NOTES

Some Small-Angle X-Ray Diffraction Measurements on Blown Polyethylene Films

Rather detailed x-ray diffraction pole figure studies on a range of blown polyethylene (PE) films have shown[1–3] that two quite distinct types of orientation occur, their properties being determined by the blowing conditions. The first, designated low-stress crystallization orientation, is the normal type and is found in most PE films. The a and c axes are at 90° and both are inclined at an angle to the plane of the film; this type of orientation is readily explicable in terms of the stress crystallization mechanism of Keller and Machin.[4] The second type of orientation, designated high-stress crystallization orientation, is analogous to that found in cold drawn polyethylene[5,6] under conditions where necking occurs and where there is considerable stress. Stress is also an important factor in the melt spinning of polyethylene fibres. Dees and Spruiell[7] have assessed its influence, by wide and small-angle x-ray diffraction, and have interpreted their results in terms of the Keller and Machin row-nucleation process. It may be surmised that, with the low-stress crystallization orientation, the conventional type of crystallization process involved will give the familiar lamellar structure in the blown films; however, this assumption has not hitherto been substantiated by small-angle x-ray diffraction measurements. In the case of the film with a significant proportion of high-stress orientation it is less certain that the lamellar structure will be present because the conversion of the lamellar folded system to a fibrillar one is readily observable in the case of cold drawn polyethylene at high drawn ratios.[8,9] This note reports the results of a brief small-angle x-ray diffraction study. Measurements have been made on two films, one each of the low- and high-stress orientation types, to confirm the presence or absence of the chain-folded lamellar morphology, and to look for other significant morphological features. The results prove to be of some interest.

EXPERIMENTAL

Two films were examined, both from the earlier pole figure studies.[3] Film 2, blown from Shell LPPE 040 high-density polyethylene, using a melt temperature of 235°C, a blow up ratio of 3, and a draw ratio of about 8, has a maximum in the sheet normal/machine direction intensity profile at about 45° and contains the conventional low-stress type of orientation. Film 23, blown from Hostalen GM 9955F high-density polyethylene, using a melt temperature of 194°C, a draw ratio of about 60, and a blow up ratio of unity, contains a substantial proportion of material of the high-stress orientation type, although some low-stress orientation is also present.

The small-angle x-ray diffraction measurements were made with a Rigaku-Denki spectrometer, using Cu $K\alpha$ radiation and step scanning with a Geiger counter detector. A sample thickness of 1 mm was used and was obtained by stacking pieces of film, using the reference grid method already described in connection with the wide-angle x-ray diffraction measurements[1] to ensure that the various pieces were all accurately aligned. Measurements were made along the machine and transverse directions. Although slit optics were used the fact that the samples are highly oriented ensures that the scattering curves obtained are similar to those that would result from pin-hole optics. Hence, no correction for desmearing is required. Corrections have been applied for Lorentz polarisation and the intensity data were multiplied by the θ^2 function.[10]

RESULTS AND DISCUSSION

The small-angle scattering curves for films 2 and 23 along the machine direction are shown in Figures 1 and 2, respectively. Low-intensity scattering only, with no maxima, was obtained from the transverse direction scans. It is clear that a well defined lamellar structure, normal to the machine direction, is present in both cases. Hence, although the orientation occurring in the case of the high-stress film is crystallographically similar to that found in heavily cold-drawn polyethylene, which contains substantial amounts of fibrillar material, there is no resemblance morphologically and lamellar structures giving well defined small-angle x-ray diffraction occur with both types of film.

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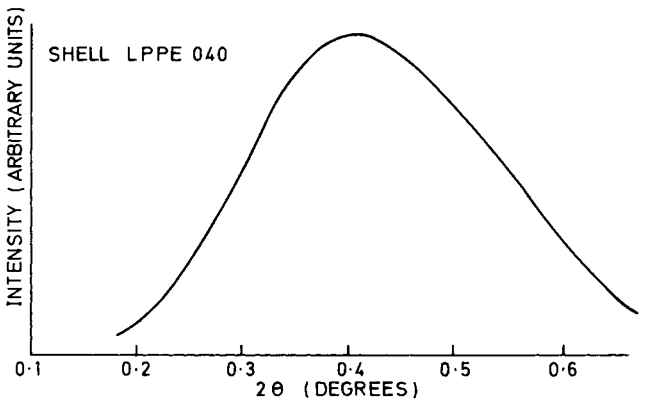

Fig. 1. Small-angle scattering curve for film 2, blown from Shell LPPE040 high-density polyethylene.

The long spacings, deduced from the positions of the two maxima, are 218 Å in the case of film 2 and 256 Å for film 23. It is well-known that the lamellar thickness is influenced by the thermal history of the sample. Vonk[11] has shown that slow crystallization leads to appreciably larger values, Statton and Geil,[12] among others, have demonstrated that lamellar thickness increases with increasing annealing temperature and among the work on the effect of crystallization temperature that of Kavesh and Schultz[13] may be cited. Hence, it is not surprising that there are differences between films 2 and 23. However, until a range of films prepared with various blowing parameters is examined it is not possible to suggest how the lamellar thickness will depend upon the melt temperature and the freeze-line height.

Nevertheless, it is of interest to compare the present limited results with the small-angle x-ray diffraction measurements of Dees and Spruiell[7] on polyethylene fibers obtained by melt spinning. With these the values of the long period spacing showed a trend towards smaller values with increasing take-up velocity, i.e., increasing spin line stress, and decreasing mass flow rate. Furthermore, they are much smaller, at similar crystallization temperatures, than those observed by Kavesh and Schultz[13] for quiescent melts, as are the present values. Dees and Spruiell[7] interpret their results in terms of a variable degree of twisting of lamellar crystals in a row-nucleated structure. They conclude that strain induced fibril nucleation causes crystallization to occur at temperatures far above those at which crystallization occurs for a quiescent melt cooled at similar rates. A further

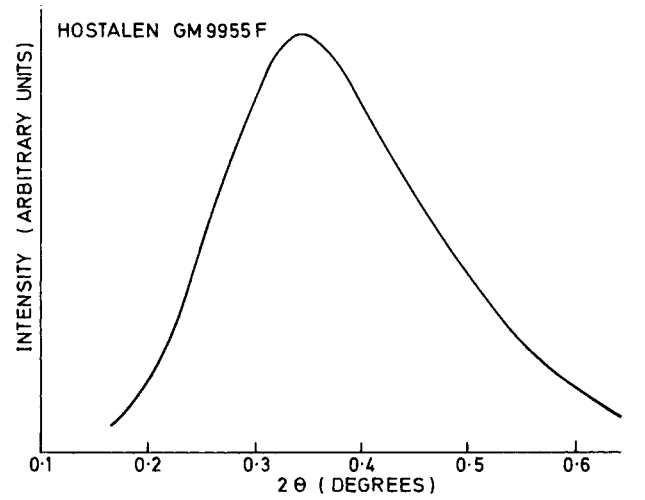

Fig. 2 Small-angle scattering curve for film 23 blown from Hostalen GM9955F high density polyethylene.

increase in the fiber take-up velocity beyond the point at which significant row nucleation first occurs causes the cooling rate to increase rapidly enough to suppress the crystallization temperature, in spite of any additional increase in crystallization rates caused by increased spin-line stresses. Crystallization under these conditions results in larger small-angle x-ray diffraction long periods. It is clear, despite the limited nature of the present work, that the results for the blown films differ fundamentally from those for spun fibers as the lamellar thickness increases with increasing stress during the blowing process. It is doubtful if the two situations are comparable because the stresses during film blowing are particularly complex, as has already been noted.[1]

The second noteworthy feature of the two intensity profiles is the considerable difference in their shapes and half-widths. These two parameters are determined both by instrumental factors and the spread of lamellar thicknesses. As the first factor is constant the observed differences must be the result of the second. The spread of lamellar thicknesses may be the direct result of a range of values or the consequence of differences in the lamellar orientation. In the case of the low-stress crystallized material (film 2) the row orientation model of Keller and Machin[4] shows that the lamellae are twisted along the *b* direction and the effect of this is to give a range of orientations and effectively of lamellar thicknesses by the small-angle x-ray diffraction technique.

With the high-stress crystallized material the lamellae are arranged in parallel stacks along the *b* direction and the effective orientation is greater. This will then lead to a sharper small-angle profile, in agreement with the experimental results and those from infrared dichroic studies.[14] Although it is not possible to separate quantitatively the effects of lamellar orientation and an actual range of lamellar thicknesses on the basis of the limited measurements reported here it seems unlikely that the latter factor can wholly account for the difference between the profiles of films 2 and 23. Hence, there is almost certainly a significant effect as the result of lamellar orientation, one that is qualitatively in agreement with the predictions of the Keller and Machin model for crystallization under low and high stress.

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