APPLICATION**NOTE**

Plastics –Temperature-Modulated DSC

Investigation of the Glass Transition-Crystallization-Melting Behaviors of PEEK Films Using the TM-DSC Method

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Introduction

PEEK is an engineering plastics material characterized as an aromatic thermoplastic; its main chain contains a repeating unit consisting of a ketone bond and two ether bonds. It has high mechanical strength, is flame retardant, and has good electrical properties as well as good resistance to heat, impact, acid and alkali, hydrolysis, abrasion, fatigue, irradiation, etc. It can be used as a high-temperature-resistant structural material and electrical insulating material, but also as a composite-reinforcing material when combined with glass fiber or carbon fiber, offering wide applications in the aerospace, medical device (as artificial bone to repair bone defects) and other industrial fields.

PEEK shows the typical behavior of semi-crystalline polymer materials; its crystallinity and crystalline morphology are greatly influenced by the thermal history during processing, which then affects its properties, such as mechanical or optical properties. Therefore, studying the crystallization and melting process of PEEK is of great practical significance.

Temperature-Modulated DSC (TM-DSC)

TM-DSC is an expansion of the traditional differential scanning calorimetry (DSC) technique. This technique superimposes a sinusoidal temperature wave on the linear temperature ramp, which yields a corresponding oscillating heat-flow curve of the sample. This oscillating heat-flow curve is then separated into two extra curves: the reversing and non-reversing heat-flow curves. Thermal effects related to the change in a material's heat capacity are on the reversing curve; these typically include the glass transition, the Curie transition, second-order phase transitions, and the change in heat capacity before and after reactions. Kinetic effects will be on the non-reversing curve, the reaction rate of which depends on the temperature and conversion rate, but not on the heating rate; e.g., cold crystallization, cross-crystallization, curing effects, etc. For polymers, TM-DSC is usually used to separate the glass transition with superimposed thermal effects such as enthalpy relaxation, cross-linking curing, and solvent volatilization; a more accurate glass transition temperature can then be obtained.

Applying TM-DSC in melt and crystallization is complex and controversial. It's proven that the melting effect cannot be separated as either reversible or nonreversible effects alone, and the separation result varies with test parameters; this is because melting is not a pure heat capacity effect or kinetic effect. However, some related publications have proven that TM-DSC is still useful in this research field; e.g., on the non-reversing curve, one can often observe an extra exothermal peak, which is frequently attributed to the recrystallization of a secondary crystalline phase. Those secondary crystals melt at lower temperatures; then, the free polymer chains attach to the surface of primary crystal grains where they recrystallize and release heat.

Note

Secondary crystal: usually with small grains, relatively imperfect lattice structure, somewhat disorderly molecular chain arrangement, and relatively lower melting temperature

Primary crystal: usually with thicker plates, more complete crystal structure, well-arranged molecular chains, and higher melting temperature

In this Application Note, TM-DSC was used to study the glass transition, cold crystallization and melting, recrystallization and remelting processes of PEEK film samples.

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Measurement Conditions

The sample was a PEEK film. Sample preparation (figure 1) consisted of punching out a series of small discs of film (approx. 5 mg) using a punching device, inserting them into an aluminum *Concavus*® crucible, and covering the crucible with a slide-in lid (the slide-in lid is an embedded crucible lid which can press onto the loose film firmly in order to improve the thermal contact).

The test atmosphere was N_2 (50 ml/min), and TM-DSC was chosen as the test mode.

1 Sample preparation

Measurement Results

The thermal effects of the sample included two stages:

1st stage: below 210°C; glass transition and cold crystallization

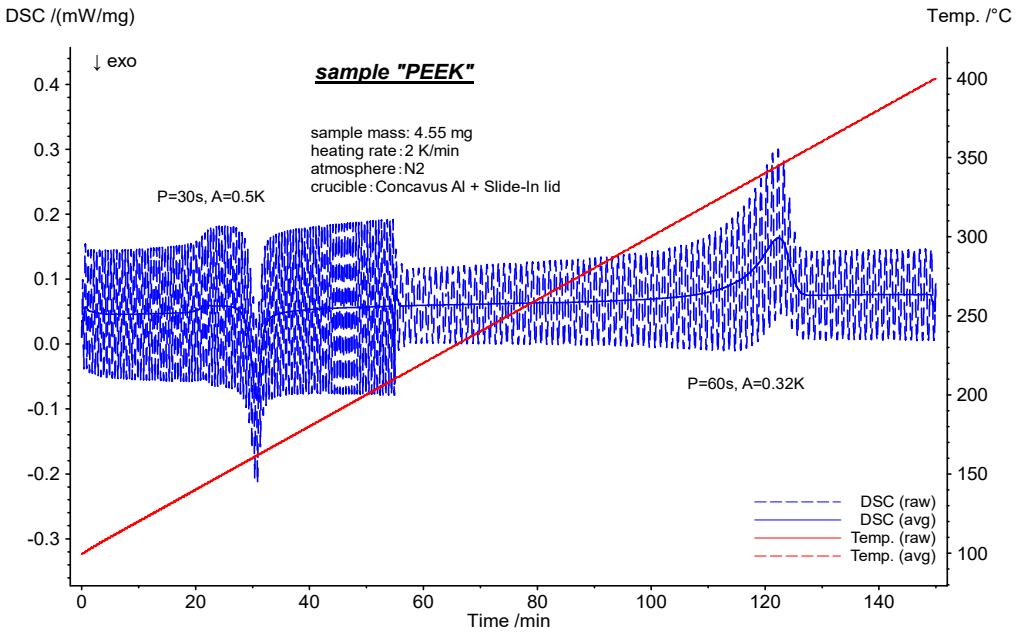
2nd stage: above 210°C; melting, recrystallization and remelting

Different modulation parameters were used for the two stages to obtain better results:

Parameters in the 1st stage: heating from 100°C to 210°C at 2 K/min, period 30 s, amplitude 0.5 K.

Parameters in the 2nd stage: heating from 210°C to 400 °C at 2 K/min, period 60 s, amplitude 0.32 K.

The raw TM-DSC signals are shown in figure 2.



2 Raw DSC signals of the TM-DSC measurement on the "PEEK" sample

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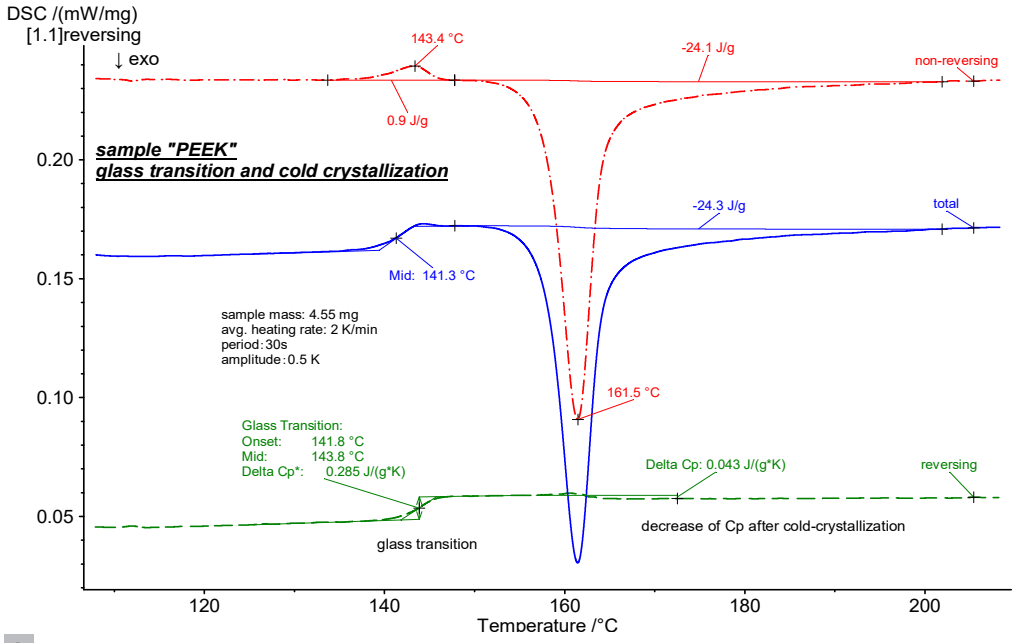
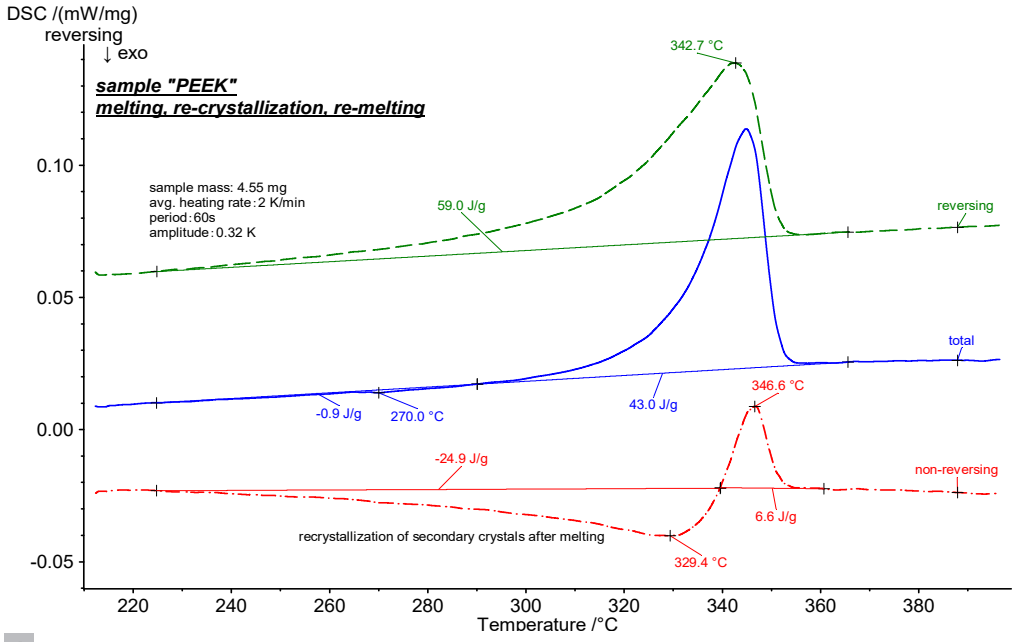
The results of the glass transition and cold crystallization are presented in figure 3. The relaxation peak (peak 143.4°C) and the cold crystallization peak (peak 161.5°C) are shown on the non-reversing DSC curve (red curve). The glass transition (T_g 143.8°C (midpoint)) can be seen on the reversing DSC curve (green curve). Besides that, the reversing curve also shows a slight drop (0.043 J/g*K) in the specific heat capacity during cold crystallization. This is due to more molecular chains being bounded to the crystalline region after cold crystallization, so the vibrational freedom of the chains decreases, and then the specific heat capacity decreases.

The results of melting, recrystallization and re-melting are presented in figure 4. The total DSC curve (blue curve) just shows a huge endothermic peak (peak 344.9°C), as



3 TM-DSC results for the glass transition and cold crystallization for the "PEEK" sample.



4 TM-DSC results for melting, re-crystallization and re-melting for the "PEEK" sample.

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well as a minor exothermic peak (270°C (peak temperature)). More information can be found after separation of the total DSC curve into the reversing DSC curve (green curve) and non-reversing DSC curve (red curve). There is a broad endothermic peak (342.7°C (peak temperature)) on the reversing DSC curve, which contains melting of the secondary crystals, remelting after recrystallization of the secondary crystals, and melting of the primary crystals [1]. The endothermic peak (346.6°C) on the non-reversing DSC curve represents the melting of a portion of the primary crystals [1]. In addition, the exothermic peak (peak 329.2°C) on the non-reversing DSC curve corresponds to recrystallization after melting of the imperfect secondary crystals [1]. The heat-flow signals of the endothermic effect of melting and the exothermic effect of recrystallization partially overlapped, so it is possible that the area of each peak is smaller than the actual value.

Conclusion

Using the TM-DSC method, it was possible to separate the reversing and non-reversing thermal effects. For the PEEK sample, more information about melting, crystallization and remelting was gleaned.

References

[1]. Temperature-modulated DSC studies of melting and recrystallization in polymers exhibiting multiple endotherms, Polymer 41 (2000) 1099- 1108

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