

# Observation of two-stage crystallization of poly(ether ether ketone) by thermal mechanical analysis

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We report the application of thermal mechanical analysis (t.m.a.) to studying the crystallization behaviour of poly(ether ether ketone) (PEEK). We are able to show that the two crystallization stages of PEEK are clearly distinguished by measuring the variation of film thickness with time during isothermal crystallization. These two crystallization stages cannot be readily distinguished by d.s.c. The distinction by t.m.a. becomes less clear with increasing crystallization temperature due to overlap of the two crystallization stages.

(Keywords: two-stage crystallization; poly(ether ether ketone); primary crystallization; secondary crystallization)

## Introduction

Poly(ether ether ketone) (PEEK) is a semicrystalline, aromatic polymer with good thermal and mechanical properties. One of the interesting features of PEEK is its double lamellar morphology<sup>1-3</sup>. The presence of these two crystal populations gives rise to two melting endotherms<sup>1-7</sup>. The thinner crystals have been found to grow in between the thicker crystals<sup>1-3</sup>. The evidence of double lamellar morphology is based on electron micrographs, which do not produce a real-time observation of the formation of these two crystal populations. Marand and Prasad<sup>2</sup> have observed the aggregation of the secondary crystals inside PEEK spherulites using optical microscopy at crystallization temperatures ( $T_c$ ) > 295°C. However, at  $T_c$  < 295°C, these secondary crystals were not seen by optical microscopy, despite the fact that two melting endotherms were still observed by d.s.c.

In this communication, we show that thermal mechanical analysis (t.m.a.) can be used to resolve the two crystallization stages for PEEK. This simple and convenient technique is a one-dimensional dilatometry, measuring the variation of film thickness with time during isothermal crystallization. It will be shown that, as PEEK undergoes isothermal crystallization, two distinct crystallization stages can be distinguished by t.m.a.

## Experimental

PEEK powder was obtained from Imperial Chemical Industries (ICI, Wilton, UK). The molecular weights were  $M_n = 16\,800$ ,  $M_w = 39\,800$ . Fully amorphous PEEK films were prepared by compression moulding at 400°C for 5 min under vacuum followed by quenching in cold water. A thermomechanical analyser (Perkin-Elmer TMS-2) was used to detect the change in thickness of PEEK films during isothermal crystallization. A PEEK film, about 0.1 mm thick, was placed on the platform of the sample tube and the probe was placed in contact with the film. An oil bath was equilibrated at the desired crystallization temperature with control of  $\pm 1^\circ\text{C}$ . The oil bath was then quickly moved to immerse the sample, and the change

of the specimen thickness with respect to time was recorded.

## Results and discussion

Figure 1 shows the direct recorded t.m.a. traces of amorphous PEEK films during isothermal crystallization at three crystallization temperatures. It can be seen that two crystallization stages are distinguished: an initial drop of specimen thickness corresponds to the first stage (primary) crystallization, and a subsequent plateau indicates an induction period before the final drop of the specimen thickness, corresponding to the second stage (secondary) crystallization. The clear distinction of these two crystallization stages for PEEK is unusual among the semicrystalline polymers, for which only one crystallization curve has generally been observed. There are two possible explanations for this observation. The first is that the secondary crystallization starts

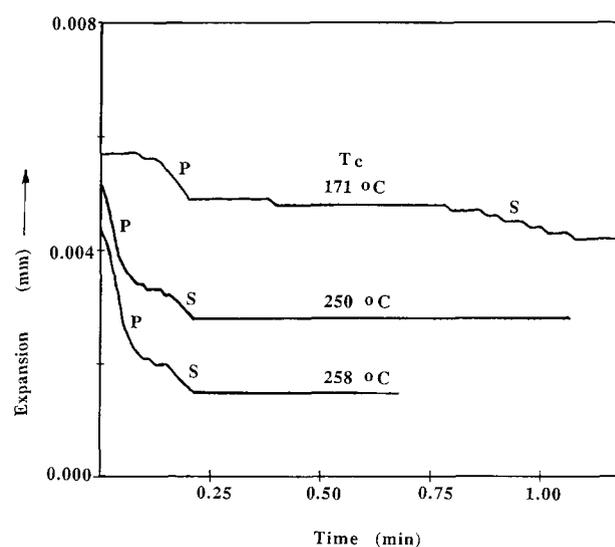
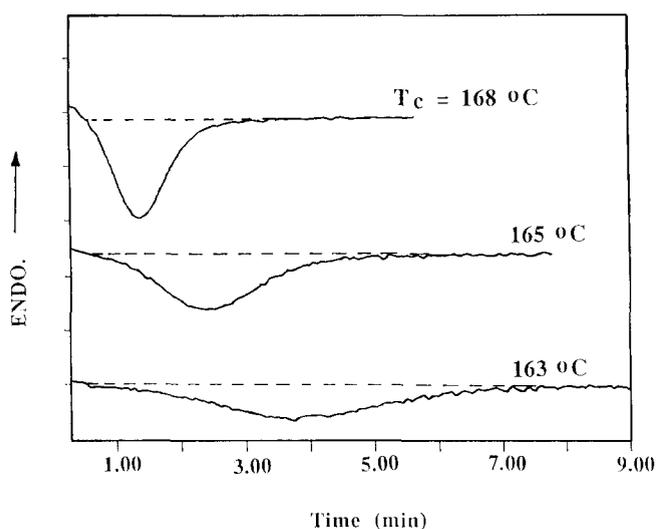


Figure 1 Direct recorded t.m.a. traces of PEEK during isothermal crystallization at 171, 250 and 258°C. In the crystallization curves, the primary crystallization is denoted by 'P', and the secondary crystallization is denoted by 'S'. The distinction of these two crystallization stages becomes less clear with increasing  $T_c$ .

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**Figure 2** D.s.c. curves of PEEK during isothermal crystallization at 163, 165 and 168°C. It can be seen that only one crystallization exotherm is distinguished

after or shortly before the conclusion of the primary crystallization. The second possibility arises from the prediction of a crystallization kinetics model proposed by Price<sup>8</sup>. This model predicts that, if the secondary crystallization proceeds much more slowly than the primary crystallization, two stages will be observed. A quantitative treatment of our data by this model, which will be reported later, concludes that the first explanation is the reason for the clear distinction of these two crystallization stages for PEEK.

Primary crystallization is normally attributed to the formation of spherulites, and secondary crystallization to crystallization taking place inside the spherulites (intraspherulitic crystallization)<sup>8</sup>. For most polymers, intraspherulitic crystallization proceeds before the conclusion of spherulite formation (i.e. impingement of spherulites). Therefore, these two crystallization stages cannot be distinguished due to overlap. However, for PEEK, intraspherulitic crystallization starts after or shortly before the impingement of PEEK spherulites, so that two crystallization stages are clearly distinguished. In principle, it is possible to test whether the time at which primary crystallization concludes corresponds to the time at which the impingement of PEEK spherulites occurs. Nevertheless, such observation by optical microscopy is very difficult at low  $T_c$  due to very high nucleation density (and hence very small size) of PEEK spherulites<sup>4</sup>.

Figure 1 also shows that as  $T_c$  is increased, the plateau between the primary and the secondary crystallization becomes shorter. This indicates the gradual overlap of these two crystallization stages with increasing  $T_c$ . It is also noted that as  $T_c$  is increased from 250 to 258°C, the crystallization rate actually decreases (this can be judged from the time at which the primary and the secondary crystallization conclude). Nevertheless, the plateau between these two crystallization stages still shortens with increasing  $T_c$ . This may imply that PEEK molecules or chain segments participating in the secondary crystallization are more sensitive to temperature change than those participating in the primary crystallization. These two crystallization stages

may overlap significantly at high  $T_c$ , such that they are not distinguishable experimentally.

The relative crystallinity can be evaluated from the t.m.a. traces in Figure 1. It is reasonable to assume that the crystallization proceeds isotropically in the film. Therefore, the relative crystallinity can be calculated from the change of the specimen thickness by:

$$X_c = \frac{1 - (l/l_0)^3}{1 - (l_\infty/l_0)^3} \quad (1)$$

where  $l_0$  is the initial specimen thickness and  $l_\infty$  is the specimen thickness after the conclusion of crystallization. Assuming that the two crystallization stages do not overlap, the secondary crystallinities of the three  $T_c$ s are evaluated directly from Figure 1. The amount of the secondary crystals is found to be 37, 20 and 16% of the total crystallinity for  $T_c = 171, 250$  and  $258^\circ\text{C}$ , respectively. This suggests that the secondary crystallinity decreases with increasing  $T_c$ . However, this disagrees with the conclusion obtained by transmission electron microscopy (TEM)<sup>1,3</sup> and d.s.c.<sup>5-7</sup>, showing that the secondary crystallinity indeed increases with  $T_c$ . In Figure 1, it can be seen that the plateaux between the primary and the secondary crystallization are not really flat for the curves of  $T_c = 250$  and  $258^\circ\text{C}$ , indicating the overlap of these two crystallization stages. Thus, the secondary crystallinities calculated above for these two  $T_c$ s are underestimated. From the d.s.c. study<sup>5-7</sup> of the melting behaviour of PEEK, it has been shown that the total crystallinity of PEEK ranges from about 30 to 40%. In addition, the enthalpy of fusion of the lower melting endotherm has been found to account for about 10% of the total enthalpy of fusion<sup>6</sup>, which is lower than the relative crystallinity calculated above. This is due to the fact that the secondary crystals undergo reorganization and recrystallization during d.s.c. heating<sup>5-7</sup>. The melting endotherm of these reorganized crystals merges with that of the primary crystals, so that the amount of the secondary crystals determined from the lower-melting endotherm is underestimated. Therefore, the amount of the secondary crystals determined by d.s.c. should be less than that determined by t.m.a.

D.s.c. is the most common technique for studying the isothermal crystallization kinetics of polymers. It is thus instructive to compare the crystallization curves obtained by d.s.c. with those obtained by t.m.a. Figure 2 shows the d.s.c. crystallization curves of PEEK during isothermal crystallization at the  $T_c$  indicated. It can be seen that there is only one rather than two crystallization exotherms, in contrast to the t.m.a. results. Figure 2 shows that d.s.c. is indeed not sensitive enough to resolve the two crystallization stages for PEEK. Nevertheless, for high  $T_c$  at which the primary and the secondary crystallization overlap significantly, the crystallization curve detected by d.s.c. should be more reliable and close to the real crystallization curve.

We have shown, by using a thermal mechanical analyser, that the two crystallization stages of PEEK can be clearly resolved. We also conclude that PEEK chain segments participating in the secondary crystallization are more sensitive to temperature change than those participating in the primary crystallization. Why is this true? This question is perhaps important for understanding the origin of the unique double lamellar morphology of PEEK. Current studies being carried out

include quantitative treatment of our t.m.a. crystallization data by a crystallization kinetics model proposed by Price<sup>8</sup> to extract the respective kinetic behaviour of these two crystallization stages, and the effect of blending with poly(ether imide) on this two-stage crystallization behaviour of PEEK.

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