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Accelerated degradation of Polyetheretherketone (PEEK) composite materials for recycling applications

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ABSTRACT

The decomposition of Polyetheretherketone (PEEK) is carried out at 623 K within 30 min using a co-solvent system comprising of ethanol and water. It has not previously been possible to carryout the decomposition of PEEK below 703 K in aqueous media. Decomposition is achieved using catalytic quantities of caesium carbonate (Cs_2CO_3), as low as 19 μmol ml^{-1}, in a high pressure bomb reactor. Carbon fibres are separated from a PEEK/carbon fibre composite and analysed by SEM-EDX. A reaction scheme is proposed for the decomposition process, producing phenol and dibenzofuran as major products. Phenol is analysed quantitatively by means of HPLC, the identification of decomposition products is performed by GC–MS. Decomposition of PEEK at 7 K above its melt temperature using Generally Recognised as Safe (GRAS) solvents represents a significant advance in the recycling of end-of-life, contaminated and deteriorated thermoplastic composite materials.

1. Introduction

Polyetheretherketone (PEEK) is a high performance engineering polymer, a member of the poly(aryl-ether-ketone) category. It is a thermoplastic, having a high melt temperature (T_m) of 616 K [1], high thermal stability [2], chemical and radiological resistance [3]. Having a glass transition temperature (T_g) of 416 K [4], it is a rigid polymer at room temperature and may be either semi-crystalline or amorphous depending on the processing technique [5]. Due to its physical properties PEEK is used in many high performance applications such as the aerospace and automotive industries [6], as well as power and energy generation [7] and biomedical industries [8,9]. Polymer processing of PEEK with supercritical carbon dioxide ($scCO_2$) allows for the manipulation of the T_g [10], it has also been shown that $scCO_2$ processing may be used to induce crystallisation below the crystallisation temperature [11]. The use of $scCO_2$ does not significantly alter the T_m and consequently does not facilitate in the low temperature polymer processing of PEEK.

PEEK may be reinforced with carbon fibres, leading to enhancement of the physical properties such as the mechanical wear and impact resistance [12]. Structural reinforcement of polymers for high performance and load bearing applications is commonplace, such as polyepoxides. Unlike polyepoxides, PEEK is a thermoplastic which means that it does not decompose upon reaching its melt temperature, allowing it to be reprocessed into another form from the melt phase. The introduction of reinforcement fibres makes this process significantly more challenging since the fibre alignment will not be the same in the recycled material. When exposed to temperatures above its continuous use temperature for extended periods of time PEEK, like many polymers, may begin to lose its physical properties. Reprocessing partially degraded or contaminated PEEK does not necessarily remove the contaminant and restore the polymer properties, potentially limiting its use and application. It is at this point that it becomes necessary to either dispose of, or recycle the polymer or composite. With recent European Union legislation aiming to drastically reduce the quantity of composite material entering landfill [13,14], there is a requirement to recycle composite materials and with the increasing trend to replace or join thermoset composites with thermoplastics composites [6] it is prudent to consider the recycling process in advance.

The repeat unit of poly(oxy-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,4-phenylene) PEEK is given in Fig. 1. At 723 K the main products of the thermal oxidative decomposition of PEEK are CO_2, CO, 4-Phenoxyphenol and 1,4-diphenoxybenzene [15].

PEEK, having a melt temperature of 616 K, does not undergo decomposition in subcritical water alone at temperatures up to 623 K. The addition of 3.33 mmol ml^{-1} Na_2CO_3 does not induce

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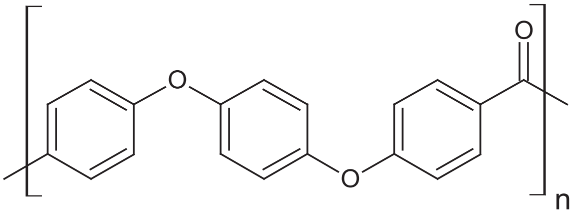

Fig. 1. Structure of poly(oxy-1,4-phenyleneoxy-1,4-phenylelecarbonyl-1,4-phenylene) PEEK.

decomposition at 623 K but can cause complete decomposition of PEEK at 703 K [16]. It is believed that the carbonate functional group is responsible for the decomposition observed in carbonate solutions, therefore the replacement of Na_2CO_3 with another carbonate species should not significantly alter the effects. Previous trial experiments showed that the addition of 3.3 mmol ml^{-1} Na_2CO_3 resulted in considerable quantities of salt residue post reaction. The solubility of salts in supercritical water is extremely low, typically leading to the precipitation from solution [17–20]. Consequently the carbonate concentration was reduced greatly until no residual salt build up post reaction was observed.

1.1. Ethanol as a co-solvent

The major decomposition products for the aqueous decomposition in supercritical Na_2CO_3 solutions are phenol and dibenzofuran [16]. Na_2CO_3 is readily soluble in water but is insoluble in ethanol, therefore a water/ethanol co-solvent system containing Na_2CO_3 was not considered feasible as the Na_2CO_3 would not be in solution at high ethanol concentrations. Cs_2CO_3 however, is soluble in ethanol and, considering the common carbonate functional group, was thought to behave in a similar way to Na_2CO_3. Ethanol has a critical temperature of 523 K and critical pressure of 6.0 MPa, significantly lower than that of water. Mixtures of ethanol and water have critical points between those of the pure compounds (ethanol 514.15 K, 6.3 MPa; water 647.15 K, 22.1 MPa). The critical point may essentially be tuned by changing the concentration of the co-solvents.

In this paper the decomposition of Victrex PEEK 150CA30, PEEK filled with 30% carbon fibre, is carried out by using a co-solvent system of ethanol and water at 623 K, the critical point of the mixture. The decomposition is catalysed by the use of 30 μmol ml^{-1}, or less, of caesium carbonate Cs_2CO_3. There is a synergistic effect of ethanol, water and Cs_2CO_3, the absence of any one component is severely detrimental to the decomposition.

2. Experimental methodology

2.1. Materials

Polyetheretherketone (PEEK), PEEK 150CA30, containing 30% by mass carbon fibre was obtained from Victrex Plc and used without further treatment. The PEEK was received in pellet form, individual pellets typically having a mass of approximately 30 mg. High Performance Liquid Chromatography (HPLC) grade water was obtained from Sigma–Aldrich, HPLC grade Ethanol (CH_3CH_2OH) and HPLC grade Acetonitrile (CH_3CN) were supplied by Fisher Scientific and used without further treatment. Phenol (C_6H_5OH) with a purity greater than 99%, caesium carbonate (Cs_2CO_3) 99% trace metal basis and Acetic acid ($CH_3C(O)OH$) with a purity of 99.7% were used as received from Sigma Aldrich without further purification. Oxygen-free Nitrogen was supplied by BOC Group Plc.

2.2. Apparatus

A Parr Instruments Company (Moline, USA) high pressure bomb reactor having a nominal volume of 100 ml was used to carryout the polymer degradation reactions. The reaction volume, accounting for the associated valves, pipework and fittings, was determined as 115 ml. A solvent loading rate of 50% by volume was used for all experiments. A Parr Instruments Company 4848 Reactor Controller and furnace were used to achieve the required reaction conditions. The reactor internal pressure was monitored by an analogue pressure gauge (SPAN, USA) and a pressure transducer with digital readout (Druck, UK).

Differential Scanning Calorimetry (DSC) was carried out using a Mettler Toledo HP-DSC827e, using 40 μl Aluminium pans. Fourier Transform Infra-Red Spectrometry (FT-IR) was carried out on a Jasco FT/IR-6300 spectrometer fitted with an Attenuated Total Reflectance accessory. Thermogravimetric Analysis (TGA) was performed on a Seiko Instruments Inc. Exstar 6000, using ceramic pans. Reverse phase High Performance Liquid Chromatography (HPLC) was conducted on a Shimadzu SCL-$10A_{VP}$ system featuring a dual channel SPD-$10AV_{VP}$ UV–Vis Detector and a RF-$10A_{XL}$ Fluorescence detector. Separation was performed across a Phenomenex Synergi Fusion reverse phase C18 column. A Waters Corporation Gas Chromatography – Mass Spectrometry (GC–MS) system utilising an Agilent HP-5MS column was used to separate and identify decomposition products. Samples were imaged using a Philips XL30 FEG ESEM Scanning Electron Microscope.

2.3. Sample preparation

2.3.1. Control sample

A control sample using a solution of Cs_2CO_3 in water, without the addition of Ethanol was used as a basis for the investigation of the effects of Ethanol in the degradation of PEEK. 0.577 g of Cs_2CO_3 was dissolved into 57.5 ml of water and poured into the High Pressure Reactor (HPR). 0.584 g of PEEK 150CA30 was placed into a stainless steel basket and placed in the reactor such that the PEEK was immersed in the solution. The reactor was sealed and heated to 623 K, the temperature was subsequently maintained for a period of 30 min prior to being cooled to room temperature. The solid material was retained within the stainless steel basket and was removed dried in a drying oven at 333 K for 2 h. The dry solid mass was then recorded and used as an initial estimate of the percentage decomposition according to equation (1).

$$\%d_g = 100 - \left(\left(\frac{Mp_i - Mp_f}{Mp_i}\right) \times 100\right) \quad (1)$$

where: Mp_i = Initial polymer mass, Mp_f = Final polymer mass, $\%d_g$ = % degradation.

TGA, GC–MS, DSC, SEM-EDX and HPLC were subsequently used to analyse the solid and liquid fractions.

2.3.2. Effect of caesium carbonate concentration

To investigate the effect of Cs_2CO_3 concentration with respect to the degradation of PEEK, the Cs_2CO_3 concentration was varied from 0 to 10 mg ml^{-1} with the solvent loading rate being constant at 50% (57.5 ml). The co-solvent solution consisted of 80% water and 20% ethanol by volume. The mass of PEEK (M_{PEEK}) was held constant at 10 mg ml^{-1}, the reaction temperature was 623.15 K and the reaction time was 30 min. The reaction schedule is presented in Table 1.

2.3.3. The significance of the co-solvent system

The ethanol concentration was varied from 0 to 100%, conversely this could be viewed as varying the water concentration

Table 1
Effect of caesium carbonate concentration $[Cs_2CO_3]$ reaction schedule.

Sample	$[Cs_2CO_3]$ (mg ml^{-1})	M_{PEEK} (g)	T (K)	t (min)	P (MPa)
1	0.00	0.57	623.15	30	16.8 ± 0.2
2	0.94	0.58			
3	2.07	0.57			
4	4.21	0.57			
5	6.17	0.59			
6	8.14	0.57			
7	10.45	0.59			

from 100 to 0%. The reaction temperature was maintained at 623 K with constant Cs_2CO_3 and PEEK concentrations of 10 mg ml^{-1}. The reaction time was held at 30 min for all experiments. The reaction schedule is given in Table 2.

2.3.4. *Effect of reaction time*

The reaction time was varied from 0 to 120 min. The 0 min experiment consisted exclusively of heating and cooling phases, with 0 min being spent at the reaction temperature. The Cs_2CO_3 and PEEK concentrations were maintained at 10 mg ml^{-1} for all experiments. The reaction mixture was a co-solvent comprising of 80% water and 20% ethanol by volume, the reaction temperature was 623 K. The HPR was cleaned using a 1 kW, 33 kHz ultrasonic bath between each experiment.

2.4. *Analytical methodology*

2.4.1. *Differential Scanning Calorimetry (DSC)*

DSC was used to investigate the existence of polymeric phase transitions in the recovered solids. A single dynamic segment was used to heat the samples, typically having a mass of 6–10 mg contained within a 40 μl aluminium pan, from 293 K to 673 K at 10 K min^{-1}.

2.4.2. *Thermogravimetric Analysis (TGA)*

To quantify the amount of degradation according to the recovered solids, TGA was used to heat the sample through the PEEK decomposition temperature in an inert atmosphere of N_2. Dried samples, typically 5–25 mg were loaded into ceramic pans and held isothermally at 298 K for 5 min to allow stabilisation. A dynamic segment was then used to heat the sample to 1150 K, followed by a second isothermal segment at 1150 K for 5 min.

2.4.3. *Fourier Transform Infra-Red Spectrometry (FT-IR)*

FT-IR was used to analyse the recovered solids to identify any functional groups present, particularly those attributed to PEEK, the solvents used and carbonates species. Analysis was carried out at room temperature, scanning over the range of 800–4000 cm^{-1} with a data interval of 0.24 cm^{-1}.

2.4.4. *High-Performance Liquid Chromatography (HPLC)*

The aqueous/organic mixture was filtered and analysed by reverse phase HPLC with a flow rate of 1 ml min^{-1}. Chromatograms were obtained by UV–Vis at 254 and 280 nm and fluorescence at 271 nm Absorbance and 300 nm Emission. The spectra associated with each of the peaks were also taken, and where applicable emission spectra were also recorded. Separation was carried out across a Phenomenex Synergi Fusion RP C18 column using a gradient method as has been carried out in previous work by other authors [21]. Phenol standards were produced containing 3.5–0.015 mg ml^{-1} and were subsequently used to carryout quantitative HPLC with respect to phenol.

Table 2
Effect of ethanol concentration $[CH_3CH_2OH]$ reaction schedule.

Sample	$[H_2O]$ (%v)	$[CH_3CH_2OH]$ (%v)	M_{PEEK} (g)	P (MPa)	T (K)	t (min)
1	100	0	0.58	15.8	623.15	30
2	90	10	0.57	16.2		
3	80	20	0.59	16.7		
4	50	50	0.59	23.8		
5	20	80	0.57	25.5		
6	0	100	0.50	23.9		

2.4.5. *Gas Chromatography – Mass Spectrometry (GC–MS)*

Separation was achieved using a constant flow of 1.2 ml min^{-1} through an Agilent HP-5MS column prior to Electron Impact ionisation at 75 eV at a source temperature of 473 K. The initial oven temperature was 308 K, held isothermally for 7 min, prior to a dynamic segment increasing to 573 K at 13.25 K min^{-1} after which the oven was held isothermally at 573 K for 15 min.

3. Results and discussion

The ethanol concentration was varied from 0 to 100% by volume, maintaining a reactor solvent loading of 50%, the PEEK and Cs_2CO_3 concentrations were 10 mg ml^{-1}. The aqueous fractions were analysed by means of HPLC and GC–MS, the concentration of phenol was used as an indicator for the decomposition as shown in Fig. 2.

By inspection of Fig. 2 it is evident that ethanol functions effectively as a co-solvent with water but water is essential in the decomposition of PEEK. When the reaction medium contains more than approximately 65% by volume ethanol the decomposition is less effective than a solution containing 0% ethanol. The optimum concentration is approximately 20% ethanol by volume, 80% water. At the reaction temperature and pressure of 623 K and 17 MPa respectively and an ethanol concentration of 20%v, the reaction medium was at the critical point for the mixture [22]. Supercritical fluids are able to swell polymers [10,23,24] and in previous work, supercritical Water (scH_2O) has produced a macro-porous structure, Fig. 3.

The creation of a macro-porous structure may assist in the rate of decomposition owing to the significant increase in surface area, as well as decreasing the depth of material that the reaction medium has to penetrate. SEM has been used to qualitatively establish

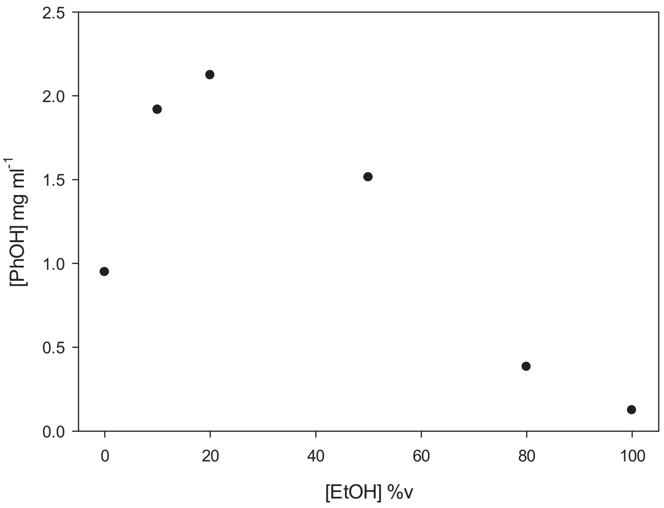

Fig. 2. Phenol concentration [PhOH] with respect to ethanol concentration [EtOH], 623 K, 30 min, 10 mg ml^{-1} Cs_2CO_3, 15.8–25.5 MPa. Determined by HPLC.

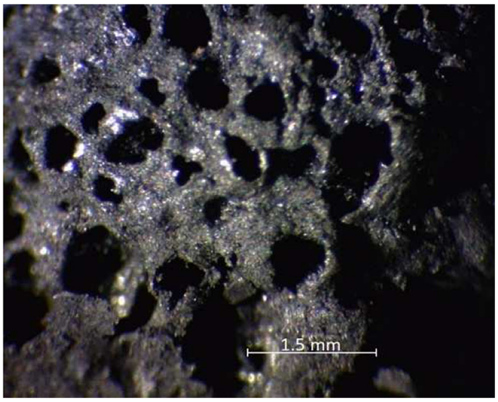

Fig. 3. Optical microscopy image of PEEK, Victrex 150CA30, post processing in scH_2O, 648 K, 25 min, 30 MPa, showing the macro-porous structure.

the relationship between Ethanol concentration and the decomposition of PEEK, and subsequent release of the carbon fibres. Fig. 4a and b show the effects of 20 and 100%v ethanol, maintaining all other reaction conditions.

Fig. 4b shows that without the addition of water the decomposition of PEEK does not readily take place, the carbon fibres are visibly confined within the polymer matrix. A co-solvent system consisting of the 80%v water, 20%v ethanol under the same conditions brings about complete decomposition of the polymer, allowing for separation of the fibres for subsequent testing and incorporation into new products. Having identified the ideal co-solvent composition with respect to ethanol concentration it was necessary to investigate the effects of the Cs_2CO_3 concentration.

3.1. Effects of caesium carbonate concentration

By maintaining the concentration of ethanol at 20%v, the reaction temperature at 623 K and a reaction time of 30 min the concentration of Cs_2CO_3 was varied from 0 to 10 mg ml^{-1}. The reaction conditions are presented in Table 1 (Experimental methodology), the results are presented in Fig. 5.

By inspection of Fig. 5 it may be seen that the reaction is 1st order with respect to the caesium carbonate concentration. Without the addition of caesium carbonate the concentration of phenol was 0.02 mg ml^{-1} indicating that the decomposition was minimal.

3.2. Fourier Transform Infra-Red Spectrometry

FT-IR may be used to analyse the functional groups of PEEK and by comparison of wavenumbers 1305 and 1280 cm^{-1} it is possible to infer the percentage crystallinity [25,26]. Therefore, if the polymer has been decomposed it would not be expected to observe functional groups associated with PEEK, crystalline or amorphous. Fig. 6 shows the FT-IR spectrum for a PEEK 150CA30 sample processed for 30 min in a mixture containing 20%v ethanol, 80%v water without the addition of Cs_2CO_3. It is evident that the polymeric functional groups associated with PEEK are still present, further indicating that the decomposition was minimal. By contrast, Fig. 7 shows the FT-IR spectrum for a sample processed under identical conditions with the addition of 10 mg ml^{-1} Cs_2CO_3.

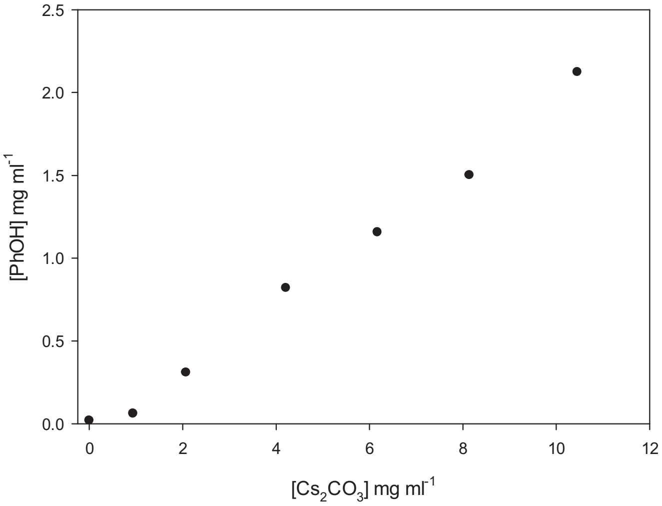

Fig. 5. Effect of caesium carbonate concentration [Cs_2CO_3] on the production of phenol [PhOH] by the decomposition of PEEK. 20%v ethanol, 80%v water, 30 min, 623 K, 16.8 ± 0.2 MPa. Determined by HPLC.

Comparison of Figs. 6 and 7 highlights the significant contribution that caesium carbonate makes in the decomposition of PEEK. The complete absence of functional groups is indicative of the FT-IR measuring only carbon fibres, a qualitative indication that the decomposition is substantial.

3.3. Differential Scanning Calorimetry

Additional information may obtained from Differential Scanning Calorimetry (DSC). PEEK 150CA30 is obtained in the semi-crystalline state, therefore crystallisation is not observed when analysing virgin samples. The crystallisation processes of PEEK is rapid, taking place at approximately 450 K [27]. The reactor cooling process is sufficiently slow (10–20 K min^{-1}) such that any PEEK in the melt phase would crystallise prior to being removed from the reactor. PEEK recovered from the reactor and analysed by DSC is

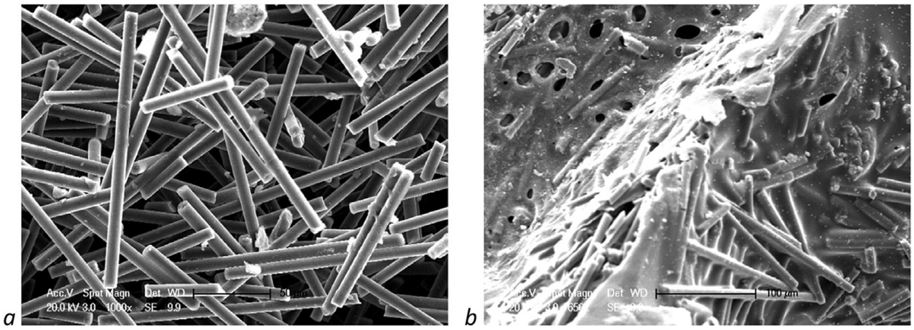

Fig. 4. SEM micrographs of post processed PEEK 150CA30, 30 min, 623 K, 10 mg ml^{-1} Cs_2CO_3, a) 20%v ethanol, 16.7 MPa, b) 100%v ethanol, 23.9 MPa.

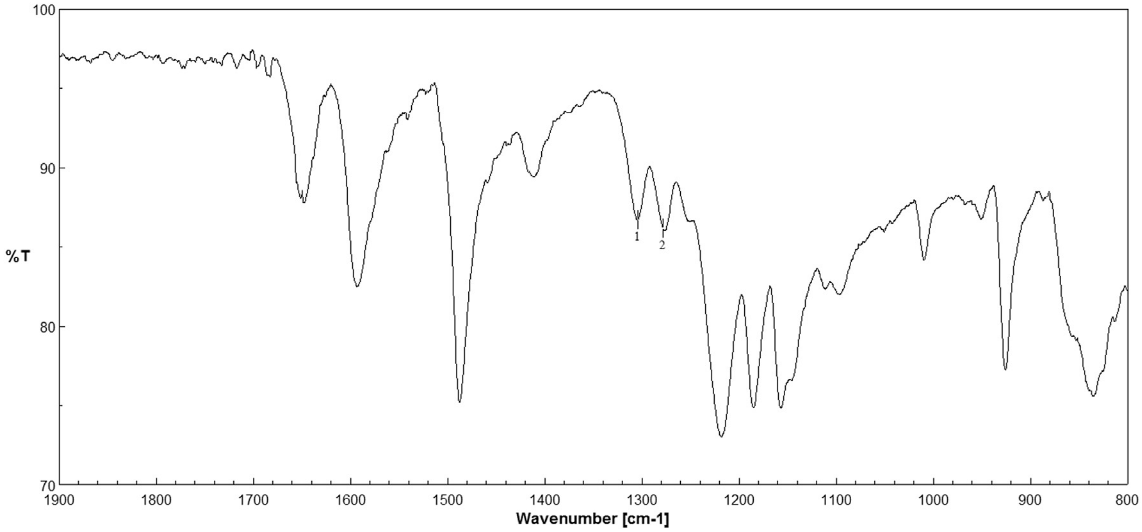

Fig. 6. FT-IR of PEEK 150CA30 post processing, 30 min, 623 K, 20%v ethanol, 80%v water, 16.8 ± 0.2 MPa, without Cs_2CO_3; Peak 1 = 1305 cm^{-1}, Peak 2 = 1280 cm^{-1}.

expected to exhibit a T_g and T_m. Fig. 8 shows the DSC curves for virgin PEEK 150CA30 and processed samples.

Fig. 8 shows that when the caesium carbonate concentration is below 6 mg ml^{-1} PEEK partially maintains its polymeric structure, hence the melt transition is observed. HPLC analysis (Fig. 5) shows that even when the caesium carbonate concentration is 1 mg ml^{-1} small quantities of phenol are produced, indicating that the decomposition has begun. Once the caesium carbonate concentration exceeds 6 mg ml^{-1} the melt transition is no longer observed and the functional groups associated with PEEK are also not seen by FT-IR, implying that the decomposition is in the advanced stages. Samples processed with a Cs_2CO_3 concentration of 1 mg ml^{-1} exhibited a T_g at 432 K, whereas samples processed with a Cs_2CO_3 concentration of 2 mg ml^{-1} exhibited a T_g at an elevated temperature of 480 K.

3.4. Effect of reaction time

Using the production of phenol as an indicator as to the decomposition of PEEK, it is possible to investigate the effects of the reaction time. A reaction time of 0 min is considered to be heating and cooling of the reactor exclusively; once the reaction temperature is reached the furnace is removed and the reactor is cooled. This study was carried out at 623 K to ensure that the PEEK was in the melt phase, and therefore amorphous. Fig. 9 shows the concentration of phenol with respect to the reaction time.

Fig. 9 shows that the production of phenol has taken place when the reaction time is 0 min (i.e. heating and cooling only). This implies that the decomposition of PEEK either takes place slightly below 623 K or that the reaction kinetics are sufficiently rapid such that the decomposition is immediate under the said conditions, leading to the production of small quantities of phenol once the temperature (623 K) is attained. At the reaction time of 0 min the phenol concentration was 0.128 mg ml^{-1} and had increased to 0.623 mg ml^{-1} at 5 min. With a reaction time of 30 min the Phenol concentration is 2.1 mg ml^{-1}, at which point doubling the reaction time to 60 min results in a phenol concentration of 2.6 mg ml^{-1}. No significant increase in phenol concentration was observed by subsequent doubling of the reaction time, indicating that the rate of degradation slowed.

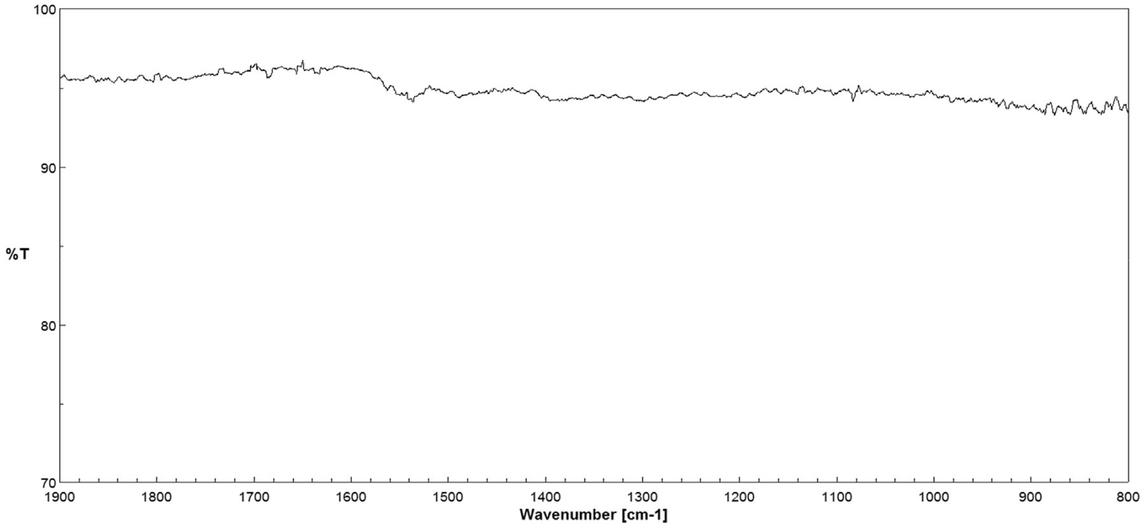

Fig. 7. FT-IR of PEEK 150CA30 post processing, 30 min, 623 K, 20%v ethanol, 80% water, 16.8 ± 0.2 MPa, 10 mg ml^{-1} Cs_2CO_3.

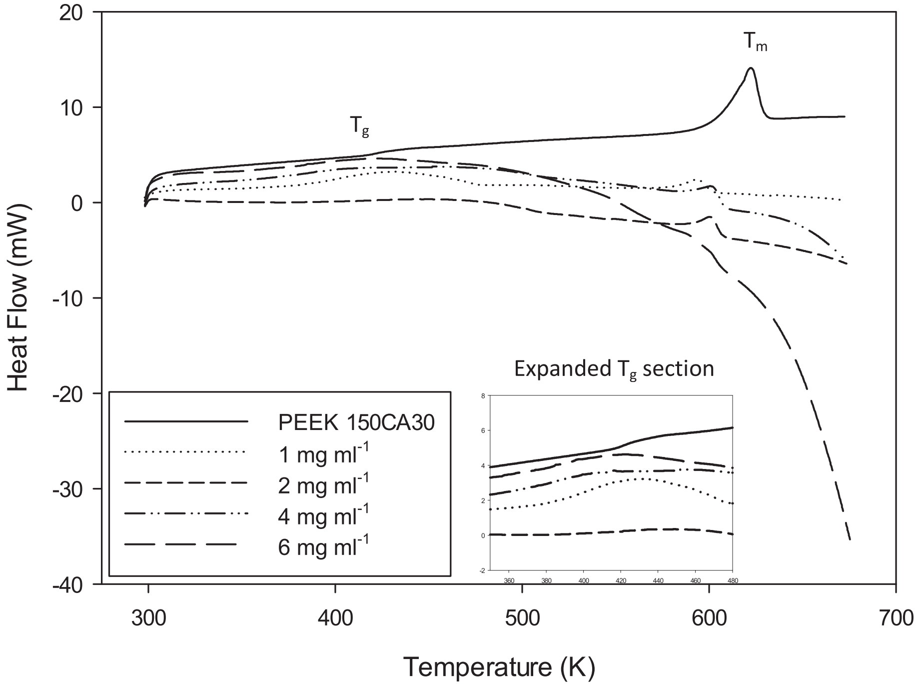

Fig. 8. DSC curves for PEEK 150CA30 processed for 30 min using 20%v ethanol, 80%v water, 16.8 ± 0.2 MPa, 1–6 mg ml^{-1} Cs_2CO_3.

3.4.1. *Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis (effect of reaction time)*

Scanning Electron Microscopy (SEM) has been used to analyse the fibres reclaimed from the polymer matrix. The fibres impregnated into PEEK 150CA30 are short, typically several millimetres in length, and therefore have not been subjected to tensile testing due to physical constraints of the testing procedure. Examination of bulk fibres shows that after 0 min the vast majority of fibres appear to be confined within the polymer matrix, although some separated fibres are present. With increasing reaction time is it possible to separate the carbon fibres from the polymer matrix. It is also evident from the increased production of phenol (Fig. 9) and the absence of polymeric functional groups (Fig. 7) that the polymer has been decomposed and is no longer present. Fig. 10a–d, show the effects of increasing reaction time on both decomposition of the polymer and release of the fibres.

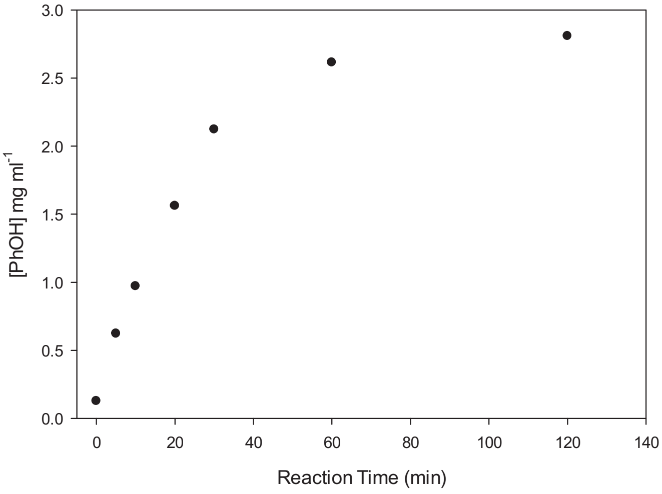

Fig. 9. Phenol concentration [PhOH] with respect to reaction time, 623 K, 20%v ethanol 80%v water, 16.8 ± 0.2 MPa, 10 mg ml^{-1} Cs_2CO_3, 10 mg ml^{-1} PEEK. Determined by HPLC.

Inspection of the carbon fibres shows that the fibres reclaimed after a reaction time of 0 min contain some solid deposition. Qualitative analysis of the liquid fraction does not show significant deposition of carbon fibres, information which further implies that the polymer integrity is not heavily degraded. FT-IR analysis shows that for a reaction time of 0 min, the PEEK functional groups remain and analysis of the peaks at 1305 and 1280 cm^{-1} show that the functional groups are not dissociated from the polymer backbone. By contrast, after 30 min the functional groups are not identified. Closer inspection of the carbon fibres by SEM shows that the fibres obtained after 0 min are partially coated, whereas those obtained from a 30 min reaction are relatively clean and free of deposition (Fig. 11).

Fibres obtained from reaction times in excess of 30 min were not, in all cases, completely free of solid deposition. There are two primary suspected causes of this deposition, one being the solidification of the non-decomposed PEEK at ambient conditions and the other being the deposition of Cs_2CO_3 that has crystallised on the dried carbon fibres. Energy Dispersive X-Ray spectrometry (EDX) was used to identify the elemental composition of the deposits for reaction times of 0 and 60 min, Fig. 12.

The EDX analysis implies that the solid deposition observed on the carbon fibres for a reaction time of 60 min is Cs_2CO_3, with Cs accounting for 8.96% of the atoms identified compared with 3.17% for a reaction time of 0 min. Considering that the Cs_2CO_3 concentration was the same in both reactions, and is not a product of the decomposition reactions, there is not sufficient evidence to suggest that there is any process leading to increased deposition of Cs_2CO_3 as a consequence of increased reaction times. In both cases, it is expected that the most abundant element in either sample would be carbon, which is indeed observed. However, in the case of the 0 min reaction there is also a significant amount of PEEK present, owing to the lack of decomposition. Almost 56% of the PEEK repeat unit is comprised of carbon atoms, and therefore should the decomposition be minimal, the relative abundance of caesium will

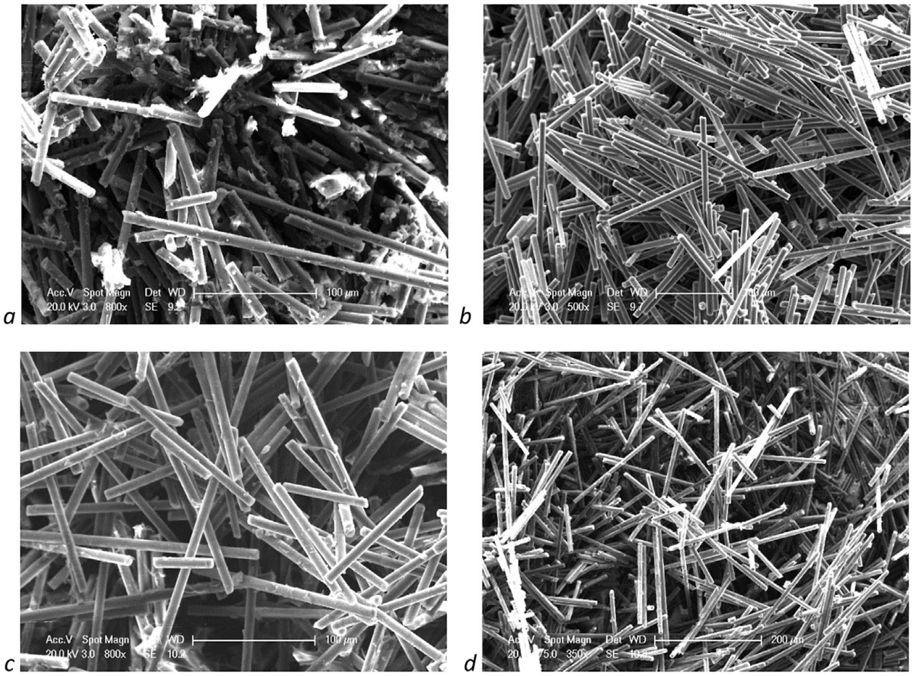

Fig. 10. Decomposition of PEEK 150CA30 and separation of the carbon fibres with increasing reaction time. 20%v ethanol, 80%v water, 16.8 ± 0.2 MPa, 623K, 10 mg ml^{-1}, a) 0 min, b) 30 min, c) 60 min, d) 120 min.

be greatly reduced. The EDX data for the two conditions are tabulated in Table 3.

The use of EDX in this context is not quantitative with respect to the entire sample, owing to its heterogeneity. EDX has been used to target deposits identified by means of SEM, allowing for the determination of their composition. Therefore, the quantitative analysis at any given point is not representative of the bulk sample.

3.4.2. *Thermogravimetric Analysis (effect of reaction time)*

Thermogravimetric Analysis (TGA) was used to determine the percentage decomposition of PEEK. The thermal decomposition temperature is 848 K [15], at which point PEEK decomposes into a range of organic compounds. The quantity and composition of the remaining char is a function of the decomposition conditions, in an inert atmosphere N_2 approximately 70% of a carbon fibre reinforced

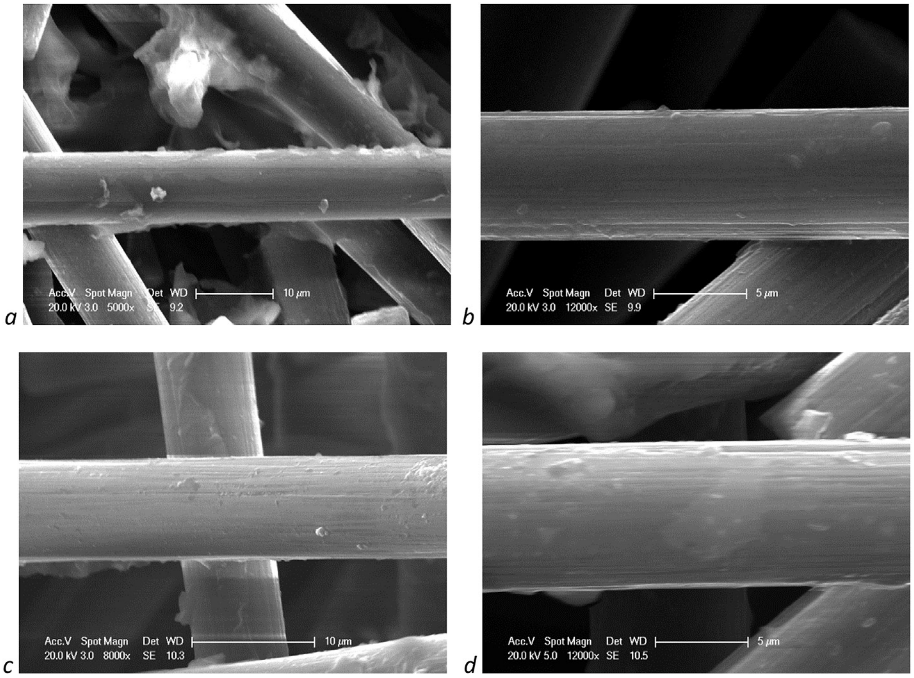

Fig. 11. Fibres reclaimed from PEEK 150CA30 using 20%v ethanol, 80%v water, 16.8 ± 0.2 MPa, 623 K, 10 mg ml^{-1}, a) 0 min, b) 30 min, c) 60 min, d) 120 min.

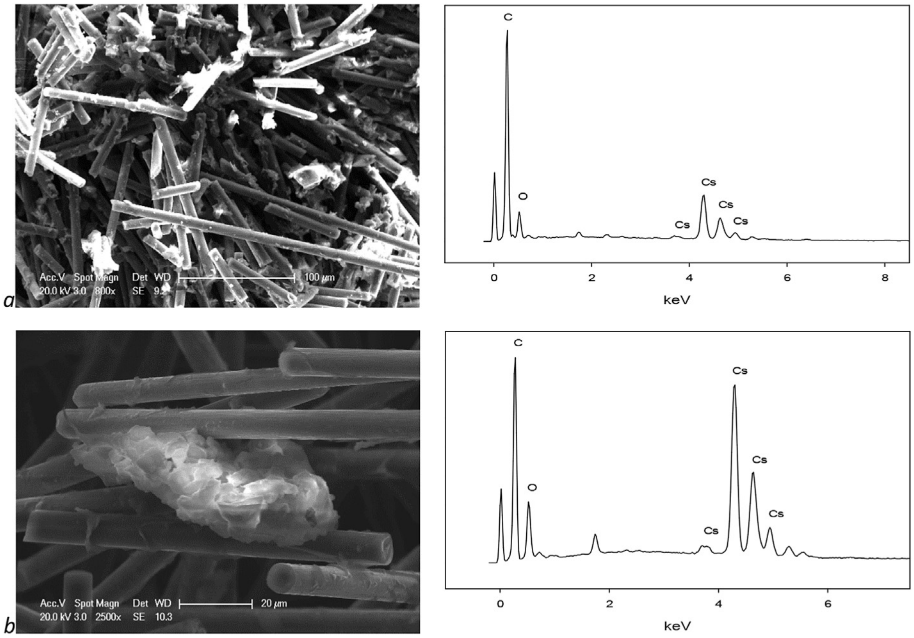

Fig. 12. Energy Dispersive X-Ray spectrometry of solids deposits using 20%v ethanol, 80%v water, 16.8 ± 0.2 MPa, 623 K, 10 mg ml^{-1}, a) 0 min, b) 60 min.

PEEK sample remains as char [15]. It is therefore expected that should the polymer be decomposed and the organic compounds solubilised during the reaction, the percentage mass loss observed by TGA would be significantly reduced. The remaining mass would be attributed char and to the carbon fibres since they are not subject to significant thermal degradation in inert atmospheres until temperatures in excess of 4273 K [28]. Fig. 13 shows the TGA curves for PEEK 150CA30 samples processed for 0–120 min.

Complete decomposition and subsequent removal of all organic compounds from the sample would leave only fibres. TGA analysis would then show approximately 4% mass loss at temperatures up to 1150 K [29], by comparison the observed mass loss by TGA is 13% or less for samples processed for 30 min or more. SEM analyses have shown that some solid deposition is present within the separated fibres, EDX has shown that some of the deposition is most likely to be Cs_2CO_3, having a thermal decomposition temperature of 873 K. It is also possible that some decomposition products, such as phenol, may have crystallised within the fibre bundles upon drying. The mass loss onset associated with the processed samples is significantly lower than that of PEEK, in some cases the mass loss appears linear below 600 K. It is therefore suggested that the TGA data for samples processed for longer than 30 min show the thermal degradation of the PEEK decomposition products, and not that of the polymer. The absence of a sharp increase in thermal degradation rate at 848 K further implies that the polymer decomposition is essentially complete for reaction times in excess of 30 min.

When the processing time is 0 min there is insufficient time for the decomposition to take place. However, prior to obtaining the reaction temperature of 623 K PEEK undergoes a transition to the melt phase at 616 K. Figs. 2 and 5 demonstrate that there is a synergistic effect between the ethanol and caesium carbonate concentrations. Experiments using 100%v ethanol have shown that decomposition of the polymer did not take place, the solid samples were swollen but not degraded. It is known that Cs_2CO_3 is soluble in both water and ethanol, and also in mixtures of both solvents. It is suggested that ethanol/water mixture, being at its critical point, swells the PEEK allowing for an increased mass transport of the Cs_2CO_3 carried in the ethanol/water mixture into the PEEK structure. Similar material expansion and subsequent porosity has been identified with supercritical water (scH_2O). This similarity in the expansion of PEEK is thought to be accountable for the ability of Cs_2CO_3 in ethanol/water mixtures to decompose PEEK at 80 K below what is possible with water/Na_2CO_3 solutions.

Table 3
EDX Analysis of solid deposits after 0 and 60 min reactions (conditions as in Fig. 12).

Reaction time (min)	C (%)	O (%)	Cs (%)
0	80.75	16.08	3.17
60	73.75	17.28	8.96

When the reaction medium consists of ethanol and the reaction time is 0 min, an increase in the solid mass recovered from the reactor is observed. The SEM data have shown that ethanol may be responsible for swelling PEEK and GC–MS has been used to identify phenol derivatives, such as 2-ethylphenol, which may indicate that ethanol may undergo some decomposition and subsequently react with the phenyl ring. Further work is required to confirm this inference, but should the substituted phenols remain within the polymer matrix post production, the mass of solids removed would be greater than the initial mass. In addition, the percentage mass loss upon decomposition would increase and thermal decomposition temperature observed by TGA would be reduced due to the degradation of the polymer structure. These effects are both observed as shown in Fig. 13 where it may be seen that the percentage mass loss after a 0 min reaction is greater than that of a virgin PEEK 150CA30 sample, the onset of decomposition being identified at approximately 700 K.

3.4.3. *Differential Scanning Calorimetry (effect of reaction time)*

Since DSC is able to identify the polymeric transitions, T_g, T_c and T_m, associated with PEEK it is possible to identify the presence of PEEK. Consequently the absence of PEEK may be used to indicate that the decomposition of the polymer chains has taken place. PEEK 150CA30 is received in the semi-crystalline state, therefore in the virgin sample only the T_g and T_m should be observed. Fig. 14 shows the DSC curves for samples processed for 0–120 min.

Fig. 14 shows that the after a reaction time of 0 min (heating and cooling only) the sample retains some polymeric properties. The

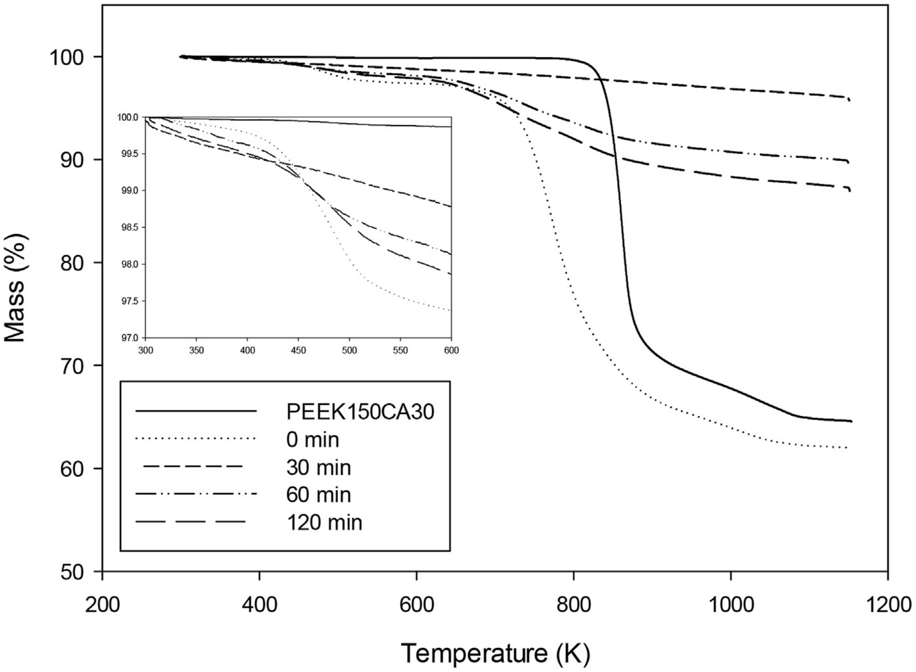

Fig. 13. Effect of reaction time on observed mass loss by Thermogravimetric Analysis. 623 K, 10 mg ml^{-1} Cs_2CO_3, 20%v ethanol, 80%v water.

melt temperature has reduced slightly to 603 K and an exotherm indicative of the onset of decomposition is visible at 634 K. For reaction times of 30 min and greater, the polymeric characteristics are completely lost and no PEEK transitions are observed. This is consistent with the TGA, FT-IR and SEM data that suggest that the polymer is decomposed into low molecular weight organic products.

All of the products shown in the proposed reaction scheme for the accelerated decomposition of PEEK, Fig. 15, were observed by GC–MS with the exception of diphenylmethanone (2). Given that the ketone group is surrounded by 2 phenoxy groups, the absence of diphenylmethanone (2) suggest that the dissociation energy of the ketone group is less than that of the ether linkage. The absence of diphenylmethanone (2) has been observed and reported in the thermal decomposition of PEEK [15]. The production of either 4-phenoxyphenol (1) or diphenylmethanone (2) would ultimately lead to the production of phenol (8, 10) and consequently phenol is a major product of the reaction. 4-Phenoxyphenol (1) undergoes

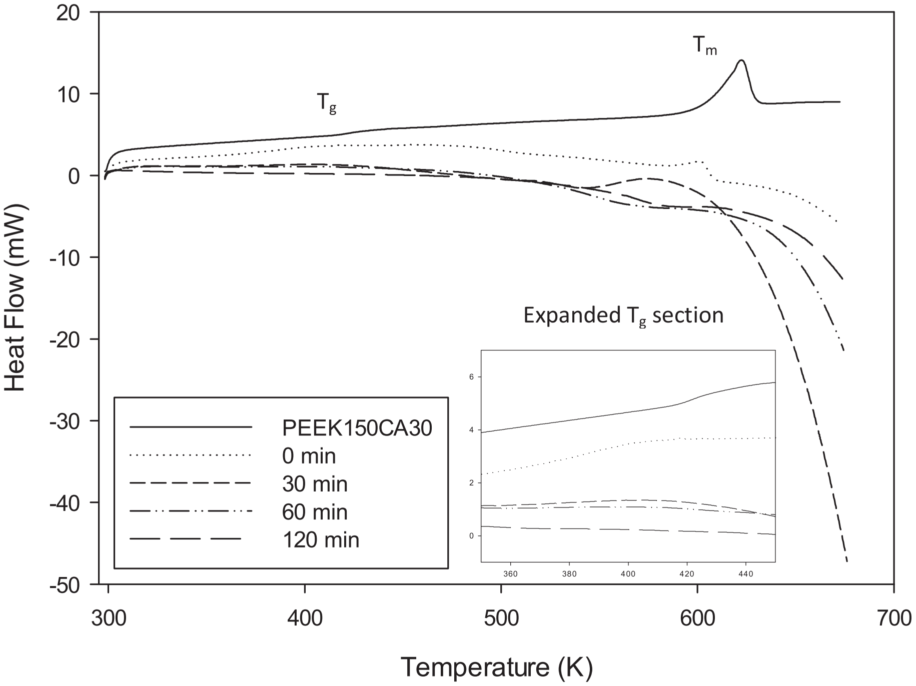

Fig. 14. Differential Scanning Calorimetry of PEEK 150CA30 and processed samples, 0–120 min, 623 K, 10 mg ml^{-1} Cs_2CO_3, 20%v ethanol, 80%v water, 16.8 ± 0.2 MPa.

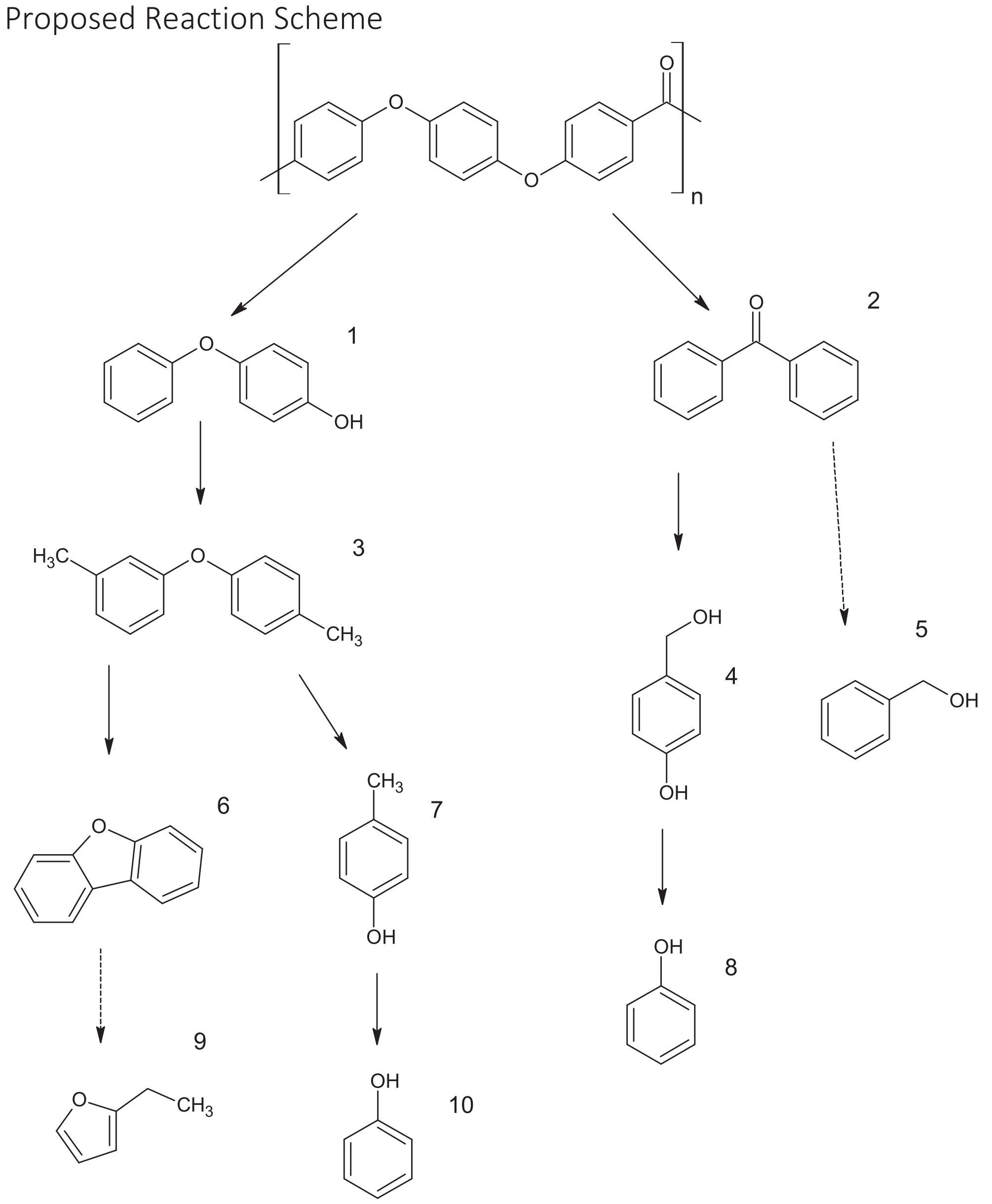

Fig. 15. Main decomposition products from the decomposition of poly(oxy-1,4-phenyleneoxy-1,4-phenylelecarbonyl-1,4-phenylene), solid arrows = major product formation, dashed arrows = minor product formation.

secondary reactions leading to the formation of 1-methyl-3-(4-methylphenoxy)benzene (3) which may undergo further reaction to form dibenzofuran (6) by radical addition [30]. The decomposition of dibenzofuran (6) to form 2-ethyl furan (9) is not thought to be dominant and is most often observed when the concentration of ethanol is 100%.

A competing reaction for the decomposition of 1-methyl-3-(4-methylphenoxy)benzene (3) is the formation of 4-methylphenol (7), which may undergo subsequent decomposition into phenol (10). Phenol was identified in all samples where the ethanol concentration was less than 100%. Moreover, when the ethanol concentration was 100% the production of phenol was not identified by GC–MS irrespective of the Cs_2CO_3 concentration and the reaction time. It may be deduced therefore, that phenol is a major product of the decomposition of PEEK near its melting temperature and that, whilst ethanol works effectively as a co-solvent for the reaction system, the predominant reaction mechanism is one of hydrolysis.

The action of the caesium carbonate catalyst may be understood by considering the decomposition reaction mechanism, leading to the production of 1,4-diphenoxybenzene, presented in the literature by other authors [15]. The mechanism essentially shows that the decomposition initiates with radical formation, followed by tautomerisation. It is postulated that by using Cs_2CO_3, the reaction may proceed in two ways. Firstly, the radicals formed may be stabilised by the positive charge of the caesium atoms, increasing their lifetime. Secondly, Cs_2CO_3 makes the solution basic which promotes the dissociation of protons into solution and therefore makes them more readily available to the radicals formed. Given that the formation of radicals is always in pairs, and that each mole of Cs_2CO_3 contains 2 Cs atoms, it thought likely that this is the reason for the decomposition reaction being 1st order with respect to the caesium carbonate concentration as each molecule of Cs_2CO_3 is able to stabilise 2 radicals.

4. Conclusion

The decomposition of PEEK/carbon fibre composites may be carried out at 623 K by using a co-solvent system comprising of ethanol and water, incorporating catalytic quantities of caesium carbonate. The decomposition is effective within a relatively short reaction time of 30 min, allowing for the separation of carbon fibres from the polymer matrix. Increased reaction times lead to an increased phenol yield, possibly due to the secondary decomposition of reaction products. Relatively clean carbon fibres are obtained without washing, however it is possible to detect the presence of residual quantities of caesium carbonate. It has not previously been possible to carryout the decomposition of PEEK below 703 K in aqueous media.

A reaction scheme for the decomposition is proposed, highlighting the production of the major decomposition products, phenol and dibenzofuran. Quantitative analysis of the phenol concentration was carried out by means of High-Performance Liquid Chromatography and used as a means of following the decomposition process. The separated carbon fibres have been analysed by Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis, confirming the decomposition of PEEK and the isolation of free carbon fibres. Differential Scanning Calorimetry has been used to investigate the presence, or absence, of polymeric transitions of the recovered solids. Functional group analysis was conducted by means of Fourier Transform Infra-Red Spectroscopy.

Using caesium carbonate as a catalyst for the decomposition in a 20%v ethanol/80%v water co-solvent system allows for a reduction in the carbonate concentration in excess of 2 orders of magnitude over the use of sodium carbonate in water, whilst simultaneously allowing a reduction in the reaction temperature of 80 K. Solutions of Cs_2CO_3 without ethanol are demonstrated to be up to 50% less effective, with respect to the phenol yield, compared to the solutions containing ethanol. Mixtures of ethanol and water not containing caesium carbonate produce virtually no phenol, the major product of the PEEK decomposition, indicating that decomposition does not take place. The use of this co-solvent system represents a significant step forward in the recycling of end-of-life, contaminated and degraded carbon fibre reinforced thermoplastic poly(aryl-ether-ketones), a process that is likely to become of high importance as they find increasing application in high performance industries.

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