

DSC CHARACTERISATION OF COMPRESSION MOULDED PEEK–PTFE PLAQUES

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Abstract

Compression moulded plaques of a range of poly(ether ether ketone) (PEEK)–poly(tetrafluoroethylene) (PTFE) blends (100, 92, 48, 29, 9.5 and 0 mass% PEEK) have been characterised using differential scanning calorimetry (DSC) and wide angle X-ray crystallography (WAXD). A shift in the melting peak of the PEEK phase from 347 to 358°C was observed with increasing proportion of PTFE in the blend. A narrowing of the melting range was also observed. Correspondingly, WAXD measurements showed a reduction in the *d*-spacings. The observed changes in morphology are rationalised in terms of a higher degree of order imparted on the PEEK crystalline phase by the transmission of an applied ‘hydrostatic’ pressure by the presence of the PTFE.

Keywords: crystal morphology, differential scanning calorimetry, poly(ether ether ketone)–poly(tetrafluoroethylene) blends, wide angle X-ray crystallography

Introduction

Poly(ether ether ketone) (PEEK) is an important engineering polymer due to its strength and high temperature resistance. PEEK, however, suffers from a high friction coefficient and excessive wear when mounted in sliding contacts [1–3]. In order to overcome the high friction and wear, PEEK–poly(tetrafluoroethylene) (PTFE) composite blends have been prepared, improving the interfacial friction characteristics. Indeed, the addition of PTFE to PEEK does reduce the interface friction and wear [1–3]. Increasing the proportion of PTFE in the composite improves the properties up to a critical blend composition, above which little further change occurs. For scratch and pin-on-disc friction and wear, this change in behaviour has been found to occur around the compositional range of 10–15 mass% PTFE [1–3].

FT-Raman characterisation of PEEK–PTFE blends has also demonstrated an influence of PTFE proportion on the morphology of PEEK–PTFE blends [4]. An increase in the relative crystallinity and degree of order in the crystalline lamellae with increasing PTFE content (again with a shift in behaviour around 10 mass% PTFE) was observed. The observation of a change in the crystalline morphology of the PEEK phase has prompted the further investigation into the influence of PTFE on the

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character of the PEEK crystallinity in compression moulded PEEK-PTFE blend plaques. In this study, this characterisation is carried out using DSC and WAXD, techniques that have been used extensively in the characterisation of the crystalline morphology of PEEK [3, 5-7].

Experimental

Compression moulded plaques (6 cm diameter and 8 mm thick) of PEEK, PTFE and PEEK-PTFE blends of 92, 48, 29 and 9.5 mass% PEEK were supplied by ICI Materials, Wilton, UK. Specimens, approximately 5×10 mm, were cut from the plaques so that they could be placed on the sample stage of a Siemens D5000 X-ray diffractometer for crystallographic analysis using CuK_{α} radiation. WAXD patterns were collected between $2\theta=10$ and 60° using a step of 0.02° with an accumulation time of 4 s per step under standard atmospheric conditions.

For DSC analysis, samples (10.0 to 10.5 mg) were cut from the specimens used in WAXD analysis with a scalpel, sealed in aluminium crucibles and placed on the sample stage of a TA Instruments MDSC 2920. The samples were heated to 240°C equilibrated and then heated to 400°C at a heating rate of 5°C min^{-1} . After the first heating program, the samples were cooled from 400 to 150°C and equilibrated for 5 min before heating to 240°C , followed by equilibration at 240°C for 5 min prior to heating once more to 400 at 5°C min^{-1} . A nitrogen purge ($150 \text{ cm}^3 \text{ min}^{-1}$) was used through out the heating program.

Results and discussion

The DSC curves for the 'as received' plaques are shown in Fig. 1 and the peak temperatures are listed in Table 1. Two characteristic peak melting temperatures are observed for the PEEK phase; a broad peak at 344°C in the 100 and 92 mass% PEEK specimens and a narrow peak at 357°C in the 48, 29 and 9.5 mass% PEEK specimens. It is notable that

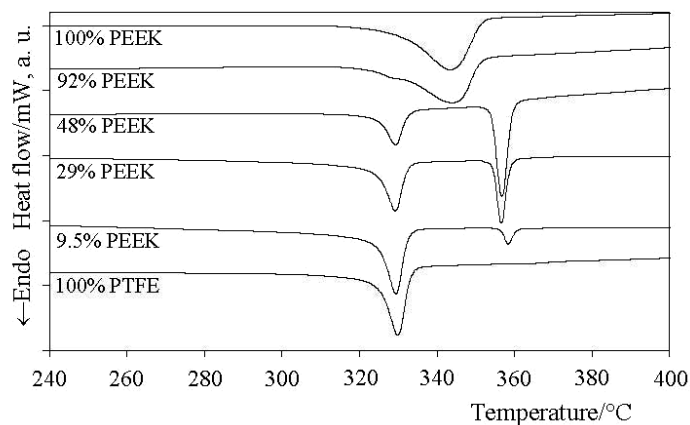
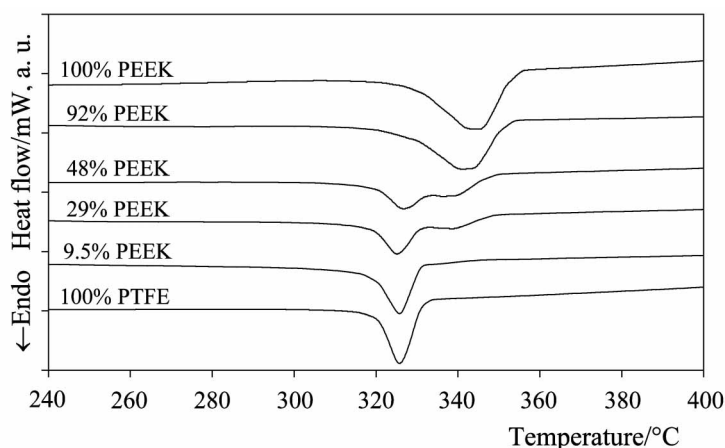


Fig. 1 DSC curves of the 'as received' compression moulded plaques

Table 1 Measured peak temperatures (°C) for the melting transitions of PEEK, PTFE and PEEK-PTFE blends for the 'as received' specimens as well as the remelted material

Specimen	'As received'		Reheated	
	PEEK	PTFE	PEEK	PTFE
100% PEEK	344	–	345	–
92% PEEK	344	shoulder	343	shoulder
48% PEEK	357	330	339	327
29% PEEK	357	329	339	326
9.5% PEEK	359	330	shoulder	326
100% PTFE	–	330	–	326

**Fig. 2** DSC curves of the blends after cycling to 400°C in Fig. 1

remelting the 48, 29 and 9.5 mass% PEEK specimens, the sharp melting peak at 357°C has been replaced by a broad shoulder to the PTFE peak around 339°C (Fig. 2). This is about 5°C lower than the position of the PEEK melting peak in the 100 and 92 mass% specimens. This difference in value is more likely to be due to overlap with the PTFE melting endotherm rather than having any physical significance. The presence of the higher temperature melting peak, observed only in the 'as received' samples, indicates that this shift is pressure induced. A strong pressure dependence of the melting transition of PEEK has been reported in the literature [7], also substantiating the possibility of a pressure-induced shift in the melting temperature of compression moulded plaques. The position of the PTFE melting peak is also observed to be at higher temperature in the compression moulded plaques relative to the position of the peak in the remelting run indicating that the degree of order of the crystalline phase of PTFE is also dependent on the compression moulding process.

In addition to the shift in temperature, there is also a difference in the shape of the PEEK melting peaks in the 'as received' specimens. The melting peaks for the

pure PEEK and 92 mass% PEEK blend are broad; the half width at half height for the pure PEEK specimen is 13°C . The 48, 29 and 9.5 mass% PEEK blends have much narrower melting peaks; the measured value for the 48 mass% PEEK blend is 3°C . The narrowing of the melting transition indicates a higher degree of order in the 'as received' plaques of the 48, 29 and 9.5 mass% PEEK blends.

WAXD measurements were only carried out on the 'as received' plaques (Fig. 3). Two sets of peak positions for the PEEK reflections are observed. The 2θ values are observed to be greater for the reflections in the PEEK crystalline phase in the 48, 29 and 9.5 mass% blends than the 100 and 92 mass% PEEK blends. An increase in the value of 2θ corresponds to a reduction in the interplanar spacings for

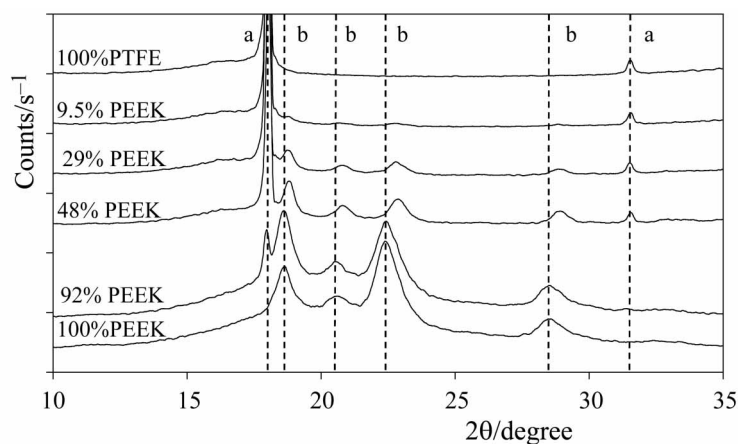


Fig. 3 X-ray diffraction patterns of the 'as received' PEEK-PTFE blends. The reflections labeled; a – correspond to the PTFE and b – to the PEEK crystallographic reflections

these reflections, indicating an increase in the degree of order in the crystalline phase. These observations correlate well with the observed melting behaviour from the DSC, as well as with the observation of a greater degree in order in the FT-Raman characterisation of PEEK-PTFE blends [4].

The higher degree of order observed in the 48, 29 and 9.5 mass% PEEK blends indicates that the PTFE itself is having an effect on the lattice spacings. It is likely that this is due to a lubricating effect of the PTFE on the PEEK phase which experiences a hydrostatic-like pressure rather than the isotactic pressure applied by the compression moulding process aiding the formation of crystallites with a higher degree of order. In the low proportion PTFE blends, this hydrostatic pressure is absent due to the reduced availability of the PTFE for lubricating the PEEK particles, hence, reducing the degree of pressure enhancement required for the formation of the higher order crystallites for these compositions.

Conclusions

A pressure-induced increase in the order of the crystalline lamellae in PEEK has been observed in the presence of PTFE and has been substantiated by both DSC and WAXD measurements. The effect of PTFE on the character of the crystallinity of PEEK in PEEK-PTFE blends, has been carried out over a wide range of compositions. As has been noted, it is in the composition range of 10 to 15 mass% that the transition in physical properties occurs. This study has noted a significant change in the morphology above and below this critical composition. It is possible that the change in properties is associated with the change in crystallinity. For this to be confirmed a closer inspection of these effects on the composition around the critical compositional range is required and will be the subject for further characterisation of the morphology of PEEK-PTFE blends.

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