Effect of the Temperature on the Drawing Behavior of Poly(ether ether ketone)

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SYNOPSIS

This study examines the drawing behavior of amorphous films of poly(ether ether ketone) (PEEK) and the effect of the drawing and the drawing temperature on some physical properties of the drawn samples. The thermal analysis shows that the amorphous films drawn at 200% of deformation and at temperatures of 80, 120, and 140°C crystallize by heating and the crystallization occurs at lower temperature with a lower crystallization enthalpy. The first effect can be related to the influence of orientation on the crystallization rate and the second to strain-induced crystallization. The dynamic–mechanical behavior of the drawn samples is in good agreement with the thermal analysis and confirms the presence of strain-induced crystallization at drawing temperatures well below 180°C. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

In the last decade, several new crystalline thermoplastic polymers, based on aromatic backbones, were developed and considered as substitutes of thermosetting matrices for high-performance composites. The good mechanical properties, along with high-temperature stability and resistance to chemical attack and to high-energy radiation, makes the use of these materials particularly suitable in severe environments.[1,2] In this family, considerable attention has been given to poly(ether ether ketone) (PEEK), whose repeat unit is
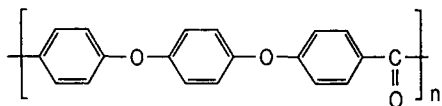
It has a glass transition of about 145°C, a melting point of about 335°C, and a heat of fusion of 130 kJ kg^{-1} for fully crystalline PEEK.[3] The maximum achievable crystallinity of PEEK is about 48%, although typical values are less than 30%.[4] Amorphous PEEK can be obtained by rapid quenching of the molten state. The crystalline form can be obtained by slow cooling the melt (melt crystallization) or by crystallization at a temperature between the T_g and the melting point (cold crystallization).[3,5-10] The cold crystallization occurs at about 180°C when the amorphous PEEK is heated at 20°C/min in a DSC.

The density of the amorphous component is 1.263 g/mL according to Blundell and Osborn[3] or 1.264 g/mL according to Hay et al.[11] The crystal structure has been studied by many authors.[11-14] According to the different parameters of the orthorombic cell, the crystal density is in the range 1.378 and 1.415 g/mL.

The present study was undertaken to determine the effects of the drawing behavior and the drawing temperature on the properties of the drawn samples of amorphous PEEK.

EXPERIMENTAL

Amorphous PEEK films (STABAR K200) 0.10 mm thick were kindly supplied by ICI. Stress–strain curves were made using a Daventest Testometric dynamometer at an extension rate of 10 mm/min on samples 15 mm long at temperatures of 80, 120, and 140°C. The actual strain was determined by photographic recording of the displacement of fiducial marks placed on the sample. Further details are reported elsewhere.[15]

Differential scanning calorimetry (DSC) was carried out over the temperature range of 0-400°C using a Mettler TA 3000 DSC, purged with nitrogen and chilled with liquid nitrogen. Runs were conducted on samples of about 12 mg at the heating rate of 20°C/min.

Infrared measurements were detected using a Nicolet 5DXB FTIR spectrophotometer with a resolution of 4 cm^{-1} (30 scans collected). The density of drawn samples was determined at 25°C by floating the samples in a solution of zinc chloride.

The dynamic–mechanical behavior of the original sample and the drawn samples was analyzed in monodirectional stretching at a frequency of 110 Hz in the temperature range 50-250°C using the dynamometer Rheovibron of Toyo Instruments. The heating rate was 3°C/min.

RESULTS AND DISCUSSION

Drawing Behavior

Stress–strain curves of amorphous PEEK detected at 80, 120, and 140°C are reported in Figure 1. At all the temperatures, the samples deform with neck propagation. At the drawing temperature of 80 and 120°C, the shape of the stress–strain plot is typical
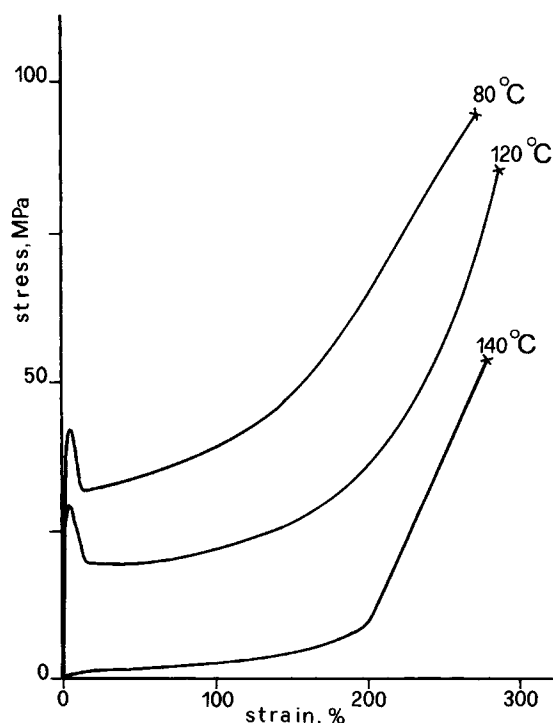

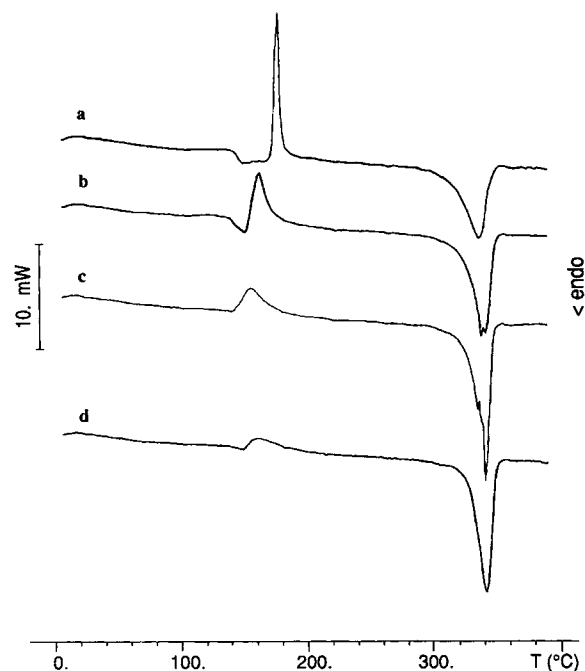**Figure 1** Stress–strain curves for amorphous PEEK at different temperatures.

Figure 2 DSC scans of (a) the original film and of the samples drawn at (b) 80°C, (c) 120°C, and (d) 140°C.

of a plastic material. After the yield at low strain, the samples deform with a neck propagation, followed by a homogeneous deformation until the break. The shape of the stress–strain curve at 140°C is quite different. The sample still deforms with neck propagation, but the stress level during the deformation drops dramatically. This is because at 80 and 120°C the amorphous PEEK is in the glassy state, whereas at 140°C, which is a temperature very close to the glass transition, the system is prevalently in the rubbery state.

The necking phenomenon can be recorded by detecting the displacement of marks on the sample.[15] The local deformation, ϵ_L, in four different volume elements is reported vs. the nominal deformation, ϵ_N, detected by recording the displacement of the extreme marks. This analysis gives information on the formation of the neck, its propagation, and the value of ϵ_N at which the deformation becomes homogeneous. In this case, the samples drawn at 80, 120, and 140°C behave in a similar way with homogeneous deformation occurring at $\epsilon_N > 150\%$.

According to these mechanical data, drawn samples at 80, 120, and 140°C with a strain value of 200% were prepared.

Differential Scanning Calorimetry

In Figure 2 the DSC traces of the amorphous PEEK and the fibers obtained at different temperatures are

reported. For all the samples, cold crystallization and melting are observed. Curve A refers to the amorphous PEEK. In this thermogram, the glass transition at 145°C is followed by a sharp exotherm at 179°C due to the cold crystallization. A broad endotherm with peak at 338°C indicates the presence of a broad distribution of crystal sizes formed during the crystallization.

In Table I, the DSC data are summarized; subscript 1 refers to the cold crystallization, whereas subscript 2 refers to the melting. ΔH_1 and ΔH_2 are quite different. This is not unusual and has been reported for PEEK[6,10] and for PET.[16] It means that between the cold crystallization and the melting there is a continuous increase of crystallinity. The increase of crystallinity consists of an increase of the total number of crystals and an increase of the average perfection of crystallites.[3,6,10,16,17] Since these phenomena take place over a wide temperature range, they are not detectable in DSC.

On increasing the temperature of drawing, a decrease in ΔH_1 is observed. This has to be ascribed to the strain-induced crystallization. It is important to verify that there is no thermal crystallization contribution because the amorphous PEEK is kept in the thermostatic cell of the dynamometer at a certain temperature for about 15 min for the preparation of drawn samples. For this purpose, a piece of amorphous film is put in the thermostatic cell of the dynamometer at the maximum temperature of drawing (140°C) and for 15 min. The DSC data on this sample are reported in Table I and reveal that there is no thermal crystallization in these conditions.

The most interesting datum is the remarkable decrease of T_1 in the drawn samples. The explanation of this must be related to the differences between the undeformed and deformed amorphous phase. In the undeformed amorphous phase, the chains are randomly arranged in the bulk. In the oriented amorphous phase, the chain extension and therefore the molecular alignment causes an appreciable crystallization rate at lower temperatures.

Table I DSC Data

Sample	ΔH_1 (J/g)	ΔH_2 (J/g)	T_1 (°C)	T_2 (°C)
Original film	20.6	34.0	179	338
Original film annealed at 140°C for 15 min	20.5	33.8	179	337
Sample drawn at 80°	18.7	40.4	163	337
Sample drawn at 120°C	11.3	44.3	158	342
Sample drawn at 140°C	6.7	44.2	165	342

Table II Crystallinity of Drawn Samples

Sample	Density (g/mL)	X_c Density (%)	X_c IR (%)
Sample drawn at 80°C	1.2742	8.4	17
Sample drawn at 120°C	1.2749	8.9	19
Sample drawn at 140°C	1.2839	15.4	21

However, the depression of the cold crystallization temperature does not show a monotonic trend on increasing the drawing temperature (Table I). The minimum in T_1 observed for the sample drawn at 120°C seems to suggest that at this temperature the best conditions in terms of mobility and alignment of chains are reached. At 80°C, the mobility is too low. At 140°C, although the mobility is higher, the system is prevalently in the rubbery state and therefore relaxation phenomena behave as competitive mechanism to the chain orientation. Finally, the increase of ΔH_2 and T_2 on increasing the temperature of drawing means that at higher temperatures of drawing (120 and 140°C) the number of chains able to crystallize increases and crystals with more perfection are formed.

Crystallinity

The crystallinity was determined with measurements of density and IR analysis. The volume percent of crystallinity X_c was obtained according to

$$X_c = (d - d_a)/(d_c - d_a)$$

where d_a is the density of the amorphous phase (1.2626 g/mL) and d_c is the density of the crystalline phase (1.4006 g/mL).[3] The values of density and crystallinity are reported in Table II. The crystallinity has been determined also with the infrared spectroscopy. In general, the spectrum of a semi-crystalline polymer is affected by changes in crystallinity in the mid-IR range. Chalmers et al.[18] found a correlation between WAXS crystallinity and the absorbance ratios 1305/1280 cm^{-1} and 970/952 cm^{-1}. The data of crystallinity were obtained by analyzing the ratio 970/952 cm^{-1} and are reported in Table II. The difference of crystallinity detected with density measurements and IR analysis is 8.6% at 80°C, 10.1% at 120°C, and 5.6% at 140°C. The difference that is particularly high in samples drawn at 80 and 120°C can be due to the fact that at these temperatures many voids are formed, as already found by other authors.[19]
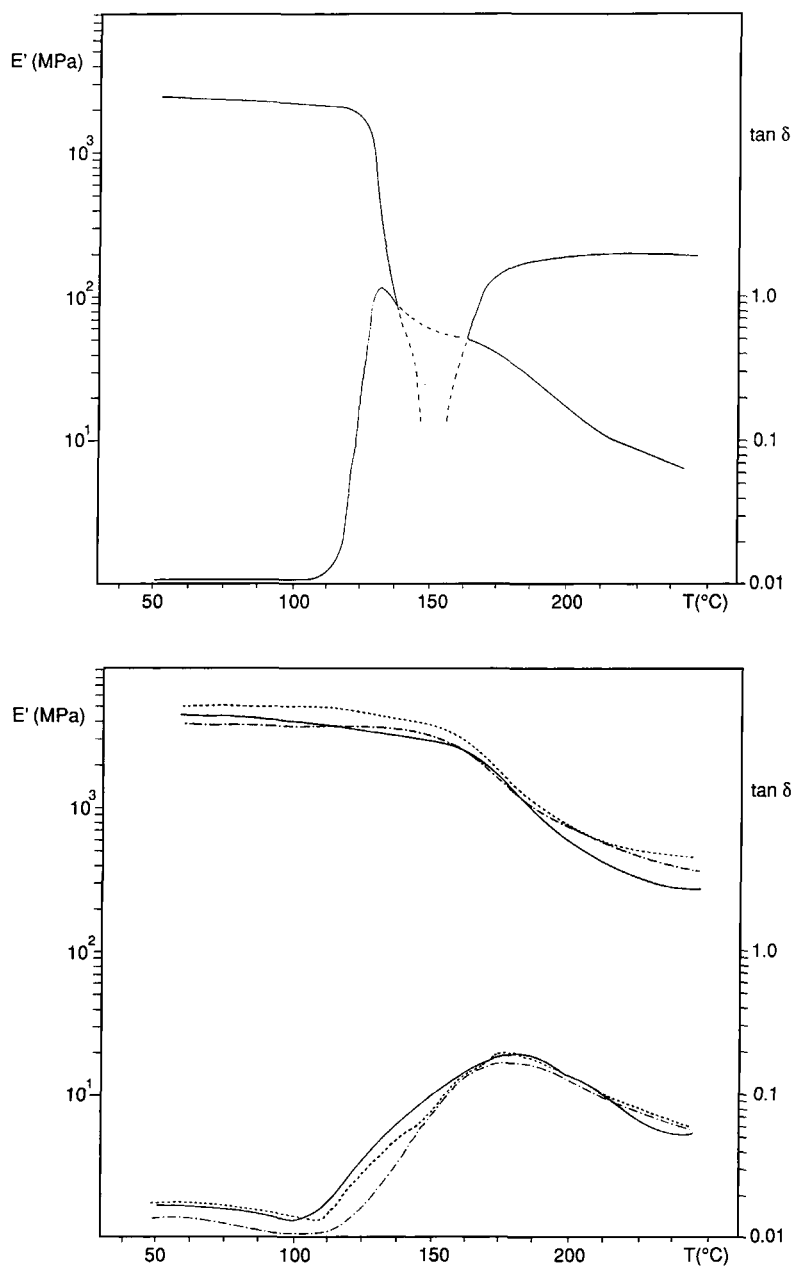
Figure 3   Storage modulus and loss factor for (a) the original film and samples drawn
at (——) 80°C, (-----) 120°C, and 140°C (b) (– • – • –).

Dynamic–Mechanical Analysis

The mechanical relaxation of PEEK has been studied by other authors,[20-22] but some assignments of molecular motion at low temperature are still not completely understood. Anyway, in this study, only the range of temperature of 50–250°C was investigated. In Figure 3, the storage modulus E' and the loss factor tan δ are reported as a function of the temperature. In the original film [Fig. 3(a)], a very

large loss peak starts at 110°C with a dramatic drop of modulus. This relaxation is associated with the glass transition. The discontinuity in the curves of E' and tan δ immediately after the T_g is due to the low sensibility of the apparatus in the detection of E' and tan δ for a material in the "liquidlike" state. E' and tan δ are again detectable as soon as the cold crystallization takes place; the reinforcing in E' is a consequence of the developed crystallinity.

In the drawn samples [Fig. 3(b)], the glass tran-

sition is shifted to higher temperatures and the peak of the loss factor is depressed. The increased T_g in the drawn samples is because the amorphous chains are oriented with many of them in the taut state. Moreover, the presence of crystals in the drawn samples is an additional element of hindering. The depression of the loss peak is due to the lower concentration of chains in the amorphous state.

Because of the presence of the crystals, the modulus of the drawn samples is higher than that of the original film, and at T_g, any effect related to the cold crystallization is not detectable. It is also worthy to note that in the lower temperature range of the transition band the observed loss factor decreases on increasing the temperature of drawing. This effect can be related to the increase of sample crystallinity that reduces the chain mobility in the amorphous state.

Another point of interest is the comparison of E' at 230°C for different drawn samples. At this temperature, the highest value of E' is for the sample drawn at 120°C followed by the samples drawn at 140 and 80°C, respectively. This is in agreement with the DSC data. The sample drawn at 120°C, although it is not the most crystalline, has the highest modulus. This means that the amorphous state in the samples drawn at these two temperatures must be different. The difference must be sought in the different orientation and tautness of the chains in the amorphous state. Further work is in progress to clarify this point.

CONCLUSIONS

Drawing behavior and physical properties on samples drawn obtained by drawing amorphous PEEK at 80, 120, and 140°C have been studied. Strain-induced crystallization occurs during the drawing of amorphous PEEK at all temperatures.

Between the investigated temperatures, 120°C seems to be the temperature at which the best conditions in terms of mobility and alignment of chains are reached. The dynamic–mechanical data are in agreement with the DSC data and support this belief. According to the DSC data, the most perfect crystals are obtained at 120 and 140°C.

Finally, the comparison of crystallinity data obtained with density and IR measurements reveals that the drawing at 80 and 120°C produces microvoids.

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