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The effects of UV irradiation to polyetheretherketone fibres – Characterization by different techniques

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ABSTRACT

The effects of UV irradiation on polyetheretherketone (PEEK) fibres were investigated in this study. PEEK fibres were manufactured with a melt spinning system and then artificially aged with simulated solar UV light. Fibres were then characterized by mechanical tests, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), rheology, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). PEEK, best known for its excellent thermal stability, suffered greatly from the effects of UV irradiation. The low UV stability manifested as embrittlement of the fibres in the mechanical tests, increased crosslinking rate in the rheological tests, formation of carbonyl and hydroxyl groups and changes in the nature of the carbon–hydrogen bonds in the FTIR, diminished thermal properties in TGA, and transverse cracks in the SEM photos. DSC was found to be an inaccurate technique for estimating the degradation level of PEEK fibres, whereas the carbonyl index measured by FTIR was found to be the most convenient technique.

1. Introduction

UV irradiation of polymeric materials is an important area of research since many polymers must withstand extended outdoor exposure. Long exposure to UV light causes polymers to degrade, which can be observed as discolouring, embrittlement, loss of mechanical properties and therefore a greatly shortened product lifetime [1–5]. The study of speciality and high performance polymers has gained more interest because their degradation behaviour, which often occurs only in extreme conditions, is not as well studied as that of commodity plastics [6–9].

Polyetheretherketone (PEEK) is a linear, aromatic, semi-crystalline and rather expensive thermoplastic (Fig. 1). It has excellent thermal properties and chemical resistance, low flammability, low water absorption and good radiation resistance. Because of these properties, PEEK is commonly used in high-tech applications such as space products, medical devices, and as a metal replacement [10,11]. Commercial PEEK fibres can be found in process belting, filtration mesh, wiring harnesses, strings, threads, and composites [12]. PEEK has a high processing temperature of 360–400 °C, which limits the processing possibilities because typical extrusion or injection moulding equipment is not capable of withstanding temperatures that high.

Most degradation studies of PEEK have concentrated on the high-temperature thermal behaviour [13–16] since PEEK has one of the highest continuous use temperatures (260 °C) among plastics. UV degradation of PEEK has been studied primarily from the chemical point of view [8,17–19] and studies of its mechanical properties are not as common [7]. Studies of the UV resistance of PEEK fibres were not found in the literature. Polymer fibres often have special characteristics in properties like mechanical strength, sample thickness, and polymer chain orientation, which makes testing of fibre form samples desirable [20–23].

PEEK, like most linear polyaromatics, degrades under UV irradiation [7,9,24]. As an aromatic chain polymer PEEK absorbs practically all UV radiation of wavelengths under 380 nm [8]. As the incident solar spectrum begins at 290 nm, natural UV radiation is strongly absorbed by PEEK generating photochemical oxidation reactions. Photooxidation forms products in the polymer sample that extend its light absorption well into the visible region, leading to an observable yellowing caused by the absorption of blue light and further accelerating the rate of photodegradation. UV light induced ageing is a major factor affecting the lifetime of PEEK products, and it can also cause great economic losses.

This article will concentrate on artificial UV testing of fibre form PEEK samples. UV testing of fibres has many advantages when

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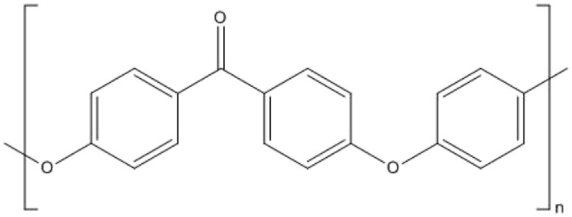

Fig. 1. The chemical structure of PEEK.

compared to the more commonly used sheets or tensile testing specimens. Fibres have a high surface area to volume ratio, which makes ageing faster because the chemical reactions occur primarily in the surface layer. Samples were irradiated for 0–1056 h, after which the mechanical properties, DSC, TGA, FTIR, SEM and rheology were measured. Rheology is rarely used for studying the ageing of materials, but provides useful information on degradation behaviour like relative amounts of competitive chain scission and crosslinking reactions [25–27]. The goal of this article is to use a wide range of characterization techniques to measure changes in the fibres and estimate the suitability of the techniques for the study of photodegraded PEEK fibres.

2. Experimental

2.1. Samples and irradiation

Samples were made of Victrex (Lancashire, UK) PEEK grade 151G. This is a semicrystalline, easy flow grade with no inherent UV stabilizers. PEEK fibres were manufactured by a melt spinning process using a Göttfert Rheograph 6000 to melt and pump the material. The processing temperature was 380 °C, capillary dimensions 30/1 mm and piston speed 0.5 mm/s. Fibres were drawn by gravity because the use of a spinning motor would have led to unnecessarily small fibre diameters. The final diameter of the fibres was very homogenous at 410 ± 10 μm.

The UV irradiation chamber (1260 × 710 × 450 mm) has four Q-Lab UVA-340 fluorescence lambs with peak intensity at 340 nm. Irradiance of the UVA-340 lambs corresponds well with sunlight in the critical short wavelength region [28]. The oldest lamp was changed every 400 h so the total working life of the lamps was 1600 h. The UV irradiation chamber was characterized using Bentham DM150 double-monochromator spectroradiometer equipped with measurement head UV-J1002 from CMS Schreder. The chamber was symmetrically divided into nine measuring points and the average of these was used. The focal plane of the measurement head was approximately at the height of 16 cm from the bottom. The dose rate at the UVB range (290–315 nm) was 0.7 W/m^2, at the UVA range (315–400 nm) 12.1 W/m^2, and at the visible range (400–600 nm) 3.1 W/m^2.

For the UV irradiation tests, PEEK fibres were cut and taped to a 600 × 400 mm frame. PEEK samples were kept in the chamber for 0, 144, 384, 720 and 1056 h so that both sides of the samples were irradiated for the same amount of time. The corresponding total doses were 0, 8250, 22,000, 41,300 and 60,500 kJ/m^2. Temperature of the UV chamber was 33 °C.

2.2. Measurements

The tensile testing of the fibres was made with an Instron 5967 according to the standard ISO 5079:1995. The initial length was 20 mm and the drawing rate 20 mm/min. Instead of the recommended 50 measurements, only 10 samples per irradiation time were measured due to the long duration of the testing procedure. The modulus was calculated by the software using linear regression techniques according to the standards EN10002 and ASTM E8. Tests were made with a 2 kN power shell.

FTIR measurements were made with a Bruker optics tensor 27 using ATR (attenuated total reflectance) mode. Samples were tested between 400 and 4000 cm^{-1}, using 16 measurements and resolution of 4 cm^{-1}. Measurements were made using four parallel fibres and the average of five measurements was used to minimize errors. The data was baseline corrected using the average absorbance of 3800–4000 cm^{-1} as a reference. The carbonyl index was calculated as the ratio of the aged and unaged peak intensities at 1716 cm^{-1}. To calculate the peak areas for the crystallization measurements, the baseline corrected FTIR data was integrated using OPUS software.

DSC tests were carried out in a Netzsch DSC 204 F1 heat-flux DSC. All the tests were performed under nitrogen atmosphere. During the DSC tests, materials were heated from room temperature to 400 °C, then cooled to room temperature and heated once more. The heating/cooling rate was 20 °C/min. To minimize errors each fibre was measured 5 times.

Oscillatory shear measurements within the linear viscoelastic range were carried out on the samples using an Anton Paar Physica MCR 301 rheometer. All the experiments were performed under a nitrogen atmosphere using a 25 mm plate–plate geometry. The measuring points with decreasing frequency in the angular frequency range of 0.1–562 rad/s were recorded at 380 °C.

TGA tests were made with a PerkinElmer TGA 6. Samples were heated from room temperature to 995 °C in synthetic air (20% O_2/80% N_2) and nitrogen (100% N_2) with a heating rate of 10 °C/min.

A Philips XL30 scanning electron microscope (SEM) was used to investigate the morphology of the PEEK fibres. The fibres were broken with liquid nitrogen for the transverse investigations.

3. Results and discussion

3.1. Tensile properties

Breaking strength, yield strength, and Young's modulus decrease only a little as the irradiation time increases (Table 1). Fibres irradiated for 1056 h lost approximately 5–15% of their original strength and elastic modulus. These changes are small when compared to the changes in their elongations, because 1056 h irradiated fibres became brittle and lost 96% of their original elongation at rupture. Pristine PEEK fibres were very ductile with over 300% elongation at rupture. The changes in the elongations at rupture are fairly linear on a logarithmic scale as can be seen in Fig. 2. An exponential trendline gives R^2-value of 0.87.

The relative variance in the elongations is the highest in the medium aged (144 h, 384 h and 720 h) samples. UV irradiation causes chain scission reactions in the polymer chains which has a special significance in the fibres since they have a high degree of orientation. In pristine PEEK the polymer chains are untouched, thus the elongation at rupture is high and the variance relatively

Table 1
Tensile properties of UV irradiated PEEK fibres.

Time [h]	Yield strength [MPa]	Tensile strength at rupture [MPa]	Elongation at rupture [%]	Modulus [MPa]
0	83.2 ± 2.0	87.6 ± 1.9	311 ± 9	2340 ± 55
144	80.5 ± 1.0	78.6 ± 0.8	173 ± 25	2290 ± 95
384	78.7 ± 1.5	78.0 ± 1.3	137 ± 23	2400 ± 71
720	79.6 ± 1.0	74.4 ± 1.0	49 ± 8	2200 ± 50
1056	77.8 ± 2.0	72.3 ± 1.6	13 ± 1	1980 ± 80