



## Physical properties of poly(ether ether ketone) exposed to simulated severe oilfield service conditions

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### ABSTRACT

The property changes occurring when poly(ether ether ketone) (PEEK) is subject to methane and carbon dioxide at high pressures ( $10^8$  Pa) and high temperatures (175–200 °C) are reported. Differential scanning calorimetry, density gradient techniques, positron annihilation lifetime spectroscopy, dynamic mechanical thermal analysis and tensile tests measurements were used to monitor the changes which occur during the ageing process. Over the period of the study an overall increase in the tensile strength was noted, with little or no change in 0.2% and 2% proof stresses, whilst there was a decrease in bending modulus and glass transition temperature due to the effects of plasticization. The Young's modulus generally increases for samples exposed to a temperature of 175 °C in the presence of a mixture of 90% methane and 10% carbon dioxide, or carbon dioxide alone, but it decreases at 200 °C in the presence of carbon dioxide alone. The observed effects are consistent with the polymer undergoing initially a densification of the matrix associated with annealing-induced crystallisation, followed by plasticization as the gases permeate into the disordered regions of the matrix. When de-pressurised, the gas dissolved in the matrix attempts to leave the matrix and morphological changes are observed. The complexity of the changes in crystallinity and plasticization in the disordered phase are reflected in changes in the positron annihilation data.

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### 1. Introduction

Thermoplastic polymeric materials are often used as seals and gaskets in harsh offshore oil and gas industry applications where sour gas attack is a problem [1,2]. The degradation of plastics in a marine environment has focussed on the effects of biodegradation, however in many applications it is the exposure to chemicals found in extraction gases and liquids which present the greatest threat to the performance of the plastic components [3,4]. In down well situations, contact with gases such as hydrogen sulfide ( $H_2S$ ), carbon dioxide ( $CO_2$ ) and methane ( $CH_4$ ), and fluids at high pressure and temperature (up to 200 °C,  $10^8$  Pa) present the most taxing of environments. Many of these chemicals alone or in combination chemically attack polymeric materials or are absorbed into the matrix and are able to induce significant changes to the chemical

and physical properties of the polymer. Degradation of properties can be a consequence of either chemical degradation or physical changes which lead to mechanical failure of the component. Therefore, it is important to understand the effects on physical properties of events such as the blistering or bubbling of polymer materials that occurs when absorption of gases by polymers is followed by rapid decompression. It is also important to identify if there is a chemical change such as chain scission which would adversely affect mechanical properties.

Ideally, polymeric materials and their structures that are intended for long-term use should be tested in real time and with realistic in-service environments. However, such a long-term approach is generally not feasible, and accelerated ageing using elevated temperature is used to assess the ageing of the material. Other accelerating factors such as mechanical stress or UV irradiation can be used depending on the application requirements [5,6].

Poly(ether ether ketone) (PEEK) is a linear aromatic semi-crystalline polymer which is widely used in extreme environments. The crystallinity of PEEK [7] ranges from zero (amorphous)

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to ~50%, depending on the thermal history of the material and the conditions used in the fabrication of the item. Semi-crystalline PEEK is a high performance thermoplastic with the characteristics common to this group – strong, stiff, hard, high temperature resistance, good chemical and hydrolysis resistance, and inherently low flammability and smoke emission [4]. PEEK has very good resistance to wear, dynamic fatigue and radiation and is used in applications such as pumps, filters, bearings and pressure seals. PEEK will encounter exposed to fuels, refrigerants, paints, coatings, and other liquid/vapours and is resistant to most organic and inorganic chemicals but it is attacked by halogens, halogenated acids and strong oxidising acids. Amorphous PEEK is plasticized and crystallises in the presence of common organic liquids and vapours such as dichloromethane, chloroform, tetrahydrofuran, toluene, acetone [8–11] and supercritical fluids such as CO<sub>2</sub> [12,13] lead to changes in the morphology and mechanical properties of the polymer. The thermal degradation of PEEK is accompanied by the selective cleavage at chain ends and chain branches to produce 4-phenoxyphenol and 1,4-diphenoxybenzene pyrolysates at temperatures of the order of 450 °C [14]. In the presence of an oxygen atmosphere degradation is observed at 400 °C and can be catalysed by the presence of branched chain moieties [15]. However, in both cases there is no evidence of degradation at temperatures of the order of 250 °C. Whilst there is a considerable body of work on thermal, photochemical and oxidative degradation of polymers, including work on lifetime prediction [16], published research on the durability of polymers under extreme conditions of high pressure and high temperature (HPHT) is lacking. In this paper we examine the effect on PEEK of exposure to high pressure mixtures of CO<sub>2</sub> and CH<sub>4</sub> at elevated temperature and the influence of fast decompression rates.

## 2. Experimental procedure

### 2.1. Materials

Moulded tensile specimens (“dog-bones”) with gauge dimensions of 12 mm long, 3.31 mm thick and 3.04 mm wide (total dimensions approximately 62 mm long, 3.31 mm thick and 9.36 mm wide at ends) of semi-crystalline PEEK (450G) with a weight average molar mass of 10<sup>5</sup> g mol<sup>-1</sup> were supplied by Victrex plc, Thornton Cleveleys, UK. These moulded tensile bars were aged at Materials Engineering Research Laboratory, Ltd. (MERL), UK. The equipment used for HPHT experiments could withstand pressures up to 10<sup>8</sup> Pa and temperatures over 200 °C. Ageing details are presented in Table 1.

PEEK specimens used in all tests, except tests 4 and 6, were virgin moulded tensile bars. Specimens used in tests 4 and 6 had previously been used to perform tests 3 and 5, respectively. This test was performed to explore the effects of repeated exposure to extreme conditions of HPHT.

**Table 1**  
Conditions used in ageing study.

Test number	Temperature, °C	Atmosphere, CH <sub>4</sub> :CO <sub>2</sub>	Pressure, Pa × 10 <sup>5</sup>	Time, days	Decompression, Rate/psi min <sup>-1</sup>
1	175	N <sub>2</sub>	1.67	5	N/A
2	175	90:10	1010	5	1.72 × 10 <sup>7</sup>
3	175	90:10	1010	5	3.45 × 10 <sup>6</sup>
4 <sup>a</sup>	175	90:10	1010	5	1.72 × 10 <sup>7</sup>
5	200	N <sub>2</sub>	1.76	4	N/A
6 <sup>b</sup>	200	90:10	1010	4	1.72 × 10 <sup>7</sup>
7	200	100% CO <sub>2</sub>	1010	90 h	5.03 × 10 <sup>7</sup>

<sup>a</sup> Specimen from test 3.

<sup>b</sup> Specimen from test 5.

### 2.2. Dynamic mechanical thermal analysis – DMTA

DMTA experiments were carried out using a Polymer Laboratories MKIII DMTA, scanning a temperature range from 30 °C to 300 °C, and operated at a frequency of 1.0 Hz at a heating rate of 3 °C min<sup>-1</sup>. The strain used was x4 while the sample was clamped using a 40N-clamping torque. Flat face clamping was used giving a sample length of 5 mm operating in a single cantilever mode. DMTA scans were obtained for all the specimens and for comparative purposes a reheat scan of a pre-analysed specimen from test 7 was also obtained.

### 2.3. Tensile measurements

Tensile tests were carried out at room temperature by using a ZWICK 2061 testing machine, which has a load capacity of 50 kN. An extensometer of gauge length of either 10 mm or 12.5 mm, was used for modulus measurements. A constant cross-displacement rate of 10 mm min<sup>-1</sup> was used for all tests.

### 2.4. Positron annihilation lifetime spectroscopy

Positron annihilation lifetime spectroscopy (PALS) measurements were obtained using a fast-slow coincidence system employing time-to-pulse height conversion and multi-channel analysis [17,18]. The radioisotope used for PALS applications is <sup>22</sup>Na in the form of <sup>22</sup>NaCl. Measurements were performed at room temperature and ~10<sup>6</sup> counts were used to record each spectrum. The lifetime spectra were obtained using the least squares fitting program POSITRONFIT [19]. Analysis was carried out fixing the two short lifetime components; τ<sub>1</sub> and τ<sub>2</sub> at 0.4 ns and 0.125 ns, respectively. The long-lived o-Ps component is well separated from the two shorter lifetime components and is therefore readily deconvoluted. The average hole size was calculated using the relationships derived by Tao [20,21]:

$$\tau_{o-Ps} = \frac{1}{\lambda} = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1} \quad (1)$$

where τ<sub>o-Ps</sub> is the o-Ps lifetime (ns) and R, (nm) the hole radius, R<sub>0</sub> equals R + DR and DR = 0.166 nm. The cavity volume is then calculated using the relationship:

$$V_c = \left( \frac{4\pi}{3} \right) R^3 \quad (2)$$

A 1 cm<sup>2</sup> sample was cut out of the dumbbell and sandwiched around the <sup>22</sup>Na source. Measurements were carried out in triplicate.

### 2.5. Differential scanning calorimetry

A TA Instruments Q1000 calorimeter calibrated with indium was used for the analysis. Analyses was carried out in an atmosphere of nitrogen (flow rate of 60 ml min<sup>-1</sup>) in an aluminium sample holder and the temperature was scanned from room temperature to 400 °C at a heating rate of 5 °C min<sup>-1</sup> using 4–5 mg samples. An empty sample holder was used as an inert reference. The enthalpy of fusion of a completely crystalline PEEK sample was taken as 130 J g<sup>-1</sup> [22].

### 2.6. Wide angle X-ray diffraction

Wide angle X-ray diffraction was carried out in the range 0–50° to the moulded tensile specimen surface using Siemens D500 high resolution diffractometer. Power for the tube is generated by a

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