Isothermal Crystallization and Melting Behavior of Short Carbon Fiber Reinforced Poly(ether ether ketone) Composites

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Abstract: Films of short carbon fiber reinforced poly(ether ether ketone) (PEEK) composite were formed by compression molding pellets for 10 min at 380 °C under air. A heating stage was used to prepare isothermally treated PEEK composites before DSC scan. The dependence of degree of crystallinity on the heating rate (10-80 °C/min) was investigated for specimens crystallized at different temperatures. The results indicated that 50 °C/min was an optimum heating rate to suppress the reorganization and to avoid the superheating of high crystallinity specimens with the sample weight of 10 mg. The upper peak temperature of double-melting peaks continued to increase with crystallization temperature. This peak temperature was related to the transition from regime II to III. The phenomenon of lower crystallinity and higher melting temperature supports the interpretation that the upper melting peak corresponded to crystals growing during the earlier stage of isothermal crystallization.

Keywords: PEEK, Composites, DSC, Crystallinity, Melting.

Introduction

Crystallinity is one of the specific physical properties of great concern during the processing of semicrystalline thermoplastic composites. Good mechanical properties as well as thermal and solvent resistance will not be achieved unless there is substantial crystallization. In order to understand the relationship between the material properties and the degree of crystallinity in a polymeric matrix composite, a reliable and accurate method for assessing this physical property is required. Differential scanning calorimetry (DSC) is a convenient technique for the evaluation of degree of crystallinity, which is often based on measuring the area underneath the melting peaks. There have been several investigations [1-14] concerning the determination of crystallinity of poly(ether ether ketone) (PEEK) and its carbon fiber composites by DSC methods at a heating rate of 5-20 °C/min. Jonas et al. [5] demonstrated that PEEK underwent reorganization during a DSC heating scan at a rate of 10 °C/min. The degree of crystallinity increased further by more than 10%. Lee et al. [15] suggested that 60 °C/min was fast enough to minimize the reorganization. This reorganization was strongly dependent on the initial crystallinity and was not visible in the DSC thermogram. These results can not be compared with each other because of different thermal treatments, different heating rates, and different calculation formulas. One of the formulas was used to subtract the exothermic recrystallization peak area from the melting peak area to obtain a measure of the initial crystallinity. This measure is quite inexact because the heat of fusion and the heat of recrystallization per unit crystallinity is quite different near 330 °C than it is at 170 °C.

In order to investigate the crystallization and melting behavior of PEEK matrices in composites, we have recently embarked upon a detailed study of the crystallization and morphology of PEEK and its composites. Thermal stability experiments [16] indicated that the PEEK matrix was stable in nitrogen up to the temperature of 400 °C for 15 min holding. After this treatment, the subsequent crystallization behavior (isothermal as well as nonisothermal) became independent of the prior thermal history, in which case the crystallization kinetics can be com-
pared precisely. This requirement is absolutely necessary to ensure valid results. For a short carbon-fiber reinforced PEEK composite, holding at 380 °C for 10 min [17] was a suitable melting condition to avoid thermooxidative degradation under air. In a previous article [18], an optical microscope equipped with a video photograph system was used to follow the growth of spherulites. Linear growth rates of crystallization of PEEK have been measured in the temperature range of 260-325 °C for melt-pressed films and solvent cast films. Detailed kinetic analysis of the isothermal growth-rate data indicated the existence of an unmistakable Hoffman regime II → III transition at 296±1 °C for PEEK specimens without degradation and crosslinking. The regime II → III transition was clearly present irrespective of the rather drastic changes in U* (the activation energy for the reptation process). In another study [19], a dynamic crystallization method via differential equations was used to measure the isothermal spherulitic growth rates of PEEK by means of an optical microscope equipped with a camera. These continuous growth rate data were further used for a kinetic analysis which indicated that PEEK exhibited an unmistakable regime II → III transition at 296 °C. It is worth speculating that the melting temperature of isothermally crystallized PEEK samples may be related to the regime transition from II to III that occurred at about 296 °C.

The maximum controlled rate of 130 °C/min, in a Linkam THMS-600 heating stage equipped with a Linkam TMS-91 temperature control system, was better than the maximum controlled cooling rate of 50 °C/min and heating rate of 80 °C/min in a DuPont 910 DSC. In addition, crystallization of the polymer occurred before thermal equilibration in DSC. Accordingly, the heating stage was used to prepare thermal treated specimens before the DSC scan in this study. The first derivative of the DSC thermogram was used to determine the DSC heating baselines. The dependence of degree of crystallinity on the heating rate as well as the melting thermogram of specimens crystallized at different temperatures were investigated. The results of crystallinity measurement indicated that 50 °C/min was an optimum heating rate to suppress the reorganization and to avoid the superheating of high crystallinity specimens.

Experimental

1. Materials and specimens

RTP 2285 is a short carbon fiber reinforced PEEK composite which contains 30% by weight carbon fiber (RTP Company, U.S.A.). A Tetrahedron MTP-14 hot press was used to make films approximately 0.1 mm thick [17]. All the films were vacuum-dried overnight at 120 °C before use. Each sample with a diameter of 6 mm and a weight of about 10 mg was cut from the film and sealed in a DSC aluminum pan for further thermal treatment.

2. Melting behavior and crystallinity at various heating rates

A Linkam THMS-600 heating stage equipped with a Linkam TMS-91 temperature control system enabled the specimen to be heated and cooled at an adjustable rate. The DSC pan containing the dried sample was placed onto the heating stage under nitrogen atmosphere and heated at 130 °C/min from room temperature to 400 °C. The samples were maintained at this molten state for 15 min, and then cooled down at 130 °C/min to the chosen crystallization temperature, Tc. The samples were held at Tc for selected times that were 30 min at 249, 260 or 269 °C and 60 min at 297 or 314 °C. A dried film in a DSC pan was placed on a small hot block regulated at 400±1 °C for melting for 15 min under nitrogen, followed by quenching the pan into a liquid nitrogen bath to make the specimen amorphous. The DSC pan containing the amorphous film was placed onto the heating stage under nitrogen atmosphere and heated at 130 °C/min from room temperature to a selected Tc (e.g. 210 °C) for 30 min. The sample was then cooled to room temperature at a maximum cooling rate of 130 °C/min.

After cooling, the specimens were ready for DSC heating scans at different rates. The melting behavior and heats of fusion of melt crystallized films were studied using a DuPont 910 DSC attached to a DuPont 9900 thermal analysis system. Both temperature and heat flow scales were routinely calibrated with indium and lead at each heating rate (10-80 °C/min) under a constant nitrogen flux. These crystallized specimens were heated with different DSC scanning rates. The first derivative of the DSC thermogram was used to identify the onset and the end of melting peaks. The heat of fusion of the specimen was evaluated by integrating the melting peaks. Finally, the amorphous specimen was heated at an optimum rate of 50 °C/min to investigate both melting behavior and the total enthalpy.

Results and Discussion

Melting traces at various heating rates from 10 to 80 °C/min are plotted in Figures 1 and 2 for specimens crystallized isothermally at 314 and 249 °C. These traces show double-melting peaks as a common feature [14,15,20-28] for PEEK. There is a