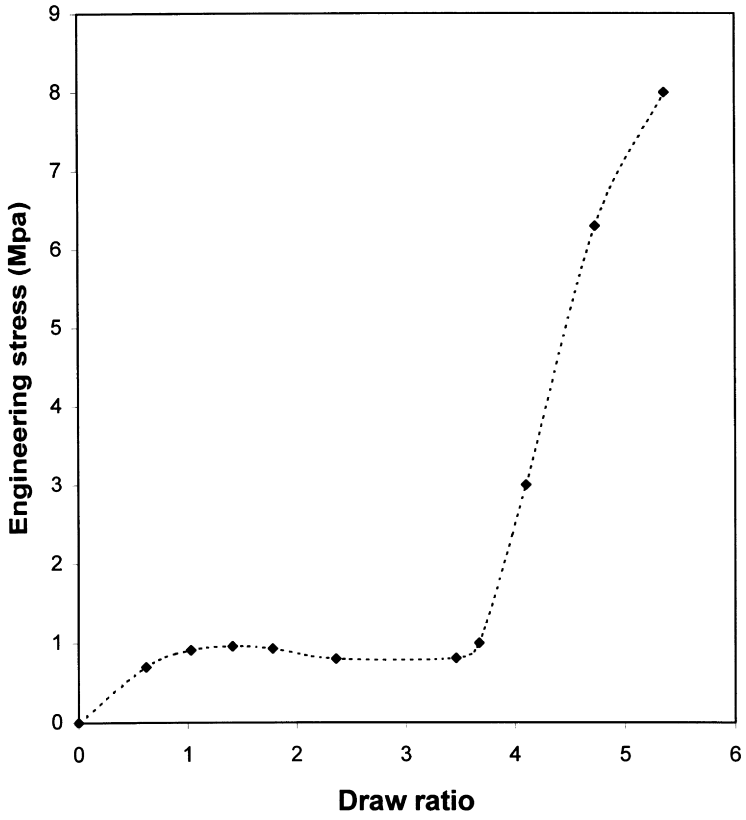

Fig. 5. Stress–strain curve for uniaxal drawing of PEN at 145°C. Here,'engineering stress = load/initial cross-sectional area'.

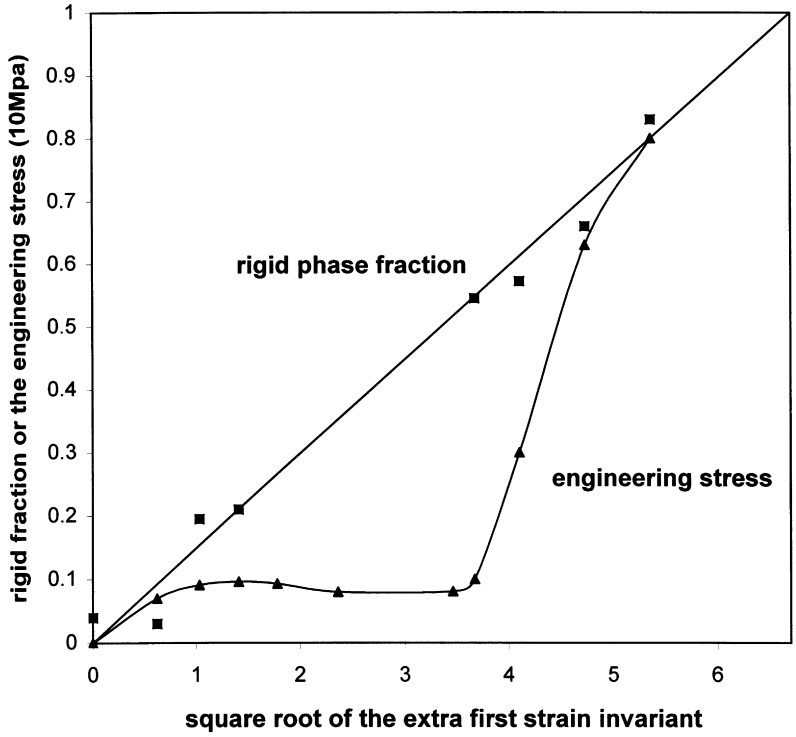

Fig. 6. Comparison between the amount of induced rigid phase f_r and the measured engineering stress as a function of the draw ratios at 145°C.

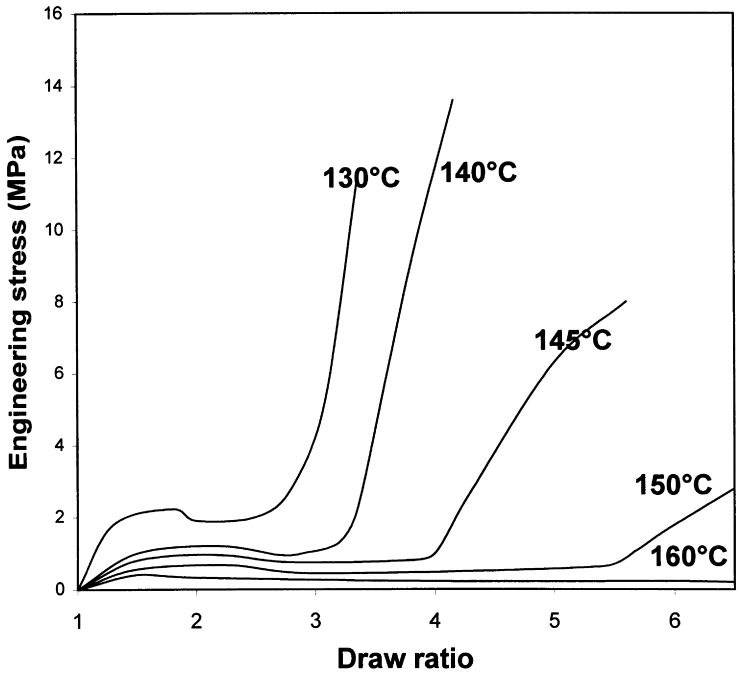

Fig. 7. Stress–strain curves for uniaxial drawing of PEN at temperatures between 130°C and 160°C. Here, 'engineering stress = load/initial cross-sectional area'.

stiffness and heterogeneity of the amorphous phase, without dramatic effects and attains the values observed for a semi-crystalline PEN material obtained after crystallization of the amorphous film at 200°C for 45 min. The orientation and formation of rigid phase structures has little influence on the behaviour of the amorphous phase, which means that the different structures are well separated.

Some of the d.s.c. scans are characterized by an exothermic peak associated with the cold crystallization. As the draw ratio is increased, the cold crystallization peak moves to lower temperatures. This is typical of the semi-crystalline polyester type polymers and is directly related to the reduction of entropy with preferential orientation during drawing. Even during d.s.c. measurements in which the structure relaxed during heating, the cold crystallization temperature was influenced by the draw ratio before the appearance of the necking behaviour ($\lambda < 2.2$). The measured values of the cold crystallization temperature T_c are represented as a function of I_{1e} in Fig. 4.

We observe that the values of T_c are directly related to the square root of the extra strain invariant I_{1e} or to the amount of rigid phase structure f_r induced during drawing at 145°C. There is a linear relationship between the cold crystallization temperature T_c and the amount f_r which suggests that the induced rigid phase structure, developed during drawing, acts as a nuclei for the crystallization of the material as the temperature is increased past the glass transition temperature.

Fig. 5 shows the stress–strain curve when the amorphous PEN film was uniaxially stretched at 145°C to the different draw ratios as indicated in Table 1. The curve shows a yield point and a necking behaviour. After necking, the stress increased very strongly with increasing draw ratio.

The draw ratios and also the resulting d.s.c. curves fall into two groups, samples drawn up to 2.2 drawing homogeneously and that drawn above 4 drawing from a neck. The measured points represented on the stress–strain curve for draw ratios between 2.2 and 4 are based on the measured distance between the ink marks on the sample. For these draw ratios the oriented sample was not drawn homogeneously and was composed of elongated and non-elongated parts. Thus, the stress value is correct for these overall imposed draw ratios, but does not represent the real draw ratio of the material. Therefore, this part of the stress–strain curve is represented as a dotted curve in order to demonstrate the variation of the stress values during necking.

Some ordered structure is obtained in the sample drawn to draw ratio of 1.7 as suggested by Table 2. The existence of some ordered structure in the sample is confirmed by infrared measurements. The infrared absorption spectrum is characterized by the appearance of absorption bands at 835 and 983 cm^{-1}, typical absorption bands of an ordered structure in PEN, and probably characteristic of a nematic structure.

If we compare this stress–strain curve with the amount of induced rigid phase f_r during drawing shown in Fig. 6, we observe that when the amount of rigid phase f_r reaches 50%, for a draw ratio of 4, a dramatic increase of the stress is measured. Actually, the increase in stress suggests a critical degree of rigid phase structure, similar to a percolation threshold accompanied by an inversion of the continuous phase, above which drawing always results in formation of

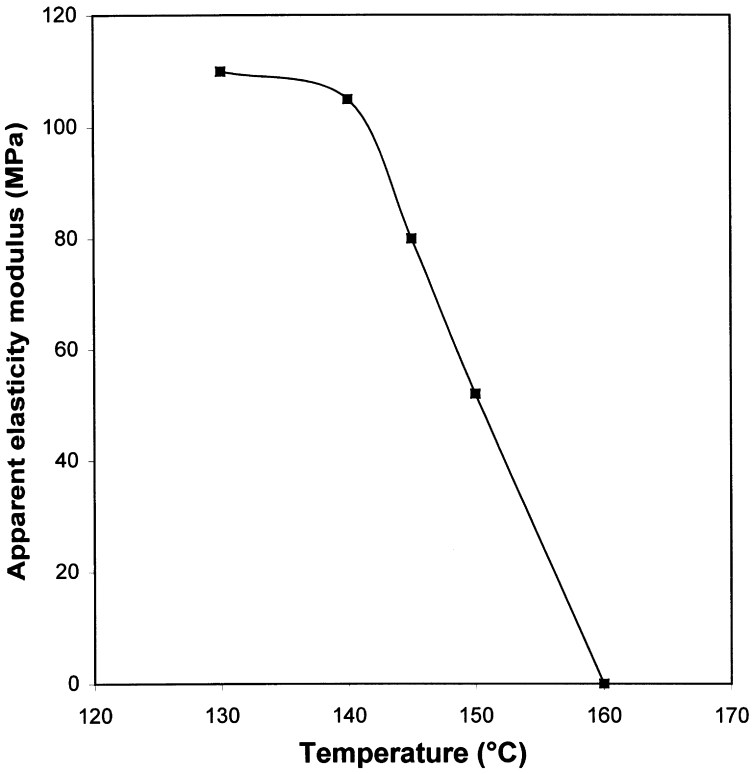

Fig. 8. The calculated values of the apparent elasticity modulus $E_{rp,a}$ after necking as a function of the temperature during isothermal uniaxial drawing of PEN samples at the indicated temperatures.

the rigid phase. When the amount of rigid phase is less than 50% the amorphous phase is the continuous phase, with the rigid phase dispersed therein. If f_r is greater than 50%, the phase inversion takes place and the rigid phase forms the continuous phase with an amorphous phase dispersed therein.

As deduced from the values of f_r and w^c of Table 2, the fraction of rigid amorphous phase is more or less constant during the necking behaviour and the degree of crystallinity is increasing from 0% to 40%. Probably, during necking, the crystallization takes place in a chain-folded structure that is subsequently unfolded during drawing comparable to the necking behaviour of semi-crystalline polymers as polyethylene, polypropylene and others. During necking, crystallization in a chain-folded structure takes place, followed directly by unfolding of the already crystallized fraction. This process continues till the plateau value of the crystallization degree is reached. Further, drawing after necking transforms the amorphous phase fraction into a more ordered phase, given an increase of the rigid amorphous phase.

The stress–strain curves at other temperatures, between 130°C and 165°C, are basically similar to the already discussed stress–strain curve at 145°C. The measured stress–strain curves are reproduced in Fig. 7.

All the characteristics of the drawing behaviour such as necking or yielding, strain hardening and the formation of a rigid phase structure as a function of the extra first strain invariant are basically similar to those observed and explained at 145°C, with a corresponding variation of the specific draw ratios with temperature. For example, the measured draw ratio after necking increases from 2.8 at 130°C to 3.2 at 140°C, 4 at 145°C to 5.4 at 150°C. The curve for 160°C does not show any necking and the film was elongated uniformly under low stresses.

Straight lines are observed after necking in the stress–strain curves for temperatures from 130°C to 150°C. From these straight lines it is possible to calculate an apparent elastic modulus $E_{rp,a}$ by considering the elongated film after necking as the starting sample for the uniaxially drawing process. Just after necking, the elongated film is characterized by a phase inversion, as already explained, with the rigid phase forming the continuous phase. By calculating the apparent elastic modulus $E_{rp,a}$ from the straight lines after necking and for temperatures ranging from 130°C to 150°C, values of $E_{rp,a}$ between 110 MPa at 130°C and 140°C and 52 MPa at 150°C are obtained. The calculated values of $E_{rp,a}$ are represented in Fig. 8.

From this figure, a value of the glass transition temperature for the induced rigid phase structure can be deduced. By taking the glass transition temperature as the mid-value between the two extremes, a value of 150°C is obtained. This implies that the induced rigid phase devitrifies at a temperature of 150°C, a value close to the one suggested from thermal measurements [12]. This can explain the stretching behaviour at 160°C. Even at 160°C, a rigid

phase structure is induced during drawing but the induced rigid phase has a very low value of elasticity modulus, practically equal to zero, and this explains the absence of the strain hardening part of the stress–strain curve at 160°C.

After necking, a phase inversion takes place and the rigid phase constitutes the continuous phase which is characterized by an apparent elastic modulus whose value is strongly influenced by the temperature between 140°C and 160°C, decreasing from a value of 110 MPa at 140°C to practically zero at 160°C with a glass transition temperature of 150°C. After necking, the drawn samples are characterized by two glass transition temperatures, a first one at 150°C from the rigid phase structure which is the most important and a second one at 120°C for the dispersed amorphous phase therein.

The influence of the thermal characteristics of this induced rigid phase structure on the shrinkage behaviour of the uniaxially drawn PEN samples will be discussed in a forthcoming article.

4. Conclusion

Differential scanning calorimetry has been used to study the structural changes in uniaxially stretched PEN films under isothermal conditions. The main conclusions drawn are as follows.

During the uniaxial drawing of amorphous PEN at temperatures between 130°C and 160°C, the amount of rigid phase that includes both the crystalline and the rigid amorphous fraction and which may be a nematic and/or mesophase structure, is linearly related to the square root of the extra first strain invariant. The stress–strain curves are characterized by a necking behaviour and the end of yielding or necking is reached when the amount of amorphous phase decreased below 50%. A rigid phase structure is induced during uniaxial drawing at the indicated temperatures and the existence of a very rigid phase in conjunction with a mobile one. The amorphous phase can explain the thermal behaviour of uniaxially drawn PEN. The stress–strain curves indicate that, after necking, the mesophase acts as the continuous phase and the stress increases very strongly. The stress–strain curves, together with the thermal analysis, indicate that the mesophase devitrifies at 150°C, a temperature well above the glass transition temperature T_g of the amorphous phase.

The stretching behaviour of amorphous PEN at temperatures above the glass transition temperature is more characterized by the strain-induced rigid phase formation than by the stress- or strain-induced crystallization.

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