

FINE-TUNING THE PROPERTIES OF POLY(ETHER ETHER KETONE)/POLY(ETHER IMIDE) BLENDS BY THE ADDITION OF CARBON NANOFIBRES

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ABSTRACT

Carbon nanofibres were used to modify the mechanical performance of a high-performance thermoplastic blend based on a semicrystalline poly(ether ether ketone) and an amorphous poly(ether imide). While the addition of 20 wt% of the PEI increased the glass transition temperature of the blend by about 20 °C compared to the pure PEEK, the nanofibres offset the accompanying reduction in the mechanical properties at a loading fraction as low as 5 wt%. Differential scanning calorimetry verified the absence of morphological variations in the crystal structure of the PEEK component, but highlighted the influence of the nanofibres on the phase separation process upon cooling. An interpretation of the composite performance by short-fibre theory showed a rather low effective reinforcement capability of these nanofibres. However, such a nanoscale reinforcement might prove especially useful in high-temperature thermoplastic components for miniature applications where conventional reinforcements cannot physically be accommodated.

1. INTRODUCTION

Applications of short fibre-reinforced thermoplastic polymer composites are mostly limited to relatively low temperatures. The development of semicrystalline thermoplastic matrices with a high glass transition and melting temperature, such as the poly(aryl ether ketone)s (PAEK), has allowed the design of modern thermoplastic composites to meet increasingly severe operating conditions. The combination of such high-performance thermoplastic matrices with conventional short fibres leads to mechanical properties rivalling those of traditional thermoset-based composites, whilst retaining the ease of processing traditionally associated with thermoplastics.

In general, all polymers belonging to the PAEK group are tough, semicrystalline thermoplastics which are mostly used for applications requiring excellent mechanical properties and a good chemical stability, even at elevated temperatures. Semicrystalline poly(ether ether ketone) (PEEK) as one example is also an attractive bearing material as it is comparatively fatigue resistant and exhibits a low creep rate up to about 250 °C, especially when fibre-reinforced [1,2]. A common approach to further enhance the glass transition temperature (T_g) and temperature range of operation of PEEK is to blend this semicrystalline

material with an amorphous high-temperature thermoplastic such as poly(ether imide) (PEI) which has a significantly higher glass transition temperature. Although the PEEK is found to crystallise to the normal bulk value (~30 % with respect to the PEEK content) at low PEI contents (up to 40 wt%), the lower mechanical performance of the amorphous PEI component leads to a reduction of the mechanical properties of the blend.

In a previous study we have shown that vapour-grown carbon nanofibres (CNF) with an average diameter of about 150 nm can be homogeneously dispersed and aligned in a semicrystalline PEEK matrix by standard processing techniques such as extrusion and subsequent injection-moulding [3]. The resulting nanocomposites revealed a linear increase in mechanical properties such as tensile stiffness and yield strength up to filler loading fractions of 15 wt%. In addition, these injection-moulded composites showed a superior wear behaviour compared to commercial PEEK compounds optimised for tribological applications when filled with additional additives such as PTFE and macroscopic carbon fibres [4]. Carbon nanofibres also hold promise as novel reinforcements for polymer nanocomposites where conventional fillers such as short glass or carbon fibres cannot physically be accommodated. For example, both CNF-reinforced PEEK [5] as well as polypropylene [6] composite fibres have been successfully spun from the melt and have revealed increased mechanical properties.

The present study was aimed at the development and characterisation of a novel carbon-nanofibre-reinforced high-performance thermoplastic blend. In particular, 20 wt% of an amorphous PEI were added to a semicrystalline PEEK to enhance the glass transition temperature. Low concentrations of the carbon nanofibres were added to the blend to offset the decrease in mechanical performance. Such polymer nanocomposites do not only allow the development of specialised composite materials with an improved physical and mechanical performance but also enable the evaluation of the intrinsic filler properties.

2. MATERIALS AND EXPERIMENTAL DETAILS

The high-performance thermoplastic polymer blend based on 80 wt% semicrystalline PEEK and 20 wt% amorphous PEI was prepared by twin-screw extrusion. The PEEK grade (Viktrex 450P) was purchased from ICI and the PEI (Ultem 1000) was obtained from General Electrics. In order to produce blends containing 5 and 10 wt% of carbon nanofibres the as-received nanofibres, obtained from Applied Sciences Inc., and the polymer were dry-mixed and added to the hopper feeding a Berstorff co-rotating twin-screw extruder with a length-to-diameter ratio of 33, operating at around 380 °C. All strands leaving the extruder were quenched in a water bath, air dried, and then regranulated. Prior to injection-moulding, the granulates were dried at 150 °C for 4 hours. Tensile bars according to the ISO 179A standard were manufactured on an Arburg Allrounder injection-moulding machine at a processing temperature of 390 °C, with the mould temperature set to 150 °C. Following a standard

procedure to ensure a similar degree of crystallinity of the PEEK matrix, all specimens were heat-treated at 200 °C for 30 minutes, followed by 4 hours at 220 °C. For comparative reasons, the processing conditions as well as the following experimental details were kept identical to those used for the previously described PEEK-CNF nanocomposites with nanofibre loading fractions up to 15 wt% [3].

Macroscopic tensile tests were performed at room temperature with a Zwick Universal tensile testing machine. The cross-head speed was set to 0.5 mm/min in the 0-0.25 % strain range and was then increased to 10 mm/min until specimen fracture occurred. Field emission gun scanning electron microscopy (JEOL 6340F) was carried out on the fracture surfaces of the tensile specimens after coating with a thin layer of gold for imaging purposes. In addition, dynamic mechanical thermal analysis (DMTA) in a bending configuration was carried out using Perkin Elmer equipment on all annealed specimens. A peak displacement of 64 µm at a frequency of 10 Hz was applied over the temperature range from -100 to 300 °C, at a rate of 2 °C/min.

The polymer matrix morphology was assessed by differential scanning calorimetry (DSC), using a Thermal Advantage DSC 2920. Samples were taken from the core of the annealed tensile specimens. All crystallisation and melting thermograms were recorded at 10 °C/min between 70 and 400 °C, with a 5 minute hold in the molten state prior to cooling to erase the thermal history.

3. RESULTS & DISCUSSION

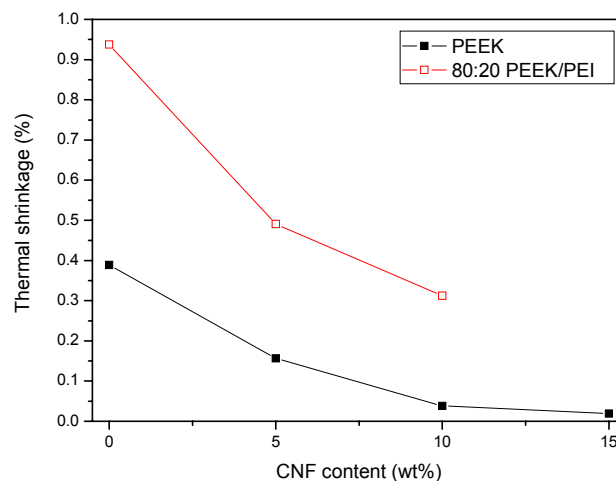
3.1 PROCESSING BEHAVIOUR

PEEK and PEI are homogeneously miscible in the liquid state, independent of the composition of the blend [7]. As in the case of the pure PEEK-CNF nanocomposites [8] the addition of up to 10 wt% of carbon nanofibres did not significantly alter the processing behaviour of the thermoplastic blend. Similarly, Lozano et al. [9] showed that the frequency-dependent rheology of a polypropylene was unaffected up to nanofibre concentrations of about 10 wt%. Only at higher filler concentrations there was a more pronounced increase of the complex melt viscosity of the polypropylene-nanofibre composites at low shear rates; however, the effect diminished in the shear rate regime typically encountered in standard thermoplastic processing technologies such as extrusion and injection-moulding.

Both the injection-moulded, pure PEEK as well as the unfilled 80:20 PEEK/PEI blend specimens were opaque, indicating that the samples were partly crystalline. All injection-moulded nanocomposites had an even black colour and an equally good surface finish as the pure reference specimens. In order to keep processing times of high-temperature thermoplastics short, the mould temperature is usually set quite low compared to the melt

temperature. The fast cooling at the cavity walls effectively suppresses crystallisation, which only takes place in the core of the injection-moulded specimens [10]. It is standard industrial practice to remove this skin-core effect by subsequent annealing at temperatures above the glass transition temperature. However, such a heat-treatment also reduces molecular orientations imposed by the shear flow and can lead to thermal shrinkage of components.

Such thermal shrinkage during heat-treatment was observed for all specimens. As shown in Fig. 1., the presence of low concentrations of carbon nanofibres in the PEEK matrix reduced the effect, especially in the axial direction, and, at a loading fraction of 15 wt%, a good dimensional stability was observed. In comparison to the pure PEEK matrix, the 80:20 PEEK/PEI blend showed a more pronounced thermal shrinkage which is a result of the phase segregation during crystallisation of the PEEK phase. The amorphous PEI is excluded from the evolving crystalline structures, and the amorphous PEEK regions are enriched in the non-crystallisable component [11]. It is interesting to note that the thermal shrinkage of the 80:20 PEEK/PEI blend could be suppressed to a similar level as the pure PEEK matrix. The overall suppression of the thermal shrinkage with an increasing nanofibre content should prove especially useful for miniature components which need to be manufactured within very narrow tolerances.

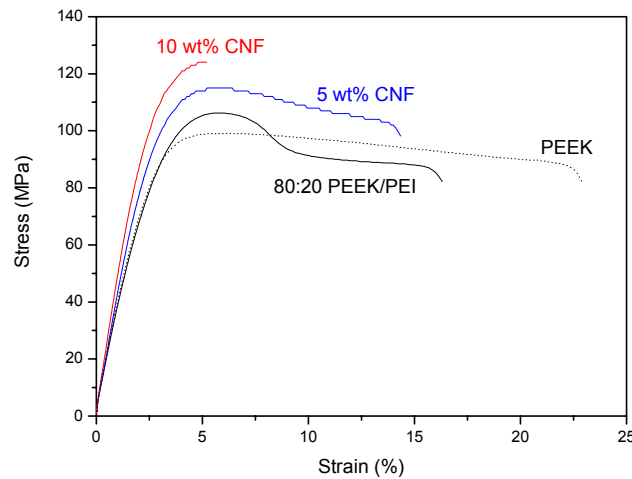


“Fig. 1. Axial thermal shrinkage during annealing of injection-moulded PEEK and 80:20 PEEK/PEI nanocomposites as a function of nanofibre loading.”

3.2 MECHANICAL PROPERTIES

Representative tensile stress-strain curves of the 80:20 PEEK/PEI nanocomposites as a function of nanofibre loading are shown in Fig. 2. The mechanical behaviour of the pure PEEK is included in b) for direct comparison. At least five specimens were tested for each composite composition and CNF loading fraction, and very small deviations in the static

mechanical properties such as Young's modulus E , yield stress σ_{\max} , strength σ_f , and strain to failure ε_f were observed. The resulting average values and standard deviations are summarised in Table 1. These experimental observations indicate a uniform dispersion of the nanofibres in all PEEK-based composites, independent of the loading fraction up to 15 wt%.



“**Fig. 2.** Representative engineering stress-strain curves for injection-moulded and annealed 80:20 PEEK/PEI nanocomposites. Data for the pure PEEK is included for comparison .”

As mentioned previously, the tensile stiffness, yield strength, and ultimate strength of the PEEK nanocomposites increased linearly up to a nanofibre content of 15 wt%, under the testing conditions chosen [3]. Furthermore, the strain to failure was found to not to decrease significantly for loading fractions up to 10 wt%.

The addition of 20 wt% of PEI to the semicrystalline PEEK led to variations in the mechanical deformation behaviour. Whereas the tensile modulus and the ultimate strength were not significantly influenced, the unfilled blend revealed an increased yield stress followed by a more pronounced ‘yield-drop’. The slight reduction in the elastic modulus at room temperature reflects the lower stiffness of the amorphous PEI as compared to the semicrystalline PEEK [7]. The increased necking behaviour and the reduced elongation at break are also a result of the PEI-enriched amorphous regions of the blend.

The addition of up to 10 wt% of carbon nanofibres led to an increase in the tensile modulus, yield stress, and strength and clearly altered the plastic deformation behaviour of the blend. The ‘yield-drop’ disappeared, although necking was still observed, as in the PEEK-CNF composites. In contrast to the PEEK-CNF reference system, the 10 wt% specimens revealed a brittle failure. These observations suggest that the nanofibres may have more influence on the plastic deformation behaviour of matrices which exhibit greater necking. Promisingly, the

addition of only 5 wt% of carbon nanofibres shifted both the tensile modulus and the yield stress of the PEEK/PEI blends to values clearly exceeding those of the pure PEEK.

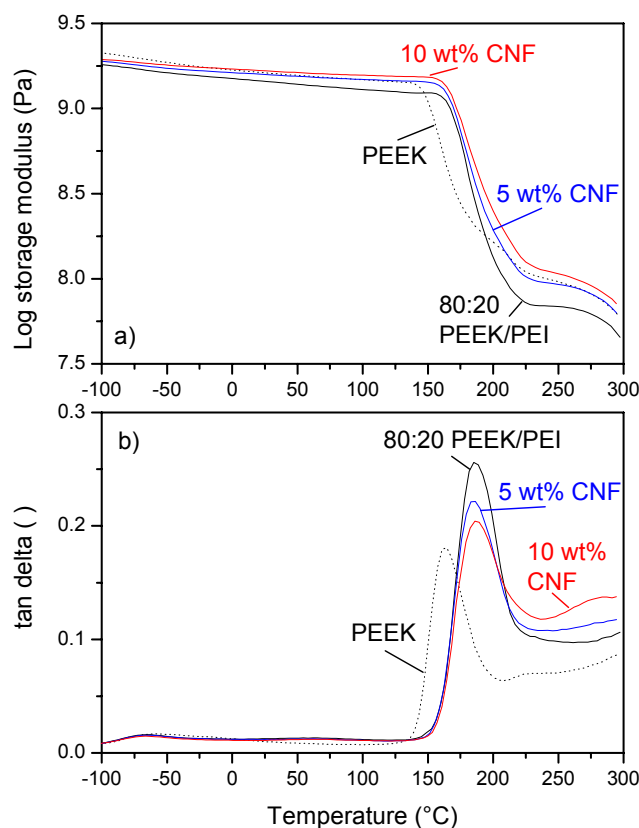
“**Table 1.** Average values and standard deviations of the composite parameters determined from the static tensile tests.”

Material	CNF content (wt%)	E (GPa)	σ_{\max} (MPa)	σ_f (MPa)	ϵ_f (%)
PEEK	0	4.0 ± 0.1	99.2 ± 0.4	80.4 ± 2.2	21.9 ± 1.2
80:20	0	3.9 ± 0.2	106.6 ± 0.3	81.8 ± 2.0	16.5 ± 0.1
PEEK/PEI	5	4.4 ± 0.2	115.1 ± 0.5	97.3 ± 1.9	12.8 ± 2.5
	10	5.0 ± 0.2	124.0 ± 0.7	124.0 ± 0.7	5.3 ± 0.7

The bending elastic modulus and damping properties of the 80:20 PEEK/PEI nanocomposites were characterised by DMTA as a function of nanofibre loading and temperature. The nanofibres were oriented parallel to the long axis of the rectangular bars and perpendicular to the direction of deformation in all cases. The elastic properties of the 80:20 PEEK/PEI blend were lower than those of the pure PEEK at temperatures above and below T_g , in agreement with the tensile test data at room temperature.

As in the case of the PEEK-CNF composites [3], Fig. 3 a) shows an increase in composite stiffness with an increasing nanofibre content, both below and above the softening point of the blend matrix. Again, over the whole temperature range explored, a nanofibre concentration of 5 wt% offset the reduction in the blend stiffness due to the addition of 20 wt% of PEI. The stiffening effect of the carbon nanofibres was more pronounced above the glass transition temperature of the blend of around 184 °C, as determined by the maximum in $\tan \delta$, the tangent of the ratio of the loss to the storage modulus (Fig. 3 b)). $\tan \delta$ is a measure of the damping within the system. In general, the temperature of this relaxation depends on the experimental probe and is very sensitive to the semicrystalline morphology of PEEK/PEI blends [12,13], which in turn is governed by the processing history.

As indicated by the data for the pure PEEK reference, the T_g of the pure blend was increased by about 20 °C. The presence of a single relaxation of for such a melt-processed and annealed blend is related to the homogenous miscibility of the two components in the amorphous phase [12]. However, the observed shift is higher than what would be predicted by the Fox equation [14] for such a homogeneously mixed blend, which would predict a shift of about 10 °C for this particular composition. The difference reflects the composition change in the amorphous phase as a result of the crystallisation of the PEEK. The increase in the PEI concentration in the amorphous phase also induced a slight broadening of the glass transition feature.



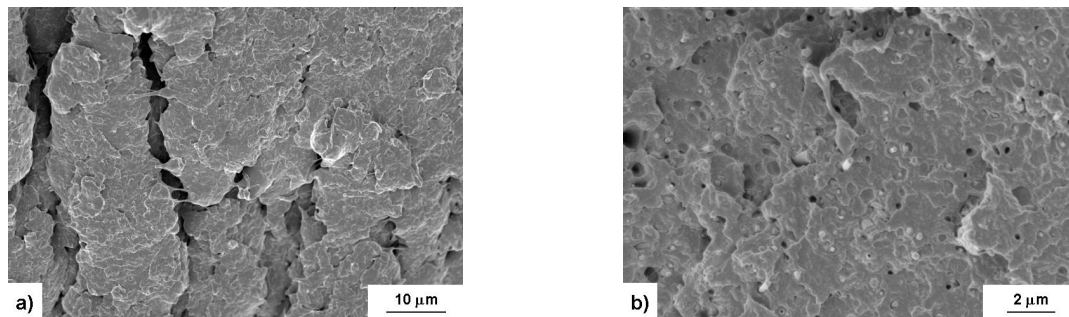
“**Fig. 3.** Dynamic mechanical analysis of 80:20 PEEK/PEI nanocomposites as a function of temperature. a) Log storage modulus and b) $\tan \delta$. Data for the pure PEEK is included as a comparison.”

As verified by the peak position of $\tan \delta$, the T_g of the blend was not affected by the addition of the nanofibres. This observation indicates that the semicrystalline morphology of the matrix was not significantly altered under the chosen processing conditions. The decreasing height of the $\tan \delta$ peak with increasing nanofibre concentration relates to the reduced fraction of polymer matrix. The onset of the glass transition temperature was also not affected by the presence of the carbon nanofibres, but there was a small broadening on the higher temperature side. As in the case of the PEEK-CNF composites [3], this effect most likely corresponds to unconstrained segments of the matrix retaining the T_g of the bulk polymer, whereas segments in the vicinity of the nanofibres are hindered in their mobility. Similar effects have been reported for other nanofibre-reinforced thermoplastic composites [15] and are typical for polymer systems filled with finely dispersed materials [16]. Greater effects would be expected for smaller diameter nanofibres or nanotubes which have higher surface areas.

3.3 MORPHOLOGY

Fig. 4 a) shows a scanning electron micrograph of the pure 80:20 PEEK/PEI blend and highlights both the crystalline nature of the matrix and its ductile deformation behaviour. In addition, the shear intensive processing led to finely dispersed carbon nanofibres in the blend

up to the highest concentration of 10 wt%, as shown in Fig. 4 b). It appears that the nanofibres are homogeneously dispersed throughout the blend; there is no evidence of preferential segregation of the nanofibres to the PEI-enriched amorphous or crystalline PEEK phases.



“Fig. 4. SEM images of fracture surfaces of a) pure 80:20 PEEK/PEI blend and b) a blend containing 10 wt% CNF.”

In order to detect potential changes in the matrix morphology due to the presence of the nanoscale reinforcement a detailed DSC analysis of the injection-moulded and annealed specimens was performed. From the melting and crystallisation patterns recorded, the thermal parameters such as the crystallisation temperature, melting temperature, crystallisation enthalpy, melting temperature, and degree of crystallinity X_c were obtained. The degree of crystallisation of the PEEK component was calculated from the peak enthalpies normalised to the actual weight fraction of the PEEK. The T_g of all the polymer blends was around 175 °C, shifted by about 20 °C compared to the pure PEEK composites, in good agreement with the DMTA data.

The onset to melting and the melting peak shape and temperature at about 340 °C were not affected by the presence of the nanofibres. However, there was a broad exotherm between the two melting features. This feature has been ascribed to reorganisation of crystals during the DSC scan and generally becomes more pronounced with increasing PEI content. The PEI effectively hinders the reorganisation of the PEEK crystals but the nanofibres did not influence this process. Taking into account the actual weight fraction of the PEEK, all composites showed an identical relative degree of crystallinity of around 30 %. This result is in good agreement with the values seen for the pure PEEK nanocomposites [3]. The onset temperature to crystallisation, as well as the maximum peak temperature during slow cooling were slightly lower for the pure PEEK/PEI blend compared to the pure PEEK. In addition, a broad tail of the exotherm on the lower temperature side could be seen. These observations indicate that crystal nucleation starts in the bulk but that the phase separation process during crystal growth is hindered by the presence of the PEI component. The crystallisation rate is generally lowered by the presence of PEI [12].

3.4 COMPOSITE PERFORMANCE

Following a previous approach [3], the tensile test data was evaluated with regard to the effective modulus of the reinforcement by the modified Krenchel rule-of-mixtures [17] for short fibre-reinforced composites. This effective modulus is the product of the intrinsic stiffness of the carbon nanofibres and two efficiency factors related to the fibre orientation and length, respectively. In the absence of significant differences in the polymer morphology this approach leads to an effective modulus of the nanoscale reinforcement of about 20 GPa, in excellent agreement with the value previously reported for the PEEK nanocomposites [3]. Further analysis of the two efficiency factors based on the experimental observations of nanofibre orientation and length lead to best estimates of the intrinsic nanofibre modulus of around 100 GPa [3,18]. A closer look at the structure of the vapour-grown carbon nanofibres used in this study implies that there is a high defect concentration in the outer part of the wall. Since only the outermost layer will be bonded to the polymer matrix, the observed low effective modulus seems consistent with expectations.

4. CONCLUSIONS

This article describes the successful industrial manufacture of a high-temperature thermoplastic polymer nanocomposite using standard processing techniques. Vapour-grown carbon nanofibres were homogeneously dispersed in a 80:20 blend of a semicrystalline poly(ether ether ketone) and an amorphous poly(ether imide) by twin-screw extrusion and subsequent injection-moulding. The addition of low nanofibre contents, up to 10 wt%, leads to a linear increase in mechanical properties such as tensile stiffness and yield stress of the blend. Due to the amorphous PEI component, the blend has an increased glass transition temperature as compared to the pure PEEK matrix. This increase in T_g is not affected by the presence of the nanofibres, however, the nanoscale reinforcement compensates the typical reduction in mechanical performance at a concentration of as low as 5 wt%. Although the nanofibres reveal a rather low effective reinforcement capability these results highlight the potential of such nanoscale reinforcements to fine-tune the dimensional stability and the mechanical and thermal properties of thermoplastic matrices, whilst maintaining the ease of processing. Such approaches should prove especially useful when optimising high-temperature thermoplastics for miniature applications.

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