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Crystallinity Increases in Semi Crystalline Polymers During High Rate Testing

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Abstract. During low rate deformation in tension semi-crystalline polymers can undergo a strain induced crystallisation during deformation which leads to increases in flow stress. This work extends studies of crystallinity in the polymers PEK, PEEK and PET to compression at high strain rates at a variety of temperatures. All three polymers show large increases in crystallinity when tested at high rates with PEK and PEEK showing increases only at rates of $10^3/s$. It is speculated that the rapid increases in flow stress reported in polymers at high strain rates may be due to the rapidity of strain induced crystallisation at these strain rates.

Résumé: Pendant une déformation à basse vitesse en traction, les polymères semi-cristallins peuvent subir une cristallisation induite par déformation qui conduit à une augmentation de la contrainte d'écoulement. Ce travail concerne l'étude de la cristallinité des polymères PEK, PEEK et PET provoquée par la déformation en compression à vitesses de déformation élevées et à différentes températures. Les trois polymères montrent une forte augmentation de cristallinité lorsqu'ils sont testés à grande vitesse; le PEK et le PEEK ne montrant qu'une augmentation qu'à partir d'une vitesse de $10^3/s$. On suppose que l'augmentation rapide de la contrainte d'écoulement révélée par les polymères à vitesse élevée pourrait être due à la rapidité de la cristallisation induite à ces vitesses de déformation correspondantes.

1. INTRODUCTION

The rapid increase in flow stress observed in many materials when tested at strain rates in the region of 10^2 and above has been the subject on some controversy. Some workers attribute the increase to instrumental effects arising from friction, inertia etc. [1] and claim that it is not a real material effect whereas others, at least in the case of metals [2], attribute the rapid increase in flow stress to dislocation multiplication and drag and have proposed theoretical models to fit their results. Similar increases in flow stress have been observed in polymers [3,4] at about the same strain rate as those that have been observed in metals and those who argue for instrumental effects would claim that this strengthens their case since it is unlikely that materials whose deformation proceeds by such different mechanisms would experience hardening at the same strain rate. During deformation semi crystalline polymers undergo a hardening mechanism caused by strain induced crystallisation (SIC) in which the alignment of polymer chains during flow gives rise to an increase in overall crystalline content in the material and hence an increase in density and hardness. The SIC is dependant on strain rate and temperature [5] and if it proceeded sufficiently rapidly could provide a mechanism for rapid increase in flow stress. The purpose of the work described here was to investigate the SIC of a selection of high performance semi crystalline polymers in order to evaluate its potential as a source of flow stress increase at high strain rates.

The materials investigated were Polyetheretherketone (PEEK) and Polyetherketone (PEK) with additional work on Polyethylene terephthalate (PET). The structures of all three materials have been extensively characterised [6,7,8]. PEEK has a glass transition temperature (T_g) of 145°C , a melting point of 335°C while PEK has a glass transition of 154°C and melts at 365°C . The PET glass transition temperature is 80°C and it melts at 230°C . Studies on PEEK have been carried out by Cebe et al. [9] but they did not carry out mechanical tests at temperatures near or above T_g and all tests were performed at a low but unspecified strain rate. Major effects on yield stress and toughness as a function of crystallinity were noted with an increase in crystallinity leading to an increase in yield stress and a reduction in toughness. Lee et al. [10] carried out an extensive study of yield and crystallinity in annealed samples of PEEK over a range of strain rates from 10^{-3} to 0.5 s^{-1} at both room temperature and at T_g . They found an increase in yield stress with strain rate and crystallinity. They also noted an additional minor melting peak in samples drawn at T_g when examined by Differential Scanning Calorimetry (DSC) whose position was always about 10 degrees above the annealing temperature. Samples drawn at room temperature did not show the additional melting peak but showed a small exothermic peak

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which was attributed to cold crystallisation. Lee et al. [10] attributed the minor melting peak to the melting of crystallites with low degree of order and the main peak to the melting of large stable spherulites. The crystalline percentage of the samples was reduced by drawing in all except the fully amorphous samples. Russo [11] also noted cold crystallisation phenomena in PEEK samples drawn at temperatures below T_g as evidenced by a cold crystallisation peak observed in samples examined by DSC after drawing. This peak decreased in size with increasing drawing temperature until it was almost absent in samples drawn at 140°C.

PET has in the past been extensively investigated by many workers. Spruiell et al [5] found a continuous increase in crystallinity with strain rate in the range 10^{-4} to $10^{-1} s^{-1}$ with very little dependence on the total % deformation for deformations > 100%. He also reports that crystallinity decreases with test temperature for samples tested above T_g . More recently Jabarin [12] carried out experiments on amorphous PET above T_g . He also observed that crystallinity increases with strain rate for samples drawn at the same temperature and that for the samples drawn at the highest rates (rates are not stated explicitly but maximum rate is probably $10^{-1} s^{-1}$) very little change in crystallisation occurred on annealing.

The general conclusion from the work on PEEK is that during tensile deformation amorphous PEEK is oriented to form aligned regions which then cold crystallise on subsequent heating. This cold crystallisation may occur during the drawing if the temperature of drawing is close to or above T_g . PEEK which is already crystallised during an annealing process before drawing suffers a reduction in crystallinity during drawing due to the destruction of part of the pre-existing crystallites. However some of this crystallinity may be recovered as cold crystallisation during subsequent DSC scans. In the case of PET the conclusions are similar except that drawing at temperatures of 20° or above increases crystallinity without the need for annealing and the strain rate has a marked influence of the crystalline content even at low rates. Spruiell et al concluded that the higher strain rates allow molecules less time to relax back to the coiled configuration after alignment under stress before other molecules are also stretched and the configurational entropy of the system becomes such that the formation of crystalline material is possible. The work described here extends investigations to higher strain rates for both materials and to the closely related polymer PEK. It also extends the investigation of SIC to compression tests, almost all previous work having been carried out in tension and, in particular, searches for crystallisation effects at strain rates of 10^2 and greater.

2. EXPERIMENTAL PROCEDURE AND RESULTS

Samples were tested in compression at a range of temperatures using a Hounsfield H50KM Universal test machine (low strain rates), a Dartec hydraulic test machine to achieve intermediate strain rates (~1) and a range of drop weight and cross-bow based high strain rate test equipment [13,14] at the higher strain rates (10^2 - 10^5). PEEK and PEK samples were machined from ICI supplied plaque grade 150G (PEEK) and grade 220G (PEK) and were small right cylinders of diameter 7mm and height 3.5mm (the plaque thickness). PET samples were prepared from 2.4mm thick granules of ICI grade B73 and were machined into 4.3mm diameter cylinders. In every case samples were heated for 30 minutes in air on a hot plate at the test temperature immediately prior to carrying out the tests. Samples were then tested in preheated test equipment. Data was recorded to total compressive strains of ~0.4 or greater. The final sample strain depended somewhat on the temperature of the test and was as high as 1.1 in some cases. After testing samples were examined by means of Differential Scanning Calorimetry (DSC) and X-ray diffraction.

2.1 Mechanical testing

Figure 1 illustrates data taken from tests on PEK and PEEK at 20°C. The rapid increase in flow stress at the higher strain rates is clearly visible as is the reduction in flow stress with strain due to adiabatic heating in tests carried out at intermediate strain rates. A summary of the flow stress at a strain of 0.1 together with crystallinity data for the PET samples is given in Table 1 and flow stress data for PEEK/PEK is included in Table 2. The PET data shows a peak in the flow stress at the high strain rate tests carried out at 50 °C which is close to the PET T_g . Due to the very low crystalline content of the PET as received samples there is relatively little pre-existing crystalline material to be destroyed during deformation and the crystallinity of all tested samples increases during deformation. The increase in flow stress for samples tested at the same temperature is directly related to the crystallinity level of the sample.

Table 1: Summary of PET results: crystallinity (%) and flow stress at strain = 0.1

Temp °C	Untested	$10^{-3} s^{-1}$	$10^2 s^{-1}$
20	9%	16% and 70 MPa	48% and 122MPa
50	11%	14 % and 33 MPa	41% and 154 MPa
90	18%	37% and 14 MPa	43% and 67 MPa

Figure 1: Stress strain data for PEEK (—) and PEK (---) tested at 20°C. PEK data is offset by 200 MPa. Strain rates (A) 2000/s, (B) 1000/s, (C) 500/s, (D) 10/s (E) 0.001/s.

2.2 Thermal analysis

Thermal analysis was performed on ~5 mg samples cut from the untested and tested samples. The equipment used was a Mettler TA3000 system. The heating rates used were either 10 or 20 °C/min. The heat of fusion obtained is directly proportional to the crystallinity. The degree of crystallinity (χ) was calculated from:

$$\chi = H/H_f \quad 1$$

where H is the heat of fusion per gram obtained from the non-isothermal DSC scan and H_f is the heat of fusion of 100% crystalline PEEK 130 J/g [7] or 100% crystalline PET 115 J/g [15]

Table 2 summarises the crystallinity of samples of PEK and PEEK after testing at a range of temperatures and strain rates. The crystallinity tabulated is calculated by subtracting the DSC induced cold crystallisation peaks from the melting endotherm before converting to crystallinity and hence represents the crystallinity of the sample at the end of the test. Modest amounts of cold crystallisation were observed in PEK and PEEK in all samples except those tested at a strain rate of 10^3 s^{-1} at temperatures above T_g and, not surprisingly, the annealed but untested samples. This is contrary to the results of previous workers who observed a far greater amount of cold crystallisation in all samples tested below T_g and an absence of cold crystallisation in samples tested at and above T_g . For tested samples up to 100 s^{-1} , the crystalline content has been reduced during mechanical deformation as shown by the crystallinity level (%). Samples tested at 1000 s^{-1} however have a greater crystalline content. The observed increase in crystallinity in all samples tested at 10^3 s^{-1} is also anomalous since all previous work on PEEK and all other PEEK results presented here show a decrease in crystallinity after strain. However other workers have not carried out tests at such high rates. The increase in 1000 s^{-1} melting endotherm might reflect either the increase in perfection of the crystallites or an increase in crystalline content. X-ray diffraction, presented below, was used to attempt to distinguish between these possibilities.

The results of the DSC measurements on PEK and PEEK can be summarised as follows. In all of the tests at strain rates from 10^{-3} s^{-1} – 100 s^{-1} the crystallinity level in the tested samples is lower than the annealed samples. This is probably due to destruction of the crystal structure and/or void formation as described by previous workers. For samples tested at very high rates i.e. 1000 s^{-1} , SIC due to the crystallisation of aligned chains gives a higher degree of crystallinity and the crystallinity level peaks for tests carried out at about T_g . In the case of PET crystallinity greatly increases with increased strain rate with the highest recorded value of flow stress being for tests conducted close to T_g . There was however no obvious link between the crystalline content and test temperature at the higher rate tests although a trend of increase in crystallinity with test temperature in low rate tests and untested material is evident. This suggests that SIC in PET cannot exceed values in the range 40–50%. Such a conclusion is supported by the results of other workers (Spruiell [5], Evstatiev et al [16]) none of whom record SIC greater than 46% before annealing. The data for PET is not yet nearly as comprehensive as that for the other materials but the general trends in behaviour seem similar to those for PEK and PEEK.

Table 2: Crystallinity levels (%) & flow stress (MPa at strain = 0.3) for PEEK and PEK at a range of strain rates and test temperatures (°C).

Temp °C	PEEK					PEK				
	Untest	10 ⁻³ /s	Strain 10 /s	Rate 10 ² /s	10 ³ /s	Untest	10 ⁻³ /s	Strain 10 /s	Rate 10 ² /s	10 ³ /s
20°	38	23&141	30&145	30&148	35&370	44	36&166	35&160	33&160	39&280
60°	33	29&131	27&135	30&133	38&340	40	35&138	33&149	33&145	44&275
80°	34	30&125	27&125	30&126	39&268	43	31&137	34&146	29&143	46&265
100°	40	29&116	30&119	30&122	45&230	41	33&125	32&134	33&134	48&230
120°	39	26&117	29&100	32&110	46&182	44	34&131	34&109	34&128	50&264
140°	36	30&112	28&96	28&108	47&210	44	31&123	34&113	32&118	53&228
160°	38	26&111	29&102	29&102	44&168	39	32&125	34&115	34&116	52&255
180°	38	27&105	28&106	30&98	46	44	34&122	30&123	37&112	51&222

2.3 X-ray Work

Wide angle x-ray diffraction (WAXD) patterns in reflection mode using CuK α radiation were recorded using a 'Unicam' camera and also a Philips PW1050/25 diffractometer. The combined WAXD of the annealed and high strain rate (1000s⁻¹) PEEK samples are shown in figure 2 for 2 θ ranging from 10°-35°. These patterns were measured on samples in which the end plane of the cylindrical sample (the plane of compression) was oriented perpendicular to the x-ray beam. The temperatures refer to the test temperature. The main (hkl) reflections are (110) at around 18.5°, (113) near 20.5°, (200) near 22.5° and (213) near 28.5° while the positions of these four major peaks observed by Fratini et.al [17] during crystal refinement work on PEEK, also using copper radiation, are at 18.76°, 20.82°, 22.72° and 28.78° respectively. In general the crystal reflection from the tested samples are very broad and poorly resolved, indicative of an imperfect crystal structure. Figure 3 shows a similar (though less comprehensive) set of data for PET.

Figure 2: Diffraction patterns of untested (—) and tested (----) PEEK samples. Temperatures indicate the test temperature. All patterns were obtained at room temperature.

Figure 3: Diffraction patterns of PET samples. Upper group Room Temperature tests, Lower group 50°C tests. In each group the lower trace is of an untested sample, middle trace is of a sample tested at a strain rate of .001/s and the upper trace is from a sample tested at 100/s.

For the PEEK/PEK samples there is a marked progressive change in the peak intensity and decrease in width with increasing temperature for the samples tested at 1000s^{-1} but this pattern is not observed for the samples tested at the other strain rates which only show a slight improvement in the peaks for samples tested at higher temperatures. Figure 2 shows that there are small changes in the reflection angles and also the disappearance of the (113) and (213) peaks in the samples tested at 10^3s^{-1} . These changes in the reflection angles indicate changes in the lattice dimension and the 'loss' of the (113) and (213) peaks indicates that orientation occurs during compression. The pattern of annealed and untested samples is virtually identical to a broadened version of the unoriented diffraction pattern reported by Fratini et al. [17]. X-rays taken in a direction perpendicular to those described above showed a similar but not as dramatic change in d spacing.

In the PEEK/PEK samples the only peak whose position that could be determined with accuracy was the (200). The corresponding lattice spacing as a function of testing temperature and rate is set out in Table 3. The refined (200) PEEK spacing reported by Fratini et al. is $3.93\text{\AA}$. Almost all the measured lattice spacings exceed this value but are close to the measured values reported by Fratini et al. of $3.96\text{\AA}$. The only exceptions are the 10^3s^{-1} samples where the 'd' spacings fall below both the reported measured and refined values. After this observation the system calibration was checked with a silicon standard and all the d spacings were observed to lie $< 0.01\text{\AA}$ from their expected values. This result indicates an increase in crystalline perfection as well as content occurs at high rates in these samples. In the case of the PET samples there was no change in the lattice spacings from the expected values after any of the tests. This would seem to indicate that crystalline content is the main factor leading to increased flow stress in high strain rate tests.

3. DISCUSSION

The results of this work show that the previously reported behaviour of PEEK [9,10,11] is representative of the behaviour of both PEEK and the closely related polymer PEK at strain rates up to 10^2s^{-1} and test temperatures up to 200°C . The observation of a large increase in crystallinity in samples tested at the highest strain rates coupled with an increase in crystalline perfection in those samples tested at high rates and high temperature provides an explanation for the increase in yield strength of samples of PEEK and PEK tested above T_g reported elsewhere [18]. There have in the past been many reports of dramatic increases in yield stress of polymers at strain rates of $10^2 - 10^3\text{s}^{-1}$ [3,4] and there is much discussion as to whether or not these are genuine material effects or merely apparent increases in yield stress caused by instrumental effects. The results presented here suggests that such increases, at least in semi-crystalline polymers are indeed genuine and are caused by a combination of increased crystallinity and crystalline perfection which appears to be induced by the high strain rate. The reason for this dramatic change at these strain rates is not clear. The possibility that it is related to the total strain has been considered, however no relationship between lattice spacing and strain has emerged and the work of Spruiell et al. showed very little strain effects on crystallinity at strains greater than 1. The adiabatic nature of tests performed at high rates means that rapid heating of the sample occurs during the test [19] so that high rate tests performed on PET close to room temperature may increase sample temperatures sufficiently close to T_g for transformation to a morphology with a much increased flow stress to occur. Calculations of the adiabatic temperature rises expected at a strain of 0.2 lead to the conclusion that the 50°C PET sample will have risen in temperature by $\sim 17^\circ$ bringing it very close to T_g . Temperature rises in PEEK/PEK are a little higher so that all tests conducted on these materials at 120° or above would lead to samples reaching T_g . Although the rate of SIC should increase with temperature upto the cold crystallisation temperature the flow stress of the material should decrease rapidly above T_g due to the viscoelastic behaviour of the material. We therefore speculate that the rate of strain hardening due to SIC should be greatest in the region of T_g and that this accounts for the increase in flow stress observed in all three materials in tests at high rates around T_g .

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