Effects of Melt Processing on Evolution of Structure in PEEK

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Abstract

We report on the effects of melt processing temperature on structure formation in Poly(ether-ether-ketone), PEEK. Real time Small Angle X-ray Scattering, SAXS, and thermal analysis are used to follow the melting behavior after various stages of processing. Assignment of peaks to structural entities within the material, the relative perfection of the crystals, and the possibility of their reorganization, are all influenced by the melt processing history. With the advent of high intensity synchrotron sources of X-radiation, polymer scientists gain a research tool which, when used along with thermal analysis, provides additional structural information about the crystals during growth and subsequent melting.

PEEK is an engineering thermoplastic polymer with a very high glass transition temperature (145 °C) and crystal melting point (337 °C). PEEK has been the subject of recent studies by X-ray scattering in which melt and cold crystallization were followed in real-time. X-ray scattering and thermal studies have been used to address the formation of dual endothermic response which has been variously ascribed to lamellar insertion, dual crystal populations, or melting followed by re-crystallization**.** Another important issue is whether all of the amorphous phase is located in interlamellar regions, or alternatively whether some is located in "pockets" away from the crystalline lamellar stacks. The interpretation of scattering from lamellar stacks varies depending upon whether such amorphous pockets are formed. Some groups believe all of the amorphous phase is interlamellar. This leads to selection of a smaller thickness for the crystals. Other groups suggest that most amorphous phase is not interlamellar, and this leads to the suggestion that the crystal thickness is larger than the amorphous layer within the stacks. To investigate these ideas, we used SAXS and Differential Scanning Calorimetry to compare results of single and dual stage melt crystallization of PEEK using a treatment scheme involving annealing/crystallization at T_{a1} followed by annealing at T_{a2}, where either $T_{a1}<T_{a2}$ or $T_{a1}>T_{a2}$.

We proposed a model to explain multiple melting endotherms in PPS, treated according to one or two-stage melt or cold crystallization. Key features of this model are that multiple endotherms: 1. are due to reorganization/recrystallization after <u>cold</u> crystallization; and, 2. are dominated by crystal morphology after <u>melt</u> crystallization at high T. In other words, multiple distinct crystal populations are formed by the latter treatment, leading to observation of multiple melting.

PEEK 450G pellets (ICI Americas) were the starting material for this study. Films were compression molded at 400 °C, then quenched to ice water. Samples were heated to 375 °C in a Mettler FP80 hot stage and held for three min. to erase crystal seeds before cooling them to T_{a1} = 280 °C . Samples were held at T_{a2} for a period of time, then immediately heated to 360 °C. In the second treatment samples were held at T_{a1} = 310 °C for different crystallization times t_c, then cooled to 295 °C and held 15 min.

In situ (SAXS) experiments were performed at the Brookhaven National Synchrotron Light Source with the sample located inside the Mettler hot stage. The system was equipped with a two-

dimensional position sensitive detector. The sample to detector distance was 172.7 cm and the X-ray wavelength was 1.54 Å. SAXS data were taken continuously during the isothermal periods and during the heating to 360 °C at 5 °C/min. Each SAXS scan was collected for 30 sec. Since the samples were isotropic, circular integration was used to increase the signal to noise ratio.

After dual stage melt crystallization with $T_{a1}<T_{a2}$, the lower melting endotherm arises from holding at T_{a1}. During cooling a broad distribution of crystals forms, and the low-melting tail is perfected during T_{a1}. Heating to T_{a2} melts these imperfect crystals and allows others with greater average long spacing to form in their place. After dual stage crystallization with $T_{a1}> T_{a2}$, the amount of space remaining for additional growth at T_{a2} depends upon the holding time at T_{a1}. The long period of crystals formed at T_{a2} is smaller than that formed at T_{a1} due to growth in a now-restricted geometry.

Perfection of crystals is seen as an increase of the intensity of the population scattering at higher s, while the intensity of the population scattering at lower s stays constant. During heating from below to above the minor endotherm, we see rapid decrease of the intensity of the X-ray scattering corresponding to the population of crystals scattering in the shoulder. Another important observation is that after the sample is annealed at 295 °C, the shoulder intensity is restored once again. The population scattering at higher s remains longer before it disappears in the sample treated to the second stage of melt crystallization, compare to the sample crystallized with a single stage. This could be interpreted as an effect of continued perfection of the less perfect population, which is also reflected in the increased melting temperature of the smaller endotherm as the holding time at 295 °C increases. In the corresponding DSC scans we see a shift in the area and the peak temperature of the lower melting endotherm with an increase of the annealing time.

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