

**Polymer Congress 2018: Near-surface crystallization in polyesters - Hazel E Assender - MA PhD, University of Oxford, UK****Hazel E Assender***University of Oxford, UK*

The near-surface properties of thermoplastic polymers are of interest, particularly where thin film coatings or other structures are to be subsequently applied. Previous work by AFM and ellipsometry has established that the glass-transition temperature in the near-surface region is depressed by up to tens of Kelvin, leaving the surface vulnerable to deformation and penetration during coating processes such as metallization. We have also shown that the near-surface region of PET shows enhanced crystallinity. This paper will report our AFM studies of PET, PEN and copolymers thereof and the near-surface crystallization that can be induced by annealing at temperatures at which the surface molecular segments are mobile, but those in the bulk underneath are not. We demonstrate the characteristic morphologies associated with the surface crystallization and changes in the crystal orientation as growth proceeds. Comparison is made with other polymer systems we have studied including near-surface phase separation and unique crystal morphologies at the surface in polyurethanes.

Comprehensive understanding of the properties of the polymer surface and polymer thin films has become more important recently, in many applications such as multi-layer films, coatings, adhesives, thin layer electronic devices (organic light emitting diodes and organic photovoltaic cells), optoelectronics, and so on. Typical polymeric crystallization processes have been fully studied using films of a few micrometres in thickness. In the case of very thin polymer films, whose thickness is less than e.g. 100 nm, however, the influence of the surface and any underlying interface increases, so that the effect of interfacial polymer chain behaviour can become the dominating feature of polymer crystallization. Various studies have been carried out for nanometre thick films, and unique thin-film crystals have been reported for several different polymers such as polystyrene, polylactide, poly(ethylene oxide), and poly(ethylene terephthalate). In this thickness range, single lamellar crystals such as flat-on and edge-on lamellar crystals are produced, whereas as the thickness becomes smaller, self-diffusion

is restricted due to the confinement of the chains within the thin layer, and a non-equilibrium crystalline morphology such as seaweed or finger pattern appears reflecting the inhomogeneity of the self-diffusion at the growth front caused by local thermodynamic fluctuations.

However, these studies have considered the crystallization processes during which the molecules whole polymer film have been mobile, and crystallization studies specific to the near-surface region have not been significantly reported. The understanding of the surface crystallization of thin films is closely linked with the study of glass transition behaviour, as the  $T_g$  is known to be modified at the near-surface. It is well-established that the polymer near an interface can show a modified  $T_g$ , with many studies reporting a decreased  $T_g$  near the free-surface, leading to an overall decrease in  $T_g$  of a thin film, within which the surface has a significant influence. Our group has also observed  $T_g$  depression by several °C in polystyrene (PS) films on a silicon substrate, by means of SFM force distance curve measurements. Cold crystallization from glassy amorphous material begins when a film is heated up above the observed  $T_c$ , which is some temperature above  $T_g$ ; previously we have reported how the low  $T_g$  near the PET free surface can be exploited to produce surface-specific crystallization by annealing at temperatures between the surface  $T_c$  and the bulk  $T_c$ . In this study we compare the surface crystallization behaviour of PET and PEN spin coated thin films, observing the influence of film thickness and annealing temperature, to consider the influence of the relatively rigid molecular structure and higher  $T_g$  of PEN on the surface crystallization behaviour, and we make a careful comparative analysis of the surface crystalline morphology for both polymers.

Each sample cast on a Si substrate was set on a specially designed in-situ heating stage placed on an AFM scanner, and annealed at elevated temperatures ranging from 50 °C to 150 °C for PET and from 70 °C to 190 °C for PEN. The heating was performed stepwise and samples were kept at each increasingly

elevated temperature for 2 hours before the morphology was recorded. The morphology change of the films during the crystallization process has been observed depending on film thickness and temperature of crystallization. An auto-probe CP microscope (Park Scientific Instruments) with V-shaped cantilever (Thermo microscopes 'Ultralever', effective nominal tip radius of 10 nm, spring constant ranging from 1.1 to 1.6 N/m) was operated in contact mode for AFM topography and LFM (lateral force microscopy) images. The scanning was performed at a rate of 0.5 - 0.7 Hz. Measurement of the surface  $T_g$  can give a better understanding of the surface crystallization phenomenon. In this study, SFM force-distance curve measurement was used to determine the surface  $T_g$  of PET and PEN films, which can detect the slight change in elasticity on the surface [26-27], by means of the same in-situ heating stage with the V-shaped cantilever, at a contact force of 0.24 nN and a scanning rate of 0.7 Hz.

In the case of PEN ultrathin films in this study, lamellae with characteristic habit of terraces emerge from the initial edge-on crystals (Fig. 9-(c) and 9-(d)). The lamellar orientation of the PEN terrace-like crystals,

however, is not directly observable from the results in this study. We can only speculate that the terrace-like crystals have flat-on orientation based on their morphological features, i.e. their height profiles are relatively flat, and the edges slightly fringed due to diffusion-limited growth [56-57]. Thus, PEN appears to favour an edge-on embryo surface crystal, which, in thicker films, can directly give rise to edge-on lamellae in all directions within the plane. In ultra-thin PEN crystals, however, the growth of ridged lamellae appears constrained (as it was in the low temperature stages of growth for the PET), but the terraced (perhaps 'flat-on') crystals can grow to a limited extent from the initial edge-on embryo. The difference between PET and PEN surface crystal development in the early stages can be accounted for by the preference for PEN to form an edge-on initial crystal, and hence, in contrast to PET, the terraced morphology is only observed in the case of the ultrathin films where, even at elevated temperatures, the surface mobility is very highly constrained.

Keywords: PET; PEN; surface crystallization; surface glass transition; force-distance curve; edge-on crystal; flat-on crystal; diffusion limited aggregation