

Frictional Surface Temperature Determination of High-Temperature-Resistant Semicrystalline Polymers by Using Their Double Melting Features

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ABSTRACT: Most semicrystalline polymers exhibit multiple melting peaks in the course of normal differential scanning calorimetry (DSC) measurements. When their amorphous versions are annealed above the glass transition temperatures, the lower endothermic temperatures (T_{m1}) appearing on the subsequent DSC heating traces are highly dependent on the annealing temperature (T_a). In consideration of the fact that temperature is the critical environmental factor controlling polymer crystallization, thermal history experienced by the material during annealing in the DSC cell is basically equivalent to that under frictional heating, and the surface temperature prevailing under sliding wear can be estimated from DSC scans taken on the worn surface. In this case, the lower melting peak temperature observed (which can be correlated with the annealing temperature) serves as an indicator for the flash temperature. In addition, this thermoanalytical method can also provide information about microstructural changes due to wearing. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 589–593, 1997

Key words: PEEK; sliding; surface temperature; multiple melting behavior; semicrystalline thermoplastics; annealing; friction

INTRODUCTION

It is well known that mechanical energy dissipated during sliding wear is mostly converted into heat, which results in a temperature rise in the region of rubbing. The contact interfacial temperature (often referred to as flash temperature) can be so high that mechanophysical and mechanochemical changes in the sliding materials are induced. Due to the fact that material's tribological performance is highly dependent on temperature,

a lot of works have targeted the calculation and measurement of the surface temperature.^{1,2} With respect to the technical viability, there are some methods available which make use of the microstructural changes caused by frictional heating. Metallographic techniques, for example, can quantify surface temperature of metals by comparing relative changes in microhardness or structural appearance. Such post-mortem characterization of the frictional surface provides more information about the wear processes than indirect techniques, such as temperature assessment by thermocouples or radiation detection.

Actually, the surface temperature of a semicrystalline thermoplastic polymer can also be estimated according to a similar concept^{3,4} if microstructural changes due to friction, rubbing, etc., can be revealed. For that purpose, the thermal response of a worn sample with that of an unworn

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sample (which before experienced precisely known heat treatment) should be compared. The current work was addressed to explore the viability of this approach for high-temperature-resistant semicrystalline polymers that underwent secondary crystallization during heat treatment.

As reported in many papers, examination of thermal behavior by means of differential scanning calorimetry (DSC) is an effective way to reveal the fundamental structure and properties relationship of semicrystalline polymers. One of the important phenomena observed in DSC traces is relying on the multiple melting behavior of polyetheretherketone (PEEK),⁵ polyphenylene sulfide (PPS),⁶ polyethylene terephthalate (PET),⁷ polyimide (PI),⁸ etc. These semicrystalline polymers, which have been crystallized either from the melt or from the rubbery amorphous state, typically display dual or multiple melting peaks. Although the interpretation of multiple melting phenomena is still very controversial, one similarity exists for polymers in general⁹: the thermal history always exerts substantial influence on the multiple melting characteristics. For instance, when amorphous PEEK is annealed at a temperature T_a between its glass transition temperature T_g and melting point T_m and then cooled, a small lower endotherm generally appears at 10 ~ 20 degrees above T_a in the reheating DSC trace besides the broad endothermic peak with a maximum in the range 330 ~ 340°C. The lower endothermic peak (T_{m1}) can be obviously related to the frictional surface temperature. During sliding wear, for example, frictional heat flows into the contacting solids, resulting in a locally high temperature at the area of contact. In the case of a steady wear condition, the sliding bodies should be regarded as being "annealed" under a certain relatively stable temperature. Therefore, the above dependence of the low temperature endothermic peak position on annealing temperature could serve as a working principle for estimation of the flash temperature.

EXPERIMENTAL

An amorphous PEEK plate kindly supplied by the Jilin University, China, was employed as the experimental material. The wide-angle X-ray scattering (WAXS) patterns of both amorphous and crystalline PEEK obtained by a Rigaku D/max III A diffractometer with Cu K_α radiation are shown

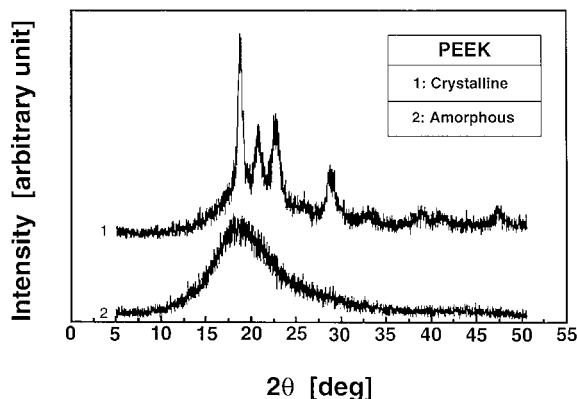


Figure 1 X-ray diffraction curves of PEEK.

in Figure 1. By means of a pin-on-disk apparatus, sliding wear tests of the stationary PEEK pins against a moving steel counterpart were carried out at a constant velocity of 0.4 m s⁻¹. The apparent contact area of the specimens was 50 mm². After the apparatus operated for 1 h under steady-state conditions, the testing was stopped in order to cut the surface layer out of the worn pins with a sharp razor blade for subsequent thermal analyses.

A Perkin-Elmer DSC-2C differential scanning calorimeter with an air flow rate of 10 cm³ min⁻¹ was used for all the thermal experiments. The worn surface layer was heated from the room temperature to 400°C at 20°C min⁻¹, giving a DSC trace. For the purpose of comparison, the unworn PEEK was rapidly heated to a desired annealing temperature T_a in the DSC cell and held there for 1 h. Then the sample was cooled down to the room temperature and heated again to 400°C at 20°C min⁻¹. This last heating scan served as a reference. It was found that the melting peak temperatures were nearly independent of annealing time in the range 15 min to 2 h.

RESULTS AND DISCUSSION

PEEK heated from the glass always exhibited a sharp cold-crystallization peak near 180°C and a melting peak at 340°C (Fig. 2). However, when the samples that had been annealed at T_a were heated up, there were two melting peaks on the DSC traces (Fig. 2). With respect to the origin of the multiple melting behavior of semicrystalline polymers, several models have been proposed. Some attributed it to the existence of different crystallites or crystalline morphologies, and oth-

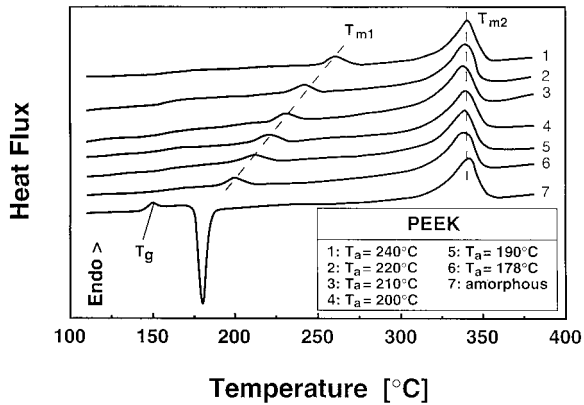


Figure 2 DSC traces of PEEK annealed at different temperatures.

ers suggested it result from reorganization. Although on the DSC traces in Fig. 2, the lower and higher temperature melting peaks are well resolved, the authors of the present paper believe that the reorganization model (i.e., melting of the less perfect crystals caused by annealing followed by their recrystallization and remelting) proposed by Lee and Porter¹⁰ is correct.

It can be seen from the curves in Figure 2 that the lower melting peak temperature T_{m1} increased with a rise in T_a , while the peak temperature of the upper melting endotherm, T_{m2} , remained constant and independent of T_a . In order to better illustrate these tendencies, both T_{m1} and T_{m2} were plotted against T_a in Figure 3. Evidently, a relatively good linear relationship existed between T_{m1} and T_a , which can be described by

$$T_{m1} = 23.97 + 0.98T_a \quad (1)$$

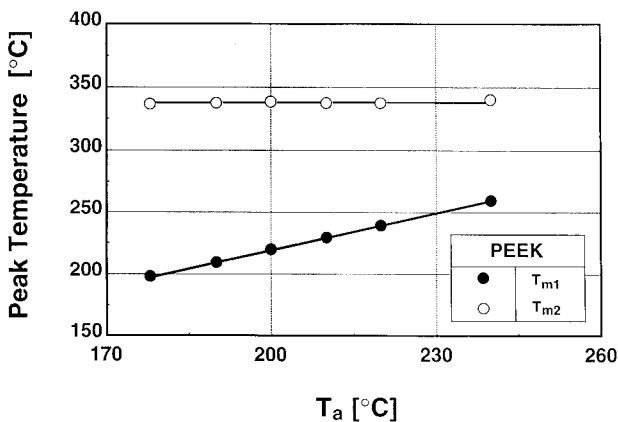


Figure 3 Melting peak temperatures (T_{m1} , T_{m2}) plotted against annealing temperature (T_a).

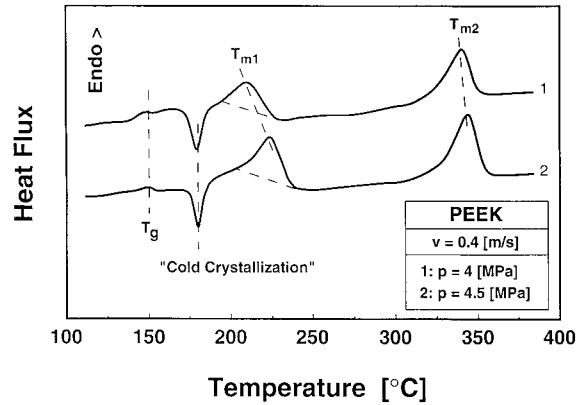


Figure 4 DSC traces of worn PEEK.

Equation (1) implies that T_a could also be estimated for a given T_{m1} . Because temperature is the critical environmental factor controlling polymer crystallization, the thermal history experienced by the polymer annealed in the DSC cell is equivalent to that experienced by the same material during frictional heating. As a result, T_a should be identical with the frictional surface temperature. Therefore, the frictional surface temperature can be quantified by considering the lower endothermic temperature in the DSC scan of the worn sample.

Figure 4 shows the thermal behavior of worn PEEK tested under different loading. The lower melting endotherms were found within $210 \sim 230^\circ\text{C}$. According to the above discussion and eq. (1), it can be easily deduced that the surface temperature (i.e., T_a) witnessed by the worn pins during sliding were 191.9°C (for 4 MPa) and 203.3°C (for 4.5 MPa), respectively. In consideration of the fact that multiple melting behavior during normal DSC scanning is found in most semicrystalline polymers, subjected to steady friction, the surface temperature of these materials can also be determined in the same way, i.e., by using T_{m1} as a temperature indicator, provided that the calibration function between T_{m1} and T_a is known.

The melting parameters of the endotherms indicated in Figures 2 and 4 were summarized in Table I. Heats of fusion of the lower melting peaks ΔH_{m1} calculated from the DSC curves of the worn pins' surface were found significantly higher than those from the endothermic response of the samples annealed in the DSC. However, heats of fusion of the upper melting peaks ΔH_{m2} of the worn samples were slightly lower than those of the annealed version. One possible explanation for this

Table I Melting Properties of PEEK Samples

	T_a (°C) (Samples Annealed in the DSC-Cell)						Load (MPa) (Worn Samples ^a)	
	178	190	200	210	220	240	4.0	4.5
T_{m1} (°C) ^b	198.6	209.9	220.0	230.0	239.6	259.2	212.1	223.2
T_{m2} (°C)	336.8	337.5	338.4	338.0	337.9	340.3	339.5	341.7
ΔH_{m1} (J g ⁻¹)	1.98	2.78	2.33	3.12	2.83	2.48	23.8	29.1
ΔH_{m2} (J g ⁻¹)	39.0	39.6	40.1	39.6	40.1	40.6	35.0	36.5

^a Sliding velocity = 0.4 m s⁻¹.

^b T_{m1} and T_{m2} denote the melting peak temperatures of the lower and upper endotherms at the DSC curves. ΔH_{m1} and ΔH_{m2} stand for the corresponding heats of fusion.

may be a change (degradation, cross-linking, etc.) in PEEK molecular structure due to tribological circumstances that also affects its crystallization. One can suppose that a larger amount of imperfect crystals that could not entirely reorganize to the higher melting forms during the subsequent DSC heating.^{3,4} Further investigations are needed to have a deeper understanding of the subject and its relation to the wear mechanism.

Another meaningful phenomenon of the two DSC curves in Figure 4 is the cold-crystallization exotherms at 180°C. It means that the material sampled from the worn PEEK pins contained an amorphous portion, which should be comprised of (1) the contactless parts on the sliding surfaces, and (2) the subsurfaces. This again demonstrated the general consideration of the contact temperature; i.e., the highest contact temperature occurred only at localized contact points between the asperities. Temperatures in the valleys and in the regions of the bulk material away from the contact points were much lower.

On the other hand, in order to overcome the difficulties of surface temperature measurement, some analytical methods have been developed and used as tools for investigators and engineers. A simple way is the application of Jaeger's work.¹¹ In the case of low speeds of sliding, the flash temperature T_f (in °C) is given by

$$T_f = \frac{0.236\mu f v}{l(k_1 + k_2)} \quad (2)$$

where μ is the frictional coefficient, f is the applied force (in N), v is the sliding velocity (in m s⁻¹), k_1 and k_2 are the thermal conductivities (in J m⁻¹ s⁻¹ °C⁻¹) of the two sliding bodies, and l is the length (in m) of the side of the contact area. Inserting the values for the current system, μ

= 0.4, $v = 0.4$ m s⁻¹, $l = 10^{-2}$ m, $k_1 = 46.7$ J m⁻¹ s⁻¹ °C⁻¹ (for steel), $k_2 = 0.25$ J m⁻¹ s⁻¹ °C⁻¹ (for PEEK), and $f = 200$ N (for 4 MPa), or $f = 225$ N (for 4.5 MPa), eq. (2) yielded the flash temperatures. Thus, the contact temperatures can be obtained by adding T_f to the bulk temperature (that was taken as the room temperature, 25°C). As shown in Table II, it is hard to find correlation between the measured surface temperatures and the calculated values. The tremendous differences suggested that great care must be taken when using the computational methods, which sometimes would not yield reliable values.

CONCLUSION

By using a thermo-analytical technique, the surface temperature of a semicrystalline polymer resulting from frictional heating was determined. In addition, some information about variations in polymeric microstructures can also be obtained. This is of particular importance for a systematic investigation of thermoplastics used in tribological applications, especially in high-temperature-resistant self-lubricat-

Table II Results of Surface Temperature Calculation and Estimation

Load (MPa) ^a	Calculated Contact Temperature Using Eq. (2) (°C)	Estimated Surface Temperature Using Eq. (1) and the Data of Table I (°C)
4.0	41.1	191.9
4.5	45.1	203.3

^a Sliding velocity = 0.4 m s⁻¹.

ing bearings. Although the method proposed in the paper is subject to some limitations, e.g., (1) only the measurement of those semicrystalline polymers presenting multiple melting behavior is allowed, and (2) the effective measurement range of surface temperature is limited (between T_g and T_m), it can successfully serve as a practical monitoring and scientific research tool.

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