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# The mechanical properties of poly(ether-ether-ketone) (PEEK) with emphasis on the large compressive strain response

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## Abstract

The mechanical properties of PEEK 450G have been extensively investigated. The compressive properties were measured at strain rates between $1 \times 10^{-4}$ and 3000 $s^{-1}$ and temperatures between −85 and 200 °C. The tensile properties were measured between the strain rates of $2.7 \times 10^{-5}$ and $1.9 \times 10^{-2}$ $s^{-1}$ and at temperatures between −50 and 150 °C. The Taylor impact properties were investigated as a function of velocity and various large-strain compression tests were undertaken to explain the results. The fracture toughness was investigated as a function of temperature and compared with previous literature. Additionally, the fracture surfaces were studied by microscopy. As with all semi-crystalline polymers the mechanical response is a strong function of the strain rate and testing temperature. A previously reported phenomenon of darkening observed in Taylor impacted samples is shown to be due to reduced crystallinity brought about by large compressive strain. For samples deformed to large compressive strains using a variety of techniques and strain-rates the measured Vickers hardness was found to decrease in accordance with reduced crystallinity measured by other techniques.

*Keywords:* Poly(ether-ether-ketone) (PEEK); Tension and compression; Large-strain discolouration

## 1. Introduction

Poly(ether-ether-ketone) (PEEK) is a relatively new semi-crystalline polymer first appearing in the literature in the early 1980s [1]. It also appears in the literature as poly(aryl-ether-ether-ketone) although its true scientific name is poly(oxy-1,4-phenylene-oxy-1,4-phenylenecarbonyl-1,4-phenylene). It has a high melt and glass transition temperatures ($T_m$ = 340 °C, $T_g$ = 143 °C), high chemical resistance and is melt processable. Thus it has been used in a variety of structural and insulation applications. A considerable body of literature exists on a number of topics related to PEEK mechanical properties. PEEK crystallizes rapidly at temperatures above $T_g$. This results in difficulty in performing absolute differential scanning calorimetry (DSC) to establish crystallinity and melt temperatures because the samples crystallinity increases during the scan. A number of investigators have looked at this problem. Jonas et al. [2] correlated DSC scans to density and infrared measurements of crystallinity. Sauer et al. [3] investigated a number of polymers exhibiting double melt endotherms to understand the equilibrium melt temperature, while Wei et al. undertook a careful analysis of the causes of the double melt endotherm [4]. The whole topic of measuring crystallinity of polymers by DSC is discussed by Kong and Hay [5]. The crystal structure has been studied by various researchers [6–9], while Bas et al. [10] have studied the crystallization kinetics.

The tensile properties have been examined by a number of authors [11–15] while the compressive properties over a wide range of strain rates have been studied by Cady et al. [16], Hamdan and Swallowe [17–19] and Walley et al. [20]. Bas and Alberola [21] used DMA to investigate the dynamic mechanical properties of PEEK in various solvents while Ivanov and Jonas used the DMA technique to examine the glass transition [62].

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The shock properties appear not to have been studied, except for two recent papers by Millett et al. [22,23].

The most complete study of the compressive properties of PEEK is described in a series of papers by Hamdan and Swallowe [17–19]. They studied PEEK 150G by varying the starting crystallinity, temperature and altering the testing strain-rate. It was found that at lower strain rates ($<10^3\ \mathrm{s}^{-1}$) the crystallinity of samples decreased when deformed to peak true strains of approximately 60%, but at strain rates above this value the crystallinity increased, particularly when the specimen starting temperature was greater than 80 °C. The yield stress associated with tests at rates above $10^3\ \mathrm{s}^{-1}$ also rapidly increased deviating from the linearly increasing trend at lower rates. The perfection of crystallites was found to be greater in samples tested at high rates and high temperatures ($>T_g$). Hamdan and Swallowe postulated that this occurs because of the adiabatic nature of the high strain-rate tests leading to sample heating and associated annealing.

Despite the relatively high fracture toughness of PEEK, the majority of investigations on fracture behavior has focused on carbon fiber reinforced PEEK composites [24–28]. However, a number of studies have been published using linear-elastic fracture mechanics (LEFM) with a compact tension geometry [29–34], a three-point bend technique [35,36,33], or a single edge notched tensile (SENT) specimen [11]. These studies are primarily focused on moderate loading rates and at room temperature, agreeing on a $G_{IC}$[1] fracture toughness of 8–12 kJ m$^{-2}$ under these conditions. Fatigue failure [37,31,38] and high rate fracture by Charpy impact [39] have also been investigated. Beguelin and Kausch [32] and Gensler et al. [33] both reported a strong logarithmic decrease in critical stress intensity with loading rate. Hashemi [40] and Arkhireyeva and Hashemi [41] have recently employed the essential work of fracture (EWF) analysis to PEEK over a range of temperatures. However, this method homogenizes the energy involved in numerous mechanical events including elastic and plastic deformations, localized necking, crack initiation, crack growth and finally failure. As such, determining a fracture criterion or comparing the data to rigorously obtained fracture data is nearly impossible. In fact these studies report critical energy values that are 150–300% above that of all other work in the literature. At least, in part, the inconsistency in their data may result from the fact that, as pointed out by Karger-Kocsis [42], the EWF method has several limitations for polymers. Not least of these is that complete yielding of the ligament must occur prior to any crack initiation, which can only rigorously be achieved in amorphous polymers. To the best of the authors' knowledge, the only other investigation on the fracture behavior of PEEK over a wide range of temperatures was performed by Karger-Kocsis and Friedrich [29]. However, they restricted their measurement technique to LEFM, which they acknowledged did not accurately capture the material behavior at elevated temperatures or rates. To overcome these issues, in the current work the authors' employ the single-specimen, *J*-integral normalization technique to capture the full elastic–plastic response of PEEK during fracture from −50 to 150 °C.

The Taylor test [43] involves firing a right cylinder of test material against a semi-infinite rigid anvil. The test was originally posed as a method for measuring the dynamic yield strength of metals, however, more recently it has been used as a dynamic validation tool for computer based models. When coupled with high-speed photography the response of visco-elastic materials such as polymers can be measured [44–47]. Recently Millett et al. published an investigation on the Taylor response of an unspecified grade of commercially supplied PEEK [47]. A number of interesting findings were noted relating to the ductile nature of the material in this test and material discolouration in the vicinity of the most deformed areas. Millett et al. report that at velocities between 152 and 349 m s$^{-1}$ PEEK failed in a ductile manner with increasing mushrooming of the impact zone and tearing. At a velocity of 408 m s$^{-1}$ a sufficient tensile stress was developed behind the impact zone to cause a ductile failure of the rod. Concave rod ends revealed significant post impact relaxation. Discolouration was noted in the rod end regions exhibiting the greatest residual deformation, which Millett et al. attributed to either shock- and strain-heating or an oxidation process from the air present during the impact.

## 2. Materials

A commercial plate of extruded PEEK 450G was purchased measuring $475 \times 475 \times 19\ \mathrm{mm}^3$. The material has been characterized in tension and compression at various temperatures and strain rates. Using helium pycnometry a density of $\rho = 1311 \pm 1\ \mathrm{kg\ m}^3$ was measured. The crystallinity calculated from density is 39 ± 2% [10]. From differential scanning calorimetry (DSC) a material crystallinity of 41 ± 2% was calculated by integrating the melt endotherm and relating it to the literature value for 100% crystalline PEEK 450G [2].

Estimates of the molecular weight of the PEEK samples were undertaken by Polymer Solutions Inc., Virginia, USA using the dissolved viscosity method from Devaux et al. [48]. Samples were dissolved in concentrated sulphuric acid and allowed to stand for equal lengths of time to normalize the sulphonation of the polymer chains. Viscosity measurements were calculated according to ASTM D2857-95(2001) at 30 °C. Devaux et al. provide a plot of weight averaged molecular weights versus intrinsic viscosity and this was used to estimate the molecular weight of our as received PEEK. It indicates a weight averaged molecular weight of ≈28 000.

## 3. Experimental

### 3.1. Differential scanning calorimetry (DSC)

Thermal properties were measured using a TA Instruments Q1000 DSC. Samples (ca. 10 mg) were loaded and sealed in

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[1] In all cases the reported studies assumed linear elasticity and thus reported fracture toughness as $K_{IC}$ with values from 5.4 to 7.5 MPa m$^{1/2}$. Where possible, values of $E$ reported to correspond to the material investigated were used for $G_{IC} = K_{IC}^2/E$, when not reported $E = 4.10$ GPa was used.