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Enthalpic relaxation in semi-crystalline PEEK

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Abstract

The effect of crystallisation on the glass transition temperature and enthalpic relaxation in poly(ether ether ketone) (PEEK) has been investigated. The increase in glass transition temperature and the activation enthalpy of ageing is explained in terms of the amorphous phase being constrained by the crystallites. The extent of enthalpic relaxation with time has been analysed in terms of the Cowie–Ferguson model and the β value was found to be dependent on both temperature and the crystalline morphology, changes in the co-operativity of the relaxations are used to explain this observation.

Keywords: Enthalpic relaxation; Amorphous poly(ether ether ketone); Semi-crystalline poly(ether ether ketone)

1. Introduction

Poly(ether ether ketone) (PEEK) is widely used as an engineering polymer because of its excellent mechanical and thermal properties together with good environmental resistance. PEEK has high tensile, flexural and impact strength coupled with good electrical properties over a wide range of temperatures [1]. It also exhibits good adhesion ability and is widely used as a resin for short of continuous fibre reinforcement, such as in the case of the carbon fibre composite APC 2. This composite material has been used in the construction of aircraft wings [2].

PEEK demonstrates excellent thermal stability, and has high chemical resistance and low flammability in addition to low gas and smoke emission [3]. The morphology of PEEK can be controlled by thermal treatment, it can be quenched from the melt into an amorphous state or crystallised to levels of 40% [3]. The glass transition temperature of amorphous PEEK is 143°C and the melting temperature is 334°C. The continuous service temperature of crystalline PEEK is 250°C and as a result, the material is used in high temperature engineering applications.

A consequence of the exposure of the material to temperatures that approach the glass transition is the development of physical ageing within the structures or components fabricated from PEEK. Physical ageing results in structural changes that increase both the density and the brittleness of the material and change the electrical properties.

Physical ageing or enthalpic relaxation is due to the non-equilibrium state of the glass and as a result there is a thermodynamic driving force to reach equilibrium [4].

Ageing is particularly important from a commercial production perspective since PEEK is often injection moulded or extruded, both processes involving a rapid quench from the melt to ambient temperature. This results in a non-equilibrium material that will exhibit physical ageing. Therefore if the product experiences service temperatures that approach the glass transition temperature, a time dependent change will occur in the properties outlined above. The process of physical ageing has been studied by a number of techniques, but in particular differential scanning calorimetry has been used extensively to measure the kinetics of the enthalpic relaxation process.

Following storage at a temperature below the glass transition temperature, an aged sample will exhibit an endotherm on the glass transition, the area of which increases with the extent of ageing.

Enthalpic relaxation has been described by the KWW function that relates the change in extent of relaxation, $\phi(t)$ to time, t,

$$\phi(t) = \exp\left(-\frac{t}{\tau}\right)^{\beta} \tag{1}$$

where τ is an average relaxation time and the exponent β ($0 \leq \beta \leq 1$) is inversely proportional to the width of a corresponding distribution of relaxation times of the relaxation processes involved in ageing [5]. The KWW

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relationship has been used as a basis of another description of enthalpic relaxation proposed by Cowie and Ferguson [6], in which,

$$\Delta H_{(T_a,t_a)} = \Delta H_{\infty(T_a)}[1 - \phi(t)] \quad (2)$$

where $\Delta H_{(T_a,t_a)}$ is the enthalpy change at time t_a, and ΔH_∞ is the equilibrium enthalpy of relaxation at the ageing temperature, T_a. This model has been used to successfully describe enthalpic relaxation in PES, PVC, PS and blends of PEEK and PEI [7–10].

There are numerous other models which have been developed to explain the development of physical ageing known as multiparameter phenomenological (MP) models. These descriptions of physical ageing, like the Cowie–Ferguson approach include non-exponentially, but the MP models also include a description of the non-linearity of the ageing process through the inclusion of a structure dependence of the relaxation time. The structure of the glass is described by the fictive temperature, which is defined as the temperature at which the glass would be in equilibrium. The MP models assume thermorheological simplicity in that the distribution of relaxation times, β, is independent of temperature. Examples of MP approaches include the Moynihan and KAHR models [11,12].

The kinetics of enthalpic relaxation in amorphous PEEK have been previously reported [13], but since high temperature applications of PEEK require a semi-crystalline morphology, the possibility of enthalpic relaxation in semi-crystalline PEEK requires investigation. In this paper, the effect of crystallisation on the glass transition temperature is reported and the development of physical ageing in semi-crystalline PEEK is measured and analysed using the Cowie–Ferguson model. The previously reported results for amorphous PEEK have been re-analysed in terms of the Cowie–Ferguson model and are compared with the kinetics of ageing measured in semi-crystalline PEEK.

2. Experimental

Poly(ether ether ketone), grade 380G was supplied by Victrex plc. The glass transition temperatures and the development of physical ageing were measured using a Perkin Elmer differential scanning calorimeter (DSC), model 2B, which was interfaced to a personal computer. The thermal response of the instrument was calibrated from the enthalpy of fusion of a known mass of indium (99.999% pure). The temperature scale of the calorimeter was calibrated using the melting points of indium, tin and lead. Plots of actual against experimental melting points were linear and used to calibrate the calorimeter temperature directly after correcting for thermal lag. Corrections were made for thermal lag by extrapolation to zero heating rate.

Samples in the form of discs (1 mm thick and 3 mm in diameter) were contained within aluminium pans, and an empty pan was used as a reference. Plots of heat capacity against temperature were obtained from the DSC at different heating rates. The glass transition temperatures were determined directly from a plot of heat capacity against temperature using the method outlined by Richardson and Savill [14].

Samples of PEEK were hot crystallised in an oven at 540 K for 30 min to enable the development of crystallites within the sample. Using the method previously described [15], the degree of crystallinity was found to be 25%.

The procedure adopted for measuring physical ageing was as follows. Samples of the semi-crystalline PEEK were heated to 30 K above the glass transition temperature, stored for 30 s and cooled at 180 K min^{-1} to room temperature to produce a sample of standard thermal history. Samples were heated to the ageing temperature and stored for various lengths of time. This sample was then cooled to room temperature prior to re-heating through the glass transition at 10 K min^{-1}. A baseline was obtained by repeating this procedure but storing at the ageing temperature for zero time. The recorded baseline was subtracted from the original trace of the aged sample and the area under the endotherm was considered the enthalpy of ageing. The enthalpic data obtained was analysed by the Cowie–Ferguson model using a double logarithm plot of $(1 - \Delta H/\Delta H_\infty)$ with $\log_{10}$ time. The β parameter was calculated from the slope of the line and the relaxation time, τ, from the intercept. Values of ΔH_∞ were calculated from the product of ΔCp and ΔT, where ΔCp is the difference between the heat capacities of glass and liquid at the glass transition temperature (T_g). ΔT is the difference between T_g and the ageing temperature (T_a). This relationship derives from the assumption that the heat capacities of the glass and the extrapolated liquid lines are linear. The values of ΔCp for amorphous and 25% crystalline PEEK were 0.28 and 0.105 J g^{-1}, respectively [13].

3. Results and discussion

The technique of DSC was used to examine the effect of crystallization on the glass transition temperature of PEEK. Fig. 1 shows the trace of relative heat flow with temperature for amorphous and semi-crystalline PEEK measured at a heating rate of 20 K min^{-1}. For the amorphous material a glass transition is apparent at 418 ± 1 K which is followed by a marked crystallisation endotherm, both features being consistent with an amorphous sample. For the semi-crystalline material, the glass transition can still be observed but the temperature at which the process occurred increased to 425 ± 1 K. The absence of any crystallisation exotherm indicated that no further crystallisation had taken place.

Although there is a measured shift in the glass transition temperature using the method described by Richardson and Savill [14], closer inspection of the transition region shows that the onset of both processes occur at almost identical temperatures and that the transitions differ in the breadth

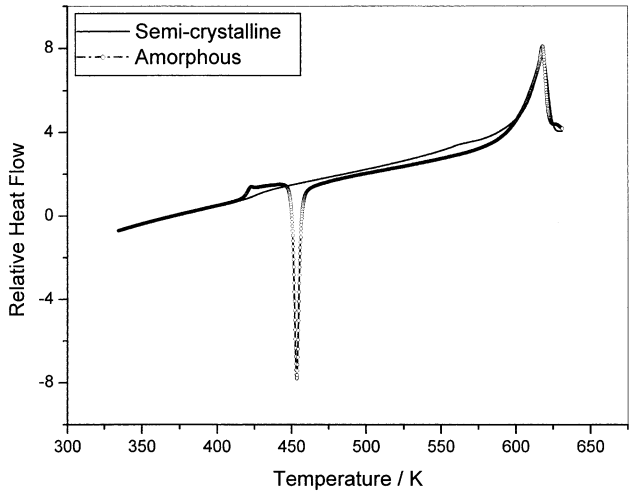

Fig. 1. Variation of relative heat capacity with temperature for amorphous and semi-crystalline PEEK.

and the size of the step change $\Delta Cp_{(T_g)}$. The latter is reduced whereas the breadth of the transition is increased. The increase in the breadth of the transition can be explained in terms of the constrainment of the amorphous material in close proximity to the crystallites. Constrainment reduces the segmental mobility of the chains and the result is a corresponding increase in the glass transition temperature. The reduction in $\Delta Cp_{(T_g)}$ on crystallisation is consistent with the two-phase model that is often used to describe a partially crystalline polymer, the model predicts a linear change in Cp with increasing degree of crystallinity. Again, it implies that regions of the amorphous material are constrained by the crystallites.

The technique of DSC was also used to measure the development of the endothermic ageing peak on the glass transition at a range of temperatures, the development of the endothermic peak for semi-crystalline PEEK with time for a supercooling of 3 K is shown in Fig. 2. It is clear that the

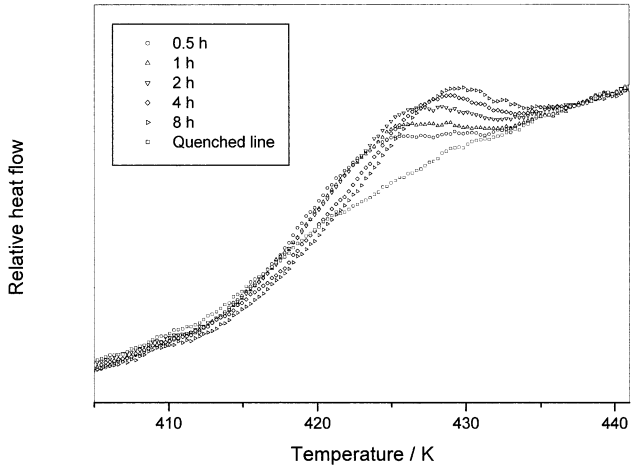

Fig. 2. Development of the endothermic peak on the glass transition at a supercooling of 3 K.

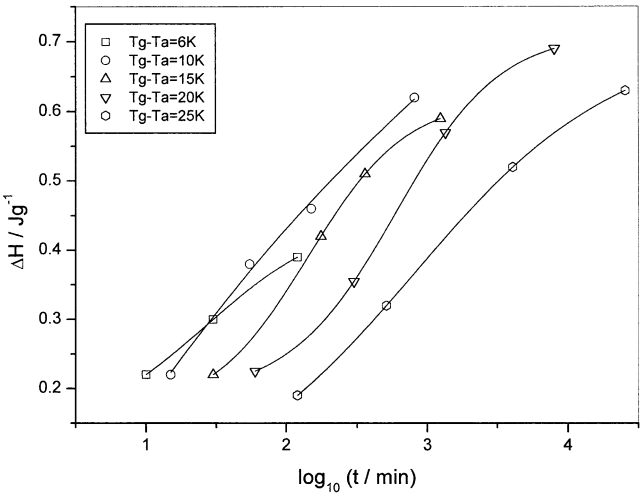

Fig. 3. Enthalpy relaxation in semi-crystalline PEEK.

extent of ageing increases with time, as is the case with amorphous polymers. Therefore it can be confirmed that semi-crystalline PEEK exhibits enthalpic relaxation. The enthalpy change (ΔH) on ageing was calculated from these traces using the procedure outlined in Section 2 and the variation of ΔH with $\log_{10}$ time for supercoolings of 6–25 K are shown in Fig. 3.

It can be seen that the rate at which enthalpic relaxation occurs decreases with increasing supercooling, but the variation in ΔH_∞ with supercooling is not apparent due to the relatively short ageing times used in this study. Longer ageing time would have revealed a maximum extent of ageing, ΔH_∞ the value of which increases with increasing supercooling. The data was initially curve fitted using a non-linear curve fitting routine but insufficient data resulted in either a poor fit or a significant error in the determination of ΔH_∞. Therefore the approximation that ΔH_∞ is equal to the product of ΔCp and ΔT was used in a double logarithm plot of $(1 - \Delta H/\Delta H_\infty)$ with $\log_{10}$ time, the kinetic parameters obtained are shown in Table 1. A number of authors has found that the approximation is not accurate [16–18]. However, the relationship is useful in situations where the datasets are too small to enable curve fitting, in these cases a double log plot will enable β and τ to be calculated from the data. The accuracy of the measured parameters will depend on the accuracy of the ΔCp, ΔT approximation. Comparison of the β values obtained from a double log plot and a curve

Table 1
Kinetic data for amorphous PEEK

ΔT (K)	β	ln τ (min)	$\Delta Cp\Delta T$
6	0.32	4.91	0.63
10	0.32	6.96	1.05
15	0.31	9.19	1.57
20	0.26	12.12	2.10
25	0.24	15.13	2.62
30	0.19	18.30	3.15

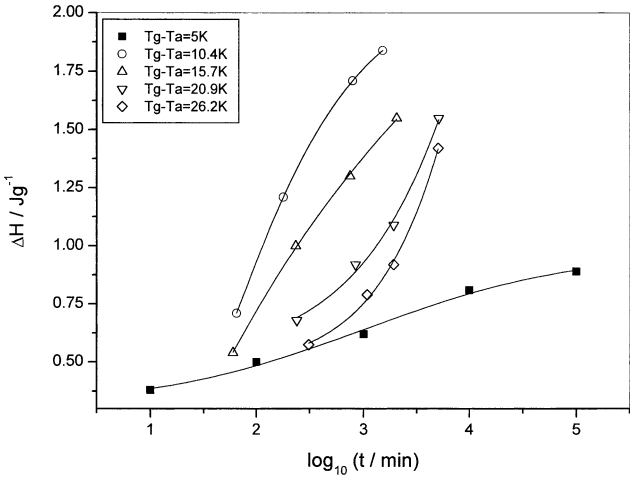

Fig. 4. Enthalpy relaxation in amorphous PEEK.

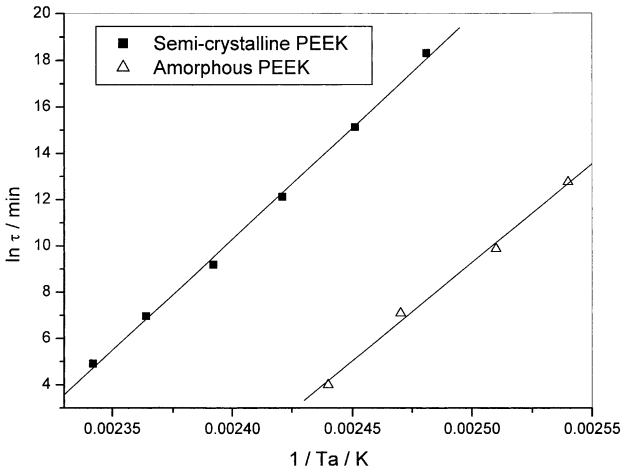

Fig. 5. Arrhenius plots for amorphous and semi-crystalline PEEK.

fit of enthalpic data measured at a ΔT of 5 K shows that the values are within 0.05 of each other, indicating a reasonably good agreement between the methods. Comparison over a wider temperature range was not possible due to poor curve fits.

Enthalpic relaxation data previously reported for amorphous PEEK [13] was re-analysed in terms of the Cowie–Ferguson model by using the double logarithm method described above. Like the data obtained for semi-crystalline PEEK, the use of curve fitting did not enable the calculation of the ageing parameters due to insufficient data at extended ageing times. The variation of the enthalpy change with $\log_{10}$ time for amorphous PEEK is shown in Fig. 4. The development of ageing is similar to that described for semi-crystalline PEEK, except the attainment of the maximum change in enthalpy is apparent for a supercooling of 5 K (Table 2).

Analysis of the data presented in Figs. 3 and 4 in terms of the Cowie–Ferguson model highlights a number of findings. Fig. 5 shows Arrhenius plots for both amorphous and semi-crystalline materials, the activation enthalpy of ageing for amorphous PEEK was found to be 708 ± 50 kJ mol^{-1} and that of 25% crystalline PEEK was found to be 800 ± 50 kJ mol^{-1}. The increase in activation enthalpy of ageing in semi-crystalline PEEK is consistent with the increase in glass transition temperature observed on crystallisation. The origin of both observations being the constrainment of amorphous material by the crystallites, results in a reduction in segmental mobility and a corresponding increase in activation enthalpy.

Table 2
Kinetic data for semi-crystalline PEEK

ΔT (K)	β	ln τ (min)	ΔCpΔT
5	0.42	4	1.40
10.4	0.39	7.1	2.91
15.7	0.33	9.88	4.39
20.9	0.29	12.77	5.85

Fig. 6 shows the variation in the measured β parameter with supercooling for both amorphous and semi-crystalline PEEK. It can be seen that the β value for the amorphous material decreases with increasing supercooling and that the values for the semi-crystalline material follow a similar trend except the values are reduced. The significance of the β value lies in the shape of the relaxation spectrum, a β value that tends towards unity indicates a narrow distribution of relaxation times whereas a β value that tends towards zero indicates a broad distribution of relaxation times. The molecular level significance of the β value is in the co-operativity of the relaxation processes [19]. Co-operative relaxation processes that are highly dependent on the relaxations of surrounding segments are associated with low β values and non-co-operative processes that relax independently are associated with relatively high β values. Therefore, it can be inferred that the formation of crystallites in PEEK results in a change in the co-operativity of the

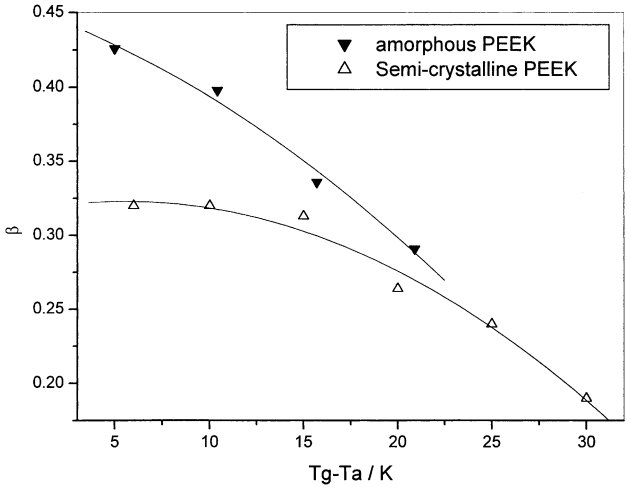

Fig. 6. Variation of β with PEEK morphology and temperature.

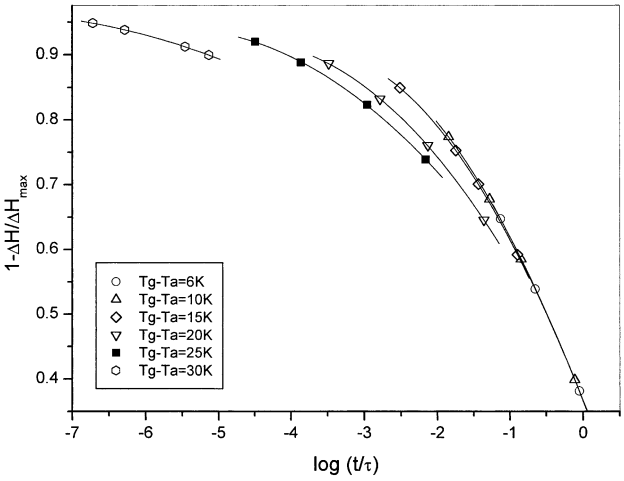

Fig. 7. Reduced variable for semi-crystalline PEEK.

relaxation processes. The constrainment effect of the crystallites increases the co-operativity of the relaxation processes in semi-crystalline PEEK. It can also be seen that the β values begin to converge at increasing supercoolings indicating a dominance of co-operative relaxations at these temperatures. Fig. 6 also shows the variation of the β value with temperature.

Even if a 5% error is inherent in the data, the variation is still significant. Fig. 7 shows a reduced variable plot of the enthalpic relaxation data obtained for semi-crystalline PEEK, a single model curve for a fixed β cannot be ascribed to the curves implying that the β parameter does vary with temperature. The variation in the breadth of the relaxation spectrum with temperature has been reported elsewhere [20–22] and has also been found to decrease with increasing supercooling [23]. The physical significance of this finding is that there is an increased tendency for the relaxations to become co-operative at increased supercoolings. The variation of the β value with temperature does not support the multiparameter phenomenological model assumption of thermorheological simplicity and also demonstrates the value of the Cowie–Ferguson approach.

4. Conclusions

The formation of crystallites in PEEK resulted in an increase in the glass transition temperature as defined by Richardson and Savill [14], but closer inspection of the process showed that the onset of the transition was almost identical to that of amorphous PEEK. The breadths of the transitions were different, the semi-crystalline process extending to higher temperatures. Semi-crystalline PEEK was also found to exhibit enthalpic relaxation, the activation enthalpy of which was found to be approximately 100 kJ mol^{-1} higher than that of amorphous PEEK. These observations are consistent with the constrainment of amorphous material by the crystallites. The presence of crystallites was also found to influence the co-operativity of the relaxation processes, the measured β values being reduced in the semi-crystalline material. A decrease in the β value with increasing supercooling was also found which indicates that the PEEK system is not thermorheologically simple.

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