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STUDIES OF THE ENTHALPY RELAXATION AND THE "MULTIPLE MELTING" BEHAVIOR OF SEMICRYSTALLINE POLY(ARYLENE ETHER ETHER KETONE) (PEEK)

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Abstract

We report the results of an investigation by differential scanning calorimetry (DSC) of two mobility controlled processes in the amorphous phase of semicrystalline PEEK – enthalpy relaxation below the glass transition (T_g) and secondary crystallization above T_g. Both result in the observation of an endothermic peak just above the annealing temperature in the DSC scan of the polymer – the enthalpy recovery peak and the low temperature melting peak, respectively. There is a striking similarity in the time and temperature dependence of the endothermic peak for these two processes. These results are reminiscent of those obtained from small strain creep studies of "physical aging" of semicrystalline PEEK below and above T_g.

Keywords: enthalpy relaxation, melting, PEEK, physical aging, secondary crystallization

Introduction

Enthalpy relaxation – the spontaneous relaxation of the excess enthalpy upon isothermal annealing below T_g, is one of the phenomena, associated with physical aging and can be studied by DSC through the observation of the enthalpy recovery peak upon heating above the annealing temperature T_a. Although studies of this phenomenon have been carried out on amorphous polymers [1], in recent years some investigations of semicrystalline polymers such as PET [2, 3], PEN [3], PEEK [4], have appeared as well. The physical aging phenomenon has also been studied through transient and dynamic mechanical measurements [5].

In recent years, a controversy has been sparked by reports that the characteristics of "physical aging" have been observed in certain semicrystalline polymers above their nominal glass transition. A model proposed by Struik [5] uses the concept of an "extended glass transition" in semicrystalline polymers. Due to the constraining effects of the crystalline lamellae on neighboring amorphous chains, the mobility of these chains is greatly reduced and their glass transition would be extended to higher temperatures, enabling them to physically age above the nominal (calorimetric) T_g of the unconstrained amorphous fraction.

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This idea has sparked our interest due to its possible relation to 1) the mobility controlled process of secondary crystallization and 2) the melting of secondary lamellae [8, 10, 12].

Experimental

The material is commercial PEEK 450G, with molecular weight M_w=38000 g mol^{-1}, obtained in the form of amorphous sheets from Atlantic Plastics, Roanoke, VA, USA. Samples were annealed for 35 min at 573 K in a convection oven under nitrogen. This initial treatment, common for all samples, produces a semicrystalline material with crystallinity by DSC of 37%. The samples were subsequently annealed in the oven for various times in a wide temperature range, encompassing the glass transition: 373, 393, 403, 413, 433, 453, 473 K, and then quenched to room temperature.

DSC scans of these samples were collected with a Perkin Elmer DSC-2C at a heating rate of 20 K min^{-1}. The heat flow output was corrected by baseline subtraction and calibrated with a sapphire standard. The enthalpy recovery peaks and the low temperature melting peaks were resolved from the total heat flow by subtraction of the DSC scan of a sample, subjected only to the initial crystallization at 573 K, common for all annealed samples. T_{max} and ΔH_a denote respectively the temperature of the peak maximum and the transition enthalpy of both types of endothermic peaks observed – the enthalpy recovery peak below T_g and the low temperature melting peak above T_g (T_g = 428 K by DSC at a heating rate of 20 K min^{-1}). Distinction between the two different peaks can be made by observing the labels for the annealing temperature T_a.

Results and discussion

Figure 1 shows the DSC scans of samples, annealed at 373 K – approximately 50 K below T_g, and at 413 K – at the lower end of the glass transition range. Although the initial state of the samples at T_a=373 K is far removed from equilibrium, the decrease in the excess enthalpy, measured by ΔH_a, is very small due to the very long relaxation times, expected at this temperature. At T_a=413 K the peak is markedly stronger, well resolved and appears superposed on the glass transition. The larger enthalpies can be attributed to the acceleration of the aging process as relaxation times decrease with increase in T_a.

Figure 2 shows the DSC scans of the samples, annealed at 433 K – at the upper end of the glass transition, and at 473 K – well above T_g. At these two temperatures, according to the standard two-phase model of semicrystalline polymers, the amorphous fraction, although somewhat constrained by the crystalline lamellae, is liquid-like and should be in equilibrium. Therefore, no enthalpy relaxation and subsequent recovery should be observed.

The scans for T_a=433 K show the appearance of an endothermic peak just above the annealing temperature. With increase in annealing time the peak increases in magnitude and shifts up in temperature. At the higher annealing temperature above

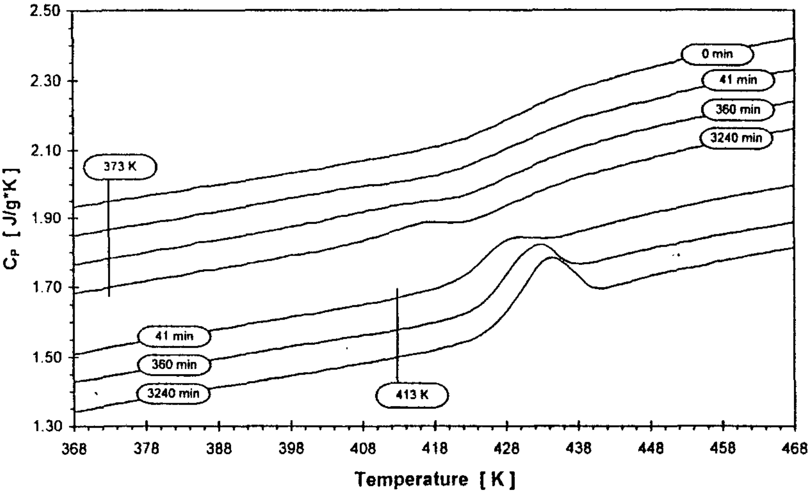

Fig. 1 DSC scans of semicrystalline PEEK, annealed at 373 and 413 K. Vertical lines indicate the annealing temperatures for the corresponding groups of scans. "0 min" is the scan of the initial semicrystalline material

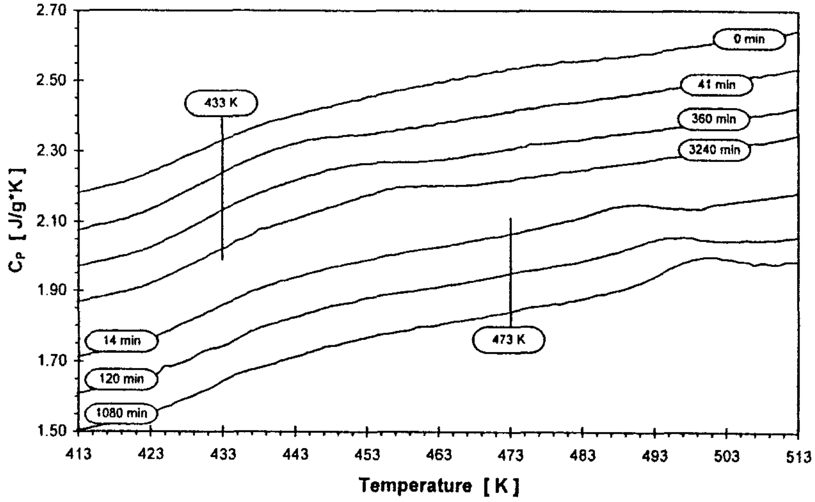

Fig. 2 DSC scans of semicrystalline PEEK, annealed at 433 and 473 K. Vertical lines indicate the annealing temperatures for the corresponding groups of scans. "0 min" is the scan of the initial semicrystalline material

T_g – 473 K, the peak evolution has the same characteristics, but appears stronger and more clearly resolved.

In PEEK [6–8], as well as many other semicrystalline polymers [9], annealing at a temperature between T_g and T_m, results in the observation of a low temperature endothermic peak just above the annealing temperature and below the main melting peak. Calorimetric [6, 8] and morphological [8] studies of the "double melting" of PEEK suggest that the origin of this peak is the melting of a population of crystalline lamellae with low thermal stability (lower than the stability of the primary lamellae, which melt at higher temperatures). Their development has been associated with the process of secondary crystallization in PEEK [8, 10].

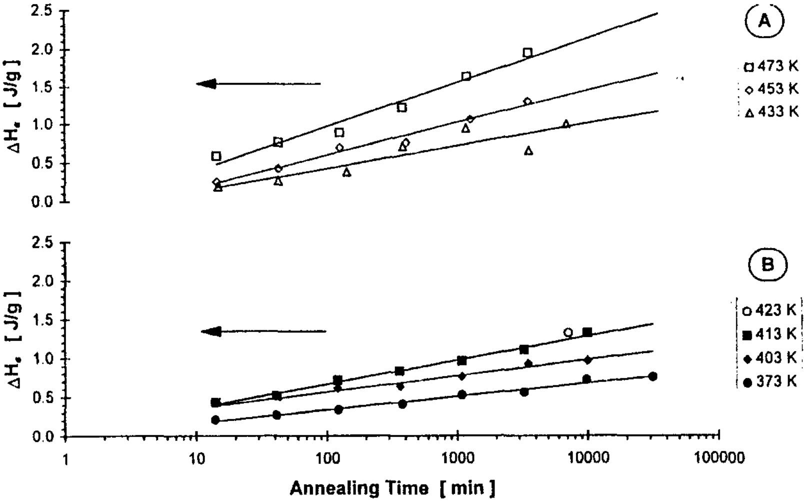

Fig. 3 Development of the transition enthalpy ΔH_a with annealing time: A) low temperature melting peak data; B) enthalpy recovery peak data

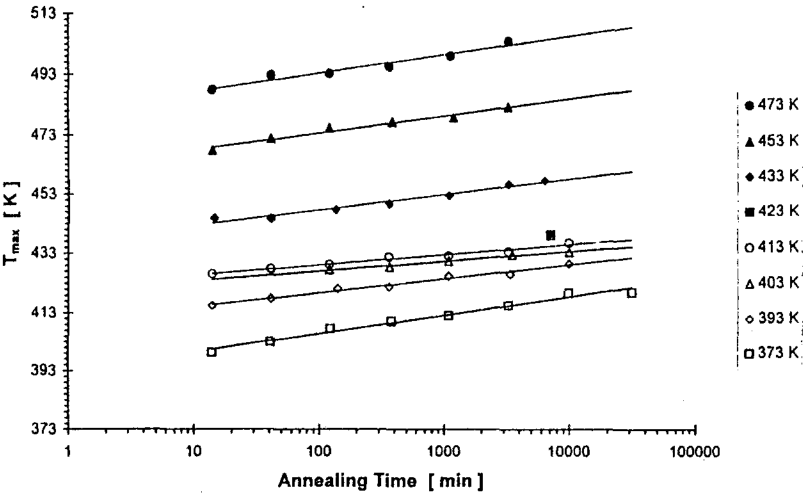

Fig. 4 Annealing time dependence of the peak maximum T_{max} for different annealing temperatures

Recently we have shown [7] that the "double melting" phenomenon in PEEK exhibits similar characteristics to the enthalpy recovery process below T_g [1]: the peak maximum temperature T_{max}(low) and the associated transition enthalpy, ΔH_m(low) increase linearly with $\log(t_a)$, and T_{max}(low) and ΔH_m(low) increase with increase in T_a.

In this study, the scans on Figs 1 and 2 are direct evidence of the similarity between the endothermic peaks which appear as a result of annealing below and above T_g, respectively. This opens at least two important questions about the observations displayed in Figs 1 and 2. First, are there more common characteristics for the enthalpy relaxation below T_g and the secondary crystallization above T_g, other than the apparent similarity in their endothermic peak? Second, what is the origin of the similarity between the enthalpy recovery and the low temperature melting peaks?

To answer the first question, we examine the annealing time dependence of ΔH_a and T_{max}. The plot of ΔH_a *vs.* $\log(t_a)$ for the enthalpy recovery peaks ($T_a < T_g$) is shown on Fig. 3B and for the low temperature melting peaks ($T_a > T_g$) – on Fig. 3A. On both plots an approximately linear increase of ΔH_a with $\log(t_a)$ is observed at any given T_a. For a fixed $\log(t_a)$ value, ΔH_a increases with increase in T_a for the low temperature melting peak (Fig. 3A), as well as for the enthalpy recovery peak (Fig. 3B). Note that the latter is somewhat unexpected. For annealing temperatures very close to T_g (as is the case with T_a=413 K and the single point for T_a=423 K), ΔH_a must decrease with increase in T_a [1] due to the decrease in the excess frozen enthalpy, which is the limiting value of ΔH_a.

Figure 4 shows the evolution of T_{max} with annealing time. Within this time range, T_{max} increases linearly with $\log(t_a)$ for all annealing temperatures. The change in the trend in the middle of the plot indicates the glass transition region, which separates the enthalpy recovery data (lower part of the plot) from the low temperature melting data (upper part of the plot).

The next step in examining the similarity between the enthalpy recovery and the low temperature endotherm is to analyze the trends shown in Figs 3 and 4. For this purpose, we fit the data with linear functions of $\log(t_a)$:

$$\Delta H_a = a + b\log(t_a) \tag{1}$$

$$\Delta T_{max} = T_{max} - T_a = A + B\log(t_a) \tag{2}$$

Below T_g the parameter A in Eq. (2) is the difference between peak and annealing temperatures, for a reference aging time of 1 min. The choice of a fixed reference time of 1 min for all aging temperatures is somewhat ambiguous as it does not reflect the change in the relaxation times with change in T_a. However, while keeping in mind this ambiguity, we can still relate A to the initial mobility of the amorphous chains at T_a. Above T_g A reflects the relative thermal stability of the secondary lamellae, extrapolated to short annealing times i.e. to the early stages of the secondary crystallization at T_a. We would speculate, that this thermal stability might be also determined by kinetic factors such as the mobility of the amorphous chains above T_g, reduced by the presence of crystalline lamellae [9].

The quantity b in Eq. (1) is physically interpreted as: 1) the rate of increase of secondary crystallinity as represented by the melting enthalpy of the secondary lamellae (for $T_a > T_g$), and 2) the rate of enthalpy relaxation (for $T_a < T_g$). In essence, both processes describe a slow approach to equilibrium. Therefore, regardless of the particular physical nature of the process, b is a measure of the rate of approach to equilibrium.

The annealing temperature dependence of the parameters b and A is plotted on Fig. 5. Below T_g the value of A decreases with increase in T_a. This is in line with the well known behavior of the enthalpic recovery peak in amorphous polymeric glasses – as T_a approaches T_g, the peak appears closer to T_a until enthalpy relaxation ceases at T_g [1]. In the glass transition region the value of A shows a significant drop. At the upper end of the glass transition region, A rises sharply again. Far above T_g it decreases with increase in T_a, which is similar to the trend found in PEEK, crystallized or annealed under various other thermal histories above T_g [9]. If the two points in the glass transition region are excluded (T_a=413 and 433 K), the rest of the data for A follows the same linear trend with T_a, regardless of the fact, that they characterize two different processes below and above T_g.

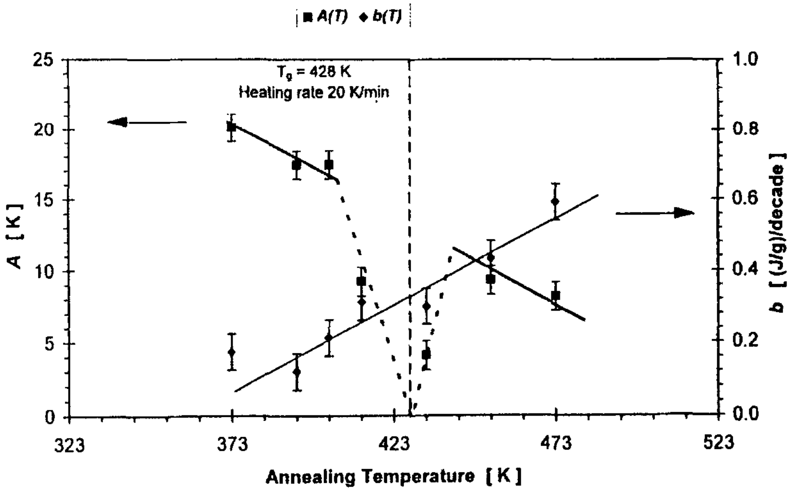

Fig. 5 Annealing temperature dependence of the parameters of the linear development of T_{max} and ΔH_a with $\log(t_a)$: $A(T)$ –Eq. (2), $b(T)$ – Eq. (1)

Even more peculiar is the fact, that the parameter b (Eq. (1)) shows a trend of continuous increase throughout the entire temperature interval studied, including the glass transition range.

Despite these striking similarities in the evolution of the endothermic peak in the heat capacity, resulting from annealing below and above T_g, one could be tempted to judge them as purely accidental.

Indeed, such a conclusion had been drawn in the case of partially crystalline PVC [11]. Two independent studies observed, that the enthalpy recovery peak, resulting from annealing below T_g, is very similar to the melting peak just above T_a, resulting from annealing above T_g. Both studies claimed that such a similarity in the evolution of these two processes is accidental.

We speculate that such a conclusion might have been rather hasty. At least in the case of PEEK, additional data exists, which clearly indicates a similarity between the structural relaxation below T_g and the slow approach to equilibrium above T_g. In a previously study by small strain creep recovery [9, 12], we have observed "physical aging" liker behavior of semicrystalline PEEK below as well as above the nominal (calorimetric) glass transition. Following the method of Struik [5], the transient creep compliance curves $J(t)$ for different annealing times t_a were reduced to master curves by a combination of horizontal and vertical shifts. The susceptibility of the material to "physical aging" is characterized by a horizontal shift rate, $\mu(T_a)$ and a vertical shift rate, $\beta(T_a)$.

These two functions [9, 12] are plotted against T_a on Fig. 6. The dependence of μ on T_a, typical of semicrystalline polymers [5], is very similar to the dependence of A on T_a from Fig. 5. In the case of the enthalpy relaxation process below T_g, both parameters are related to the temperature dependence of relaxation times. The vertical shift rate β shows the same type of annealing temperature dependence as the rate of approach to equilibrium – the parameter b on Fig. 5. In the case of the secondary crystallization process above T_g, both b and β characterize the secondary crystallization rate.

In summary, the kinetics describing "physical aging" of PEEK below and above T_g, as observed by creep recovery studies, is similar to the kinetics of enthalpy relaxation and secondary crystallization of semicrystalline PEEK, as observed by DSC.

$$\mu = \frac{\partial \log(a_t)}{\partial \log(t_a)} = \frac{\partial \log[\tau(t_a)]}{\partial \log(t_a)} \qquad \beta = -\frac{1}{J_e(t_{ar})}\frac{\partial J_e(t_a)}{\partial \log(t_a)}$$

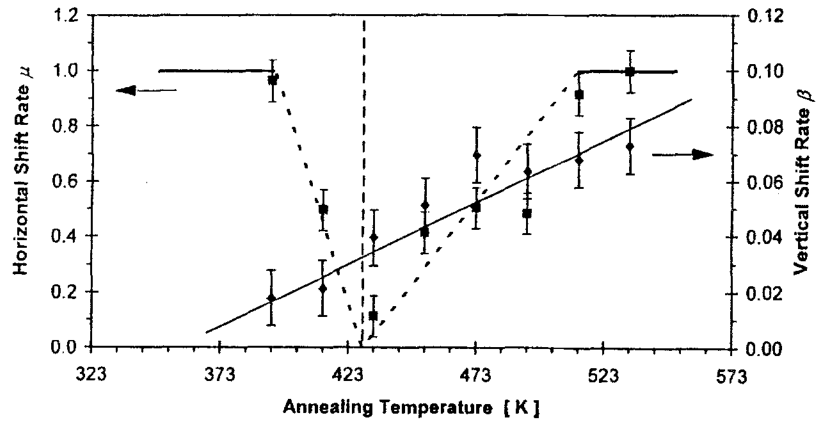

Fig. 6 Temperature dependence of the horizontal and vertical shift rates during annealing of semicrystalline PEEK below and above T_g by momentary short strain creep compliance measurements [9,12]

We would like to point out that although the two processes described above exhibit similar kinetic signatures, annealing above T_g should not be viewed as a genuine process of physical aging. We believe the shift in the momentary creep curves to longer creep time with increase in annealing time is a direct consequence of the secondary crystallization process. Amorphous chains in the vicinity of, or between crystalline lamellae are more contrained than these located further away from lamellae. In analogy with crosslinking, we view the secondary crystallization process as one that leads to an increase in the fraction of "more constrained" amorphous chains (the crystalline lamellae playing the role of crosslink sites). An increase in the fraction of constrained amorphous chains would be similar to an increase in the degree of crosslinking and result in the shift of the relaxation spectrum to longer times. This concept differs from that proposed by Struik but is supported by a number of observations: 1) the horizontal shift rate, μ, decreases for temperatures approaching T_g and increases again as secondary crystallization is allowed (always slightly above T_g), 2) the increase in the vertical shift factor, β, during annealing above T_g follows qualitatively the increase in crystallinity measured by calorimetry [9], and 3) the glass transition temperature increases linearly with the logarithm of annealing time in isothermal conditions above T_g [9, 10]. In the context of this new interpretation of the effect of annealing above T_g, the concept of a rigid amorphous fraction takes a different meaning. The fact that the magnitude of the heat capacity change at T_g is less than that expected on the basis of the two phase model, is not explained by the existence of a rigid amorphous phase having a higher glass transition temperature, T_g^{μ}, but by the fact that the heat capacity of the amorphous fraction is a function of the constraints exerted by the crystals (in the same fashion as one should expect a decrease in the heat capacity of the liquid phase of an amorphous material with increasing the degree of cosslinking).

The correlation of the results from two independent methods – DSC and small strain creep recovery, leads to the conclusion that the similarity between the effects of structural relaxation below T_g and secondary crystallization above T_g is probably not accidental. Independent studies of the two processes have established already the fact, that both are mobility controlled phenomena. The polymeric glass with frozen excess enthalpy below T_g and the partially crystalline polymer with crystallinity less than unity above T_g, are away from their respective equilibrium states. Therefore, both processes are also a manifestation of the slow approach to equilibrium. The correlation between the two phenomena could lie in the nature of the molecular motions required en route to the final equilibrium state.

A full answer to the second question posed above would need a more extensive experimental and theoretical investigation of the kinetics and molecular nature of structural relaxation below T_g and secondary crystallization above T_g in semicrystalline polymers. Further studies of the effect of initial crystallinity on the magnitude of these phenomena will be very helpful in clarifying the nature of their apparent similarity.

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