

Observation of two-stage crystallization of poly(ether ether ketone) by thermal mechanical analysis[☆]

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Abstract

We report the application of thermal mechanical analysis (TMA) to study the crystallization behavior 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 can not be readily distinguished by DSC. The distinction by TMA becomes less clear with increasing crystallization temperature due to overlap of these two crystallization stages.

Keywords: Crystallization; DSC; PEEK; TMA

1. Introduction

Poly(ether ether ketone) (PEEK) is a semicrystalline, aromatic polymer with good thermal and mechanical properties. One of the increasing features of PEEK is its double lamellar morphology [1–3]. The presence of these two crystal populations gives rise to two melting endotherms [1–7]. The thinner crystals have been found to grow in between the thicker crystals [1–3]. 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 [2] have observed the aggregation of the secondary crystals inside

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PEEK spherulites using optical microscopy at crystallization temperatures $\theta_c > 295^\circ\text{C}$. However, at $\theta_c < 295^\circ\text{C}$, these secondary crystals were not seen by optical microscopy, despite the fact that two melting endotherms were still observed by DSC.

In this paper we show that thermal mechanical analysis (TMA) can be used to resolve the two crystallization stages for PEEK. This simple and convenient technique is 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 TMA.

2. Experimental

PEEK powder was obtained from Imperial Chemical Industries (ICI), Wilton, UK. The molecular weights are $M_n = 16\,800$, $M_w = 39\,800$. Fully amorphous PEEK films were prepared by compression molding at 400°C for 5 min under vacuum followed by quenching in cold water. A Perkin-Elmer TMS-2 thermomechanical analyzer was used to detect the thickness change 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 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.

3. Results and discussion

Figure 1 shows the direct recorded TMA 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, 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 between these two crystallization stages for PEEK is unusual among semicrystalline polymers for which generally only one crystallization curve has been observed. There are two possible explanations for this observation. The first is that the secondary crystallization started after or shortly before the conclusion of the primary crystallization. The second possibility is from the prediction of a crystallization kinetics model proposed by Price [8]. 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 between these two crystallization stages for PEEK.

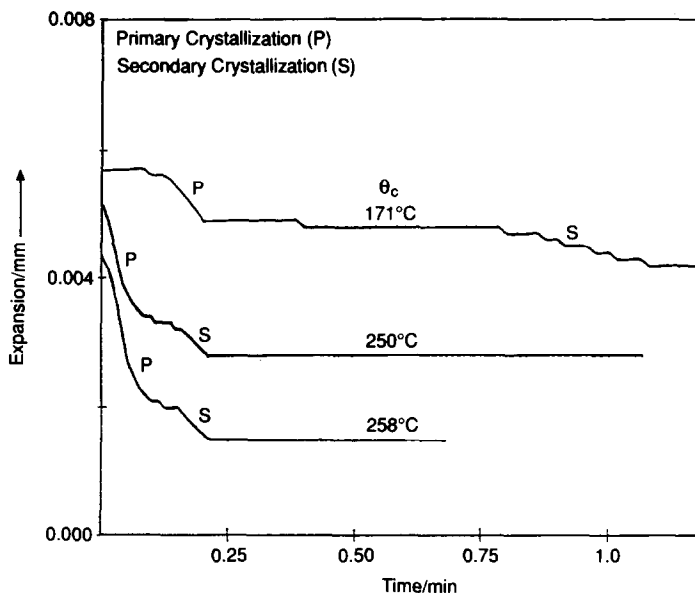


Fig. 1. Direct recorded TMA traces of PEEK during isothermal crystallization at θ_c indicated. In the crystallization curves, the primary crystallization is denoted by P, and the secondary crystallization is denoted by S. The distinction between these two crystallization stages becomes less clear with increasing θ_c .

Primary crystallization has normally been attributed to the formation of spherulites, and secondary crystallization has been attributed to crystallization taking place inside the spherulites (intraspherulitic crystallization) [8]. For most polymers, intraspherulitic crystallization proceeded 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 started after or shortly before the impingement of PEEK spherulites, so that two crystallization stages are clearly distinguished. In principle, it is possible to test if the time where the primary crystallization concluded corresponds to the time where the impingement of PEEK spherulites occurred. Nevertheless, such observation by optical microscopy is very difficult at low θ_c due to very high nucleation density (and hence very small size) of PEEK spherulites [4].

Figure 1 also shows that as θ_c was increased, the plateau between the primary and the secondary crystallization becomes shorter. This indicates the gradual overlap of these two crystallization stages with increasing θ_c . It is also noted that as θ_c was increased from 250 to 258°C, the crystallization rate actually decreased (this can be judged from the time at which the primary and the secondary crystallization concluded). Nevertheless, the plateau between these two crystallization stages still shortens with increasing θ_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 θ_c , such that they are not experimentally distinguishable.

The relative crystallinity can be evaluated from the TMA traces in Fig. 1. It is reasonable to assume that the crystallization proceeded 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_∞ is the specimen thickness after the conclusion of the crystallization. Assuming the two crystallization stages do not overlap, the secondary crystallinities of the three θ_c s are evaluated directly from Fig. 1. The amount of the secondary crystals is found to be 37%, 20%, and 16% of the total crystallinity for $\theta_c = 171^\circ\text{C}$, 250°C , and 258°C , respectively. This suggests that the secondary crystallinity decreases with increasing θ_c . However, this disagrees with the conclusion obtained by transmission electron microscopy (TEM) [1,3] and DSC [5–7] showing that the secondary crystallinity indeed increased with θ_c . In Fig. 1, it can be seen that the plateaus between the primary and the secondary crystallization are not really flat for the curves of $\theta_c = 250$ and 258°C , indicating the overlap of these two crystallization stages. Thus, the secondary crystallinities calculated above for these two θ_c s are underestimated. For the DSC study of the melting behavior of PEEK, it has been shown that the total crystallinity of PEEK ranges from about 30% to 40% [5–7]. 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 [6], which is lower than the relative crystallinity calculated above. This is due to the fact that the secondary crystals undergo reorganization and recrystallization during DSC heating [5–7]. The melting endotherm of these reorganized crystals merged 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 DSC should be less than that determined by TMA.

DSC is the most common technique used to study the isothermal crystallization kinetics for polymers. It is thus instructive to compare the crystallization curves obtained by DSC with those obtained by TMA. In Fig. 2 are the DSC crystallization curves of PEEK during isothermal crystallization at θ_c s indicated. It can be seen that there is only one, rather than two, crystallization exotherm, in contrast to the TMA results. Figure 2 shows that DSC is indeed not sensitive enough to resolve the two crystallization stages of PEEK. Nevertheless, for high θ_c s at which the primary and the secondary crystallization overlap significantly, the crystallization curve detected by DSC should be more reliable and close to the real crystallization curve.

4. Conclusions

We have shown by using a thermal mechanical analyzer that the two crystallization stages of PEEK can be clearly resolved. We also conclude the PEEK chain segments

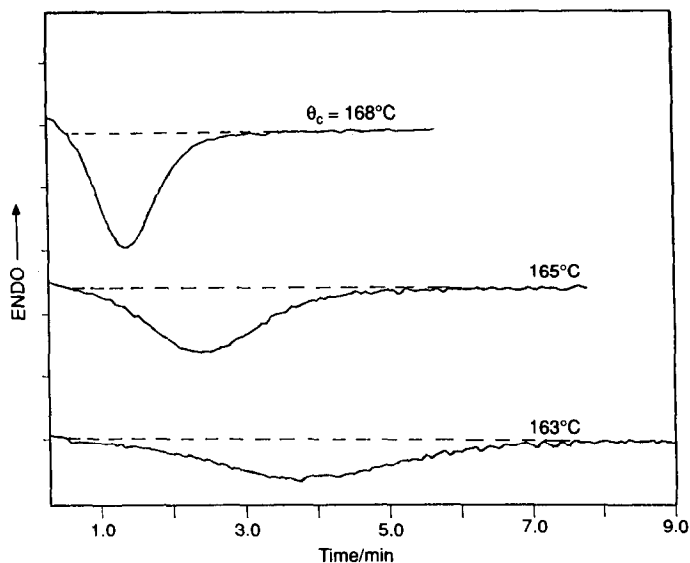


Fig. 2. DSC curves of PEEK during isothermal crystallization at 163, 165, and 168°C. It can be seen that only one crystallization exotherm is observed.

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 to understand the origin of the unique double lamellar morphology of PEEK. Current studies being carried out include quantitative treatment of our TMA crystallization data by a crystallization kinetics model proposed by Price [8] to extract the respective kinetic behavior of these two crystallization stages, and the effect of blending with poly(ether imide) (PEI) on this two-stage crystallization of behavior of PEEK.

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