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Studies on the reprocessability of poly(ether ether ketone) (PEEK)

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ABSTRACT

Whilst demonstrating desirable mechanical properties, corrosion resistance and the ability to retain structural integrity over extended temperatures, PEEK (poly(ether ether ketone)) remains expensive, restricting broader usage. The reuse and recyclability characteristics of PEEK are therefore commercially important, where the most prevalent manufacturing process for PEEK is injection moulding. This study comments on the reprocessability of PEEK specifically applied to the injection moulding process, comparing the effect of repeated reuse on mechanical properties. Recycled PEEK retains its tensile properties through at least three moulding and regrinding cycles. XRD and DSC measurements confirmed that reused PEEK shows no degradation in crystallinity.

1. Introduction

Poly(ether ether ketone) (PEEK) is an engineering thermoplastic polymer known for its high melting temperature, chemical and abrasion resistance, and excellent mechanical properties, particularly toughness (Jones et al., 1985). Consequently, PEEK is used extensively in high strength and stiffness applications, such as the advanced composite systems reviewed in detail by Nguyen and Ishida (1987). PEEK is now finding ever greater usage in diverse engineering applications including bearings, piston parts, pumps, HPLC columns, compressor plate valves, and cable insulation and ultra-high vacuum systems. It is also extensively used in the aerospace and automotive sectors. Its chemical and wear resistance to hostile environments, along with its ability to withstand thermal sterilisation processes, also makes PEEK a suitable material for medical applications such as orthopaedic and spinal implants (Kurtz and Devine, 2007).

PEEK is however an expensive polymer, currently more than four times the price of other engineering thermoplastics such as PBT, POM and PMMA, so there is a strong economic incentive to recycle PEEK and the industrial recycling possibilities are therefore commercially significant.

To date, recycling studies have focused on PEEK reinforced with carbon fibre (CF). For example, Buggy et al. (1995) used concentrated sulphuric acid to recover PEEK from APC-2 composites, although DSC analysis indicated the presence of impurities in the reclaimed material. For industrial purposes, the favoured approach is mechanical reprocessing. Day et al. (1994) extruded a blend of granulated APC-2 CF/PEEK prepreg offcuts with injection moulding grade PEEK. Test pieces were produced from the blend by injection moulding and were found to have greater tensile strength and Young's modulus than a commercial material containing a similar loading of CF. It was also observed that the viscosity-average molecular weight of the recycled PEEK did not decrease greatly after an additional injection moulding cycle. Sarasua and Pouyet (1997) evaluated the effect of several successive injection moulding cycles on 10% and 30% short carbon fibre (CF) reinforced PEEK. Damage to fibres as well as degradation of the matrix led to a fall in mechanical properties and the authors suggested that the degradation of PEEK was due to the presence of carbon fibres which may have led to a chemical reaction between PEEK structure and pyrolysis products of CF. The presence of fillers can therefore hinder understanding of the behaviour of the matrix polymer in recycling operations.

In past studies, the mechanical behaviour of PEEK has been investigated in relation to crystallinity, molecular weight and thermal history. Improvements in Young's modulus and strength together with ductility reductions are generally obtained as crystallinity increases in both neat PEEK and its composites. For example, Chivers and Moore (1994) showed that both modulus and strength of PEEK improve with increasing crystallinity, but the effect was accompanied by embrittlement, as indicated by decreasing toughness. Molecular weight also had an indirect effect, where maximum crystallinity attainable was found to fall at high M_w. Studies on the effect of thermal history on PEEK crystallisation behaviour (and therefore resulting mechanical properties) have shown that the quality and quantity of the crystalline regions depend on the cooling kinetics and can be altered by the presence of inclusions such as fibres (Sarasua et al., 1996), or by self-nucleation (Jonas and Legras, 1991). Jonas and Legras (1991) also examined the degradation, in terms of branching, induced

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Table 1
Injection moulding parameters used for manufacturing different percentages of virgin/1st regrind parts.

Virgin/1st regrind	Temperatures				Screw speed (mm/s)	Injection speed (cm/s)	Injection pressure (bar)	Cooling time (s)
	Die	Zone 3	Zone 2	Zone 1				
100/0	380	365	365	360	60	100	1210	25
75/25	380	365	365	360	60	100	1210	25
60/40	380	365	365	360	60	100	1210	25
50/50	380	365	365	360	60	100	1210	25
40/60	380	365	365	360	60	100	1210	25
25/75	380	365	365	360	60	100	1210	25
0/100	380	365	365	360	60	100	1210	25

Table 2
Injection moulding parameters applied for manufacturing of 1st–5th regrind parts.

Material regrind cycle	Temperatures				Screw speed (mm/s)	Injection speed (cm/s)	Injection pressure (bar)	Cooling time (s)
	Die	Zone 3	Zone 2	Zone 1				
Virgin	380	365	365	360	60	100	1210	25
1st	380	365	365	360	60	100	1210	25
2nd	380	365	365	360	60	100	1210	25
3rd	380	365	365	360	60	100	1210	25
4th	380	365	365	360	60	100	1210	25
5th	380	365	365	360	60	100	1210	25

when held in the molten state, and found that the structural defects created by branching reduced the crystallinity, whilst the restricted molecular mobility associated with increased molecular weight decreased the crystallisation rate. Abu Bakar et al. (1999) reported a 2% drop in the crystallinity of pure PEEK for every 10 °C rise in melt processing temperature, although this effect was absent in composites containing 5% or 10% hydroxyapatite. Although Sarasua et al. (1996) observed that pure PEEK maintained its degree of crystallinity during ten successive injection moulding cycles, the mechanical properties of moulded PEEK samples resulting from the successive moulding cycles were not presented in the work, as the main focus of the study was on the short fibre PEEK composites.

In comparison with the lab scale research studies described above which focused on increasing time and temperatures in order to elucidate the degradation mechanisms at work, this study aimed to determine at what point PEEK reuse becomes unfeasible in an injection moulding process, due to degradation and subsequent deterioration in mechanical performance. To achieve this aim, the effect of reprocessing unfilled PEEK was investigated. Thus, injection moulded PEEK test pieces were reground and processed a further five times by injection moulding to study the effect of successive moulding cycles on the mechanical properties. In addition, first regrind and virgin PEEK were co-processed in varying proportions in order to assess the effect of reprocessed material on the properties of virgin material.

2. Materials

The material used for injection moulding was Victrex High Performance PEEK™ 450G. All regrind PEEK grades were prepared in-house. Each regrind batch (1st, 2nd, 3rd, 4th, 5th and 6th) was produced by processing the material once in a Battenfeld HM 40/130 injection moulding machine followed by mechanical grinding in order to produce pellets for further reprocessing through injection moulding. The process was repeated six times in order to achieve all six regrind batches. Different percentages of virgin PEEK were then mixed with 1st regrind PEEK (virgin/1st regrind) in the following percentages: 100/0; 75/25; 60/40; 50/50; 40/60; 25/75; 0/100 and then injection moulded into test bars.

3. Experimental procedures

3.1. Injection moulding

The injection moulding parameters used for manufacturing the different percentages of virgin/1st regrind PEEK samples and the 1st, 2nd, 3rd, 4th and 5th regrind batches are presented in Tables 1 and 2, respectively.As can be seen in Tables 1 and 2, no change in the processing parameters was required throughout the moulding work, where all batches could be used to mould good quality parts using the recommended parameters for virgin PEEK moulding.

3.2. Tensile testing

The parts moulded were dog bone shape tensile testing specimens (40 mm × 5.5 mm × 2.0 mm). Tensile testing was carried out using a LLOYD instruments EZ20 mechanical testing machine. Testing speed for all samples was 10 mm/min and gauge length 35 mm. 8–10 samples were tested for each batch and the testing was performed at ambient temperature (20 °C).

3.3. X-ray diffraction (XRD)

X-ray diffraction analysis (XRD) was performed on the injection moulded parts directly using a Bruker D8 Advance X-Ray Diffractometer with a LynxEye detector, operating at 40 kV voltage and 40 mA current using Cu Kα radiation ($\lambda = 0.1542$ nm) in the $2\theta = 5°–35°$ range in 0.03° increments. The specimens had no additional treatment prior to analysis.

3.4. Differential scanning calorimetry (DSC)

Thermal analysis measurements were carried out using a Mettler-Toledo DSC 821e under a 60 ml min^{-1} nitrogen flow. Both sets of samples (regrind cycles and mixtures of virgin/1st regrind) were heated and cooled between 30 °C and 400 °C at 10 °C min^{-1}. Three repeat measurements were carried out on samples cut from the tensile testing specimens. The sample was always taken from the middle and core of the dog bone specimens, in order to avoid producing any additional variation in data due to differences in