Double Melting Behavior Study of PEEK by ADSC

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Abstract

ADSC was applied to the study of the double melting behavior for isothermally melt crystallized and glass crystallized PEEK. We got almost the similar results with William G. Kampert's on the melt crystallized PEEK. In addition, the difference of the out-of-phase Cp and complex Cp between the melt and glass crystallized PEEK was also found. It seems that, there two kind of stable crystalline exited in the melt crystallized PEEK. At the same time, recrystallization contributed to both of the glass crystallized and melt crystallized PEEK.

Introduction

Poly(ether ether ketone)(PEEK) is a kind of thermoplastic with exellent physical and chemical properties. There are two opposing models proposed to explain the double melting endotherms resulting from isothermally annealing of the glass or the melt crystallized PEEK. The first model[1,2] supposed that the crystals with lower melting temperature may transform into a higher melting form during heating; the second model[3,4] proposed that the two peaks are due to two separate crystal morphologies.

Alternating DSC is a relatively new technique[5] which adds a sample to a linear heating ramp of standard DSC with a superimposed low frequency small amplitude temperature oscillation resulting in a modulation in the heating profile. By deconvolution the total heat flow can be separated into a heat capacity-related (reversing) component and a time-dependent non-reversing (NR) component. The reversing signal provides excellent resolution of the glass transition by separating the heat capacity from other non-reversing processes. All exothermic behavior is detected only in the NR signal.

We applied ADSC in the study of the double melting behavior for isothermally melt crystallized and glass crystallized PEEK and got the similar result with William G. Kampert's.[6] The results seemed to show that the double melting behavior of PEEK could be explained by combination of the two models.

Experimental

Materials. The commercial grade of PEEK 450G was obtained from ICI. Amorphous films about 0.5mm thick of PEEK were obtained by melting the samples into a laboratory press heated at 400°C for 5min, followed by rapid quenching in the water. The obtained films were found to be amorphous by WAXD diffraction test.

Instrumentation and Method. A Mettler Toledo DSC821e was used in these experiments and the signal processing was provided by the manufacturer. The experiments utilized ADSC heating ramps of 2°C/min with a modulation amplitude of 0.32°C with a period of 60s. A N2 purge was used for all experiments. Careful baseline calibration is critical for these films and was performed regularly.

Annealing Experiments. Glass-crystallized PEEK was prepared in an oven by heating amorphous films directly at the annealing temperature Ta. Melt-crystallized samples were

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prepared in a Mettler Toledo DSC821^e stage by melt at 390°C 15min then quenched to the annealing temperature Ta at about 200°C/min and crystallized different times.

Results and Discussion

PEEK was glass crystallized at 280°C for 10min and 300min separately and the ADSC scans at 2°C/min. **Figure 1**, **Figure 2** and **Figure 3** show the heatflow curves of ADSC for glass crystallized PEEK at 10min and 300min. They show the similar trends for the different times. The non-reversing curve consists of a low endotherm which starts a few degrees before the endothermic drop in the reversing signal (**Figure 2**) at the temperature a little higher than 280°C, immediately followed by relatively high levels of exothermic recrystallization. It's the recrystalllization which resulted in the obscure broad melting endotherm of the primary crystals in the total heat flow signal in **Figure 3**. The low endotherm of the total heatflow curves consists of two parts: one is the non-reversing melting peak, the other is the reversing melting peak. They are all caused by the melting of secondary crystal formed during the annealing at 280°C. The higher endotherm is a combination of the endotherm from initially formed primary crystals, which overlaps with the endotherm from the large fraction of higher melting crystals formed during DSC heating.

Figure 4 and **Figure 5** show the outp-of-phase Cp and complex Cp curves of the PEEK melt and glass crystallized at 280°C for 300min. From the comparison, we could find that they had the similar trends, however, there are wide range peaks in the melt crystallized curves and none in the glass crystallized curves. It seems that there was a stable crystalline melted in the temperature rang of 300°C to 316°C when PEEK was melt crystallized and none when it was glass crystallized.
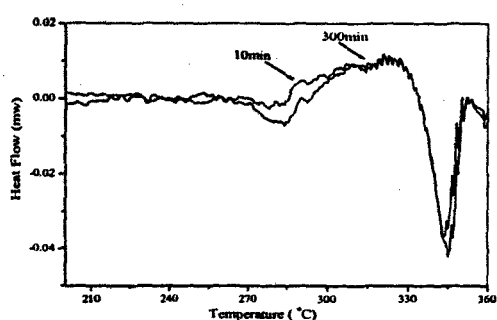

Figure 1. Reversing heat flow curves of ADSC data for PEEK crystallized at 280°C for 10min and 300min.
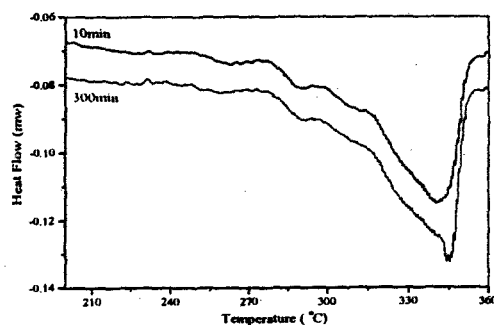
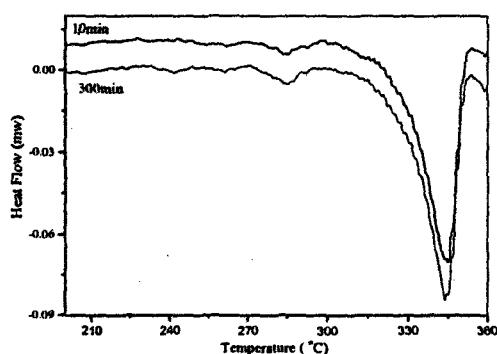**Figure 2.** Nonreversing heat flow of ADSC data for PEEK crystallized at 280°C for 10min and 300min.

Figure 3. Total heatflow curves of ADSC data for PEEK crystallized at 280°C for 10min and 300min.
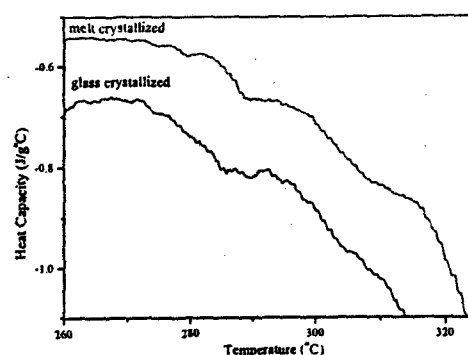
Figure 4. Out-of-phase Cp curves of ADSC data for PEEK melt crystallized and glass crystallized at at 280°C for 300min.
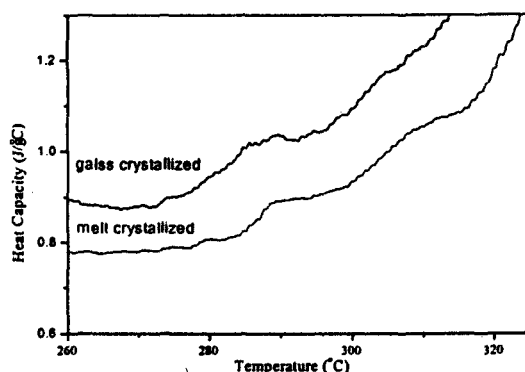
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Figure 5. Complex Cp curves of ADSC data for PEEK melt crystallized and glass crystallized at 280°C for 300min.

Conclusions

We studied the double melting behaviors of PEEK by ADSC. The melt crystallized and glass crystallized PEEKs were both investigated. We got almost the similar results with William G. Kampert's on the melt crystallized PEEK. In addition, the difference of the out-of-phase Cp and complex Cp between the melt and glass crystallized PEEK was also found. It seems that, there two kind of stable crystalline exited in the melt crystallized PEEK. At the same time, recrystallization contributed to both of the glass crystallized and melt crystallized PEEK.

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