Formation and Peculiarities of Heterogeneity in Polyethylene Samples Obtained by Extrusion

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Synopsis

Three-layer structure was observed in the polyethylene strips obtained under definite conditions of extrusion, with the high degree of orientation of the core layer being most remarkable. The wide- and small-angle X-ray investigation of the different layers of the strips and the pole figures analysis were performed. In the outer layers *a* texture is formed. Crystalline structure formed in the core is characterized by almost regular cylindrical arrangement of *a* and *b* axes around the extrusion direction. The *c* axes direction almost coincides with the extrusion direction. In the core of the extruded strand, lamellae are arranged in parallel stacks. The angle value between the normal to the lamellae surface direction and the extrusion direction is about 30°.

The processes of structure formation are very important for working out optimum production conditions of materials with specified physical and chemical properties on the basis of commercially available polymers. Structure of polymeric materials is as a rule far from being equilibrium (within temperature and shear stresses gradient) due to realization of certain crystallization conditions. The latter factor causes structural heterogeneity of polymers in the form of macroheterogeneity in transverse direction. In materials prepared by extrusion from melt, in particular, multilayer structure is observed. The surface layer is highly oriented and the inner one is isotropic.[1,2] The same is typical for polypropylene films prepared by extrusion.[3]

Earlier we observed a very specific phenomenon involving formation of macroheterogeneity in the polyethylene film obtained by extrusion with the melt coming from the die fed to the rolls.[4] It was found that under certain conditions of extrusion a very pronounced three-layer structure was obtained. In contrast to the preferential orientation of the surface layer common for these methods of polymer processing, in our case the core of the film is highly oriented. Since such effects have not been studied yet it was deemed reasonable to investigate the structure peculiarities of polyethylene films obtained by extrusion with a special emphasis on the texture of highly oriented core.

EXPERIMENTAL

To prepare the films high-density polyethylene with a melt index 4 g/10 min was used. Extrusion was performed at the laboratory extruder, the melt coming from the die fed to the rolls.[4] Temperature of the melt in the extruder was 185°C; temperature of the rolls was 30°C. The melt strip was passed between the rolls at the rate of 12 mm/s. The strip was 0.8 mm thick and 10 mm wide with the roll nip 0.5 and 0.8 mm, respectively. The melt flow rate through the die was varied within 4–8 mm/s. Structure of the layers was studied on the samples cut

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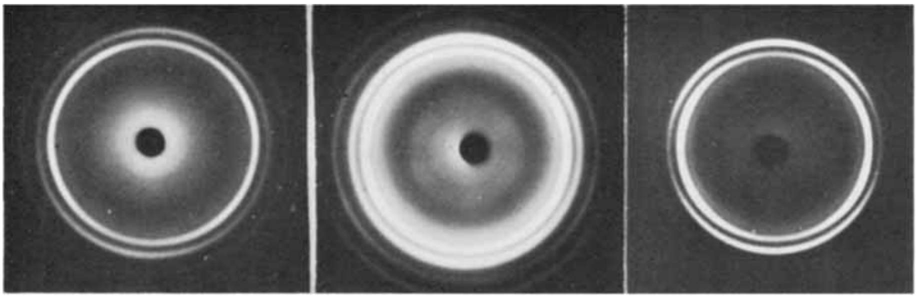


(a) (b) (c)

Fig. 1. Wide-angle X-ray patterns of the extruded polyethylene strip obtained at various conditions of extrusion. (Here and at the subsequent X-ray patterns, direction of extrusion is vertical. X-ray beam is perpendicular to the sample plane.) (a) Flow rate of the melt 4 mm/s, without subsequent rolling; (b) flow rate 4 mm/s and the roll nip 0.5 mm; and (c) flow rate 8 mm/s and the roll nip 0.8 mm.

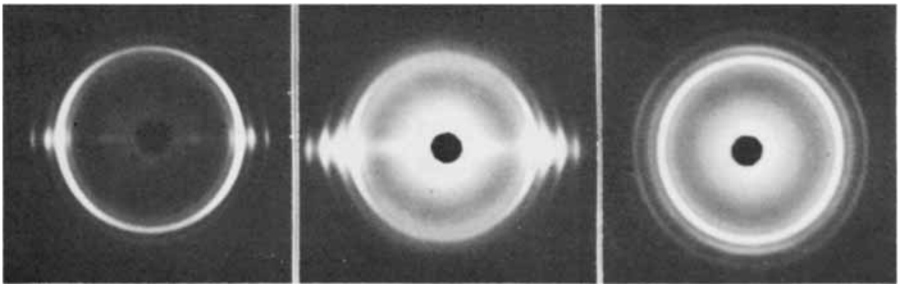
from the extruded strip, the inner layer being 0.2 mm thick and the outer one —0.15 mm thick.

Wide-angle X-ray patterns were taken with the flat-plate camera mounted on the table of a X-ray unit URS-55. Small-angle X-ray patterns were taken by the vacuum X-ray camera with the point collimation of the primary beam. Texture diffractograms were taken with DRON-2,0 diffractometer. In all X-ray experiments radiation of the copper anode with the nickel filter was used.

RESULTS

Figure 1(a) is the wide-angle X-ray pattern of the strip prepared at the extrusion rate of 8 mm/s without rolling. Figure 1(b) is the same for the strip prepared at the extrusion rate of 4 mm/s, rolled, with the roll nip 0.5 mm. Figure 1(c) is the same for the strip prepared at the extrusion rate of 8 mm/s, rolled, with the roll nip 0.8 mm. At the X-ray patterns, more or less perfect *a* texture is observed, which is common for the polyethylene films prepared by extrusion.[5]

Figure 2(a) shows the wide-angle X-ray pattern of the film prepared at the extrusion rate of 8 mm/s and the roll nip 0.5 mm. At this X-ray pattern is contrast to those shown in Figure 1, one can see diffraction arcs for the two types



(a) (b) (c)

Fig. 2. Wide-angle X-ray patterns of the extruded polyethylene strips obtained at the flow rate of the melt 8 mm/s and the roll nip 0.5 mm. (a) Entire cross section of the sample; (b) inner layer of the sample; and (c) outer layer of the sample.

of textures. Distinction of the effects was done by taking X-ray patterns of different layers—in Figure 2(b) the core of the specimen, in Figure 2(c) surface layers are shown. Figure 2(b) shows only reflections of the highly oriented texture, and Figure 2(c) shows only those of the usual *a* texture.

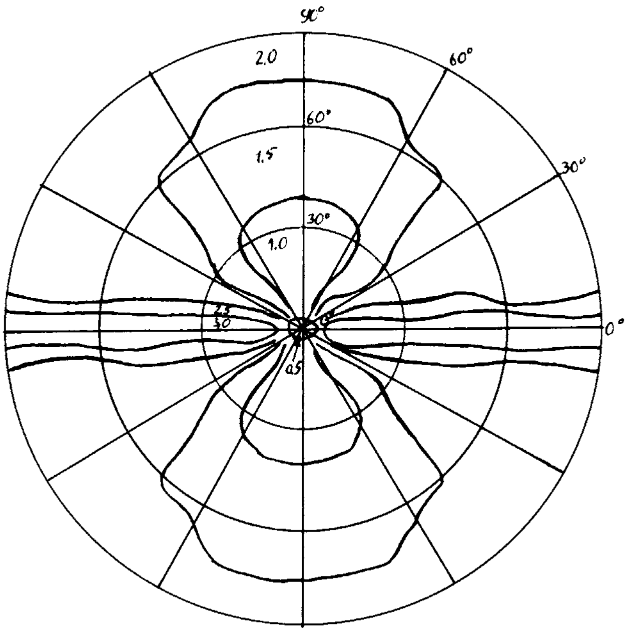
Figure 3 shows pole figures (200), (020), and (002). From the pole figure (200) follows more or less circular arrangement of the *a* axes of the polyethylene crystalline lattice around the extrusion direction. It is however necessary to note that in the plane of the film and in the direction perpendicular to the extrusion direction azimuthal spread of these axes decrease. An essentially similar picture of normal arrangement in the pole figure is typical for the plane (020) as well. In the pole figure (002) very good orientation of the crystalline lattice *c* axes of polyethylene in the extrusion direction is seen.

Figure 4(a) shows the small-angle X-ray pattern of the specimen with highly oriented texture. This pattern was taken at the X-ray direction perpendicular to the plane of the strip. In this X-ray pattern, superposition of almost isotropic scattering (diffuse ring) and meridional spot like reflections are seen. The X-ray pattern of the core of the strand in similar placement of the specimen shows only spotlike reflections [Figure 4(b)]. On the contrary, the X-ray pattern of the core of the strand taken with the beam direction parallel to the strand plane and perpendicular to the extrusion direction shows a four-point reflection [Figure 4(c)].

DISCUSSION

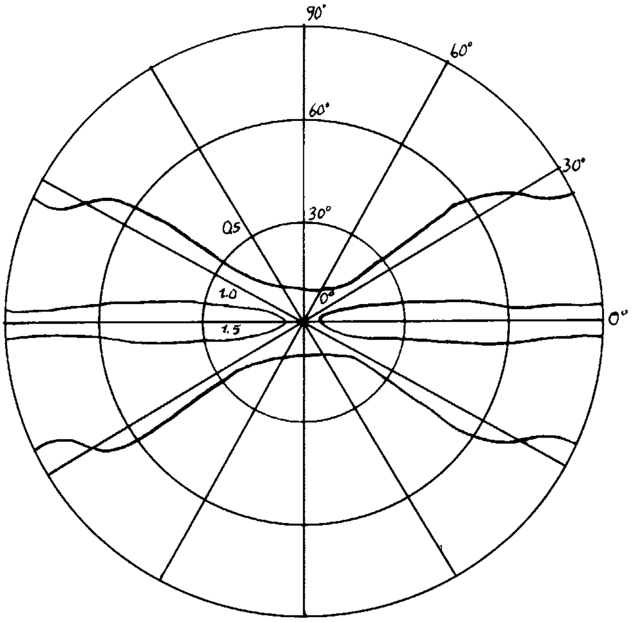
As it follows from Figure 1 at some extrusion conditions in extruded strands so-called *a* texture is formed.[5-9] Peculiarity of such a strand lies in that *b* axes of crystalline lattice and is oriented perpendicular to the extrusion direction in the strand plane. In this case directions of *a* and *c* axes depend on the extrusion conditions and are due to the shear stresses that occur in the melt passing through the die and to the subsequent relaxation processes.[8,9] It is shown that with increased shear stresses *c* axes form smaller angles with the extrusion direction. Regularities of occurence of such textures are well described by the row crystallization theory of Keller.[10,11] These peculiarities lie in the fact that crystallization of the drawn melt takes place due to the initiation of this process is extended along the extrusion direction chains of high-molecular fractions and is realized with preservation of radial symmetry around them.

Occurence of these two types of textures at the X-ray patterns in Figure 2 proves that the process causing formation of *a* texture in surface layers is taking place with the process causing formation of highly oriented *c* texture in the core of the specimen. Crystallization in both cases evidently takes place under different temperatures and mechanical conditions. In fact, crystallization of the surface layers takes place with specific distribution of shear stresses in the melt coming from the die. Crystallization of the core occurs during pressing of the melt, which crystallizes in passing between the rolls by the surface layers that had already crystallized and experience pressure from the rolls. Therefore squeezing of the melt takes place from the core of the specimen in the direction opposite to the draw direction, as is the case with any paste squeezed out from the tube. This process is evidently accompanied by high stresses. Values of the latter are connected with thickness of the melt strand fed to the rolls and with



(200)

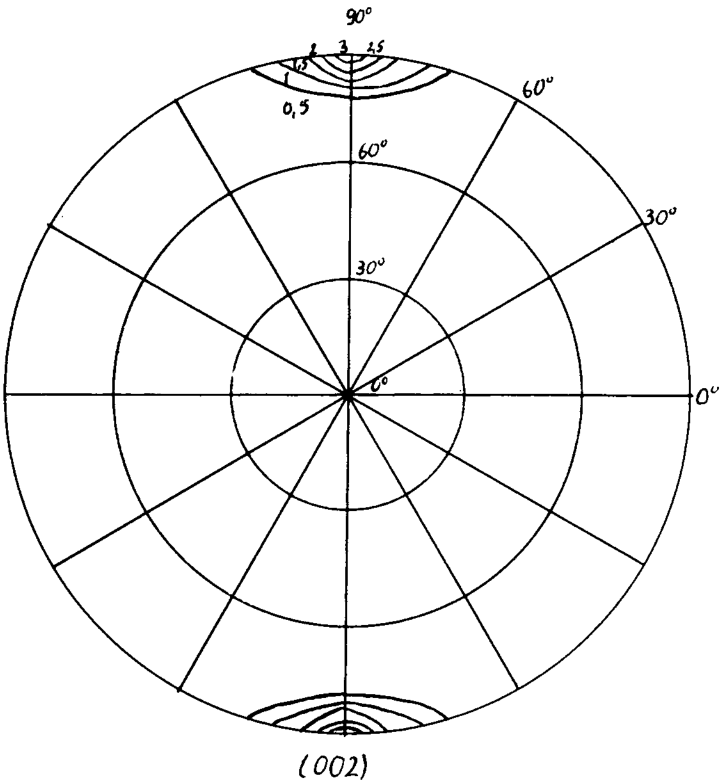
(a)



(0 2 0)

(b)

Fig. 3. Pole figures of the high oriented inner layer of the extruded strand obtained at flow rate of 8 mm/s and the roll nip 0.5 mm; *a*, *b*, *c* correspond to the pole figures for the polyethylene reflections 200, 020, and 002.



(c)

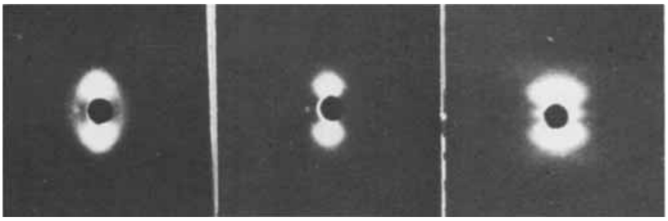
Fig. 3. *(Continued from previous page.)*

roll nip. The greater amount of the material is fed to the rolls and the narrower the roll nip, the higher are shear stresses.

This accounts for the formation of highly oriented texture under certain conditions of extrusion, which evidently correspond to the level of shear stresses necessary for the formation of *c* texture.

It follows from Figure 3 that crystalline structure formed in the central layer is characterized by almost regular cylindrical arrangement of *a* and *b* axes around the extrusion direction. The angle between the axes and the extrusion direction is about 90°. The *c* axes have very small scattering around the extrusion direction.

As is seen from Figure 4, in the core of the extruded strip lamellae are arranged



(a) (b) (c)

Fig. 4. Small-angle X-ray patterns of the high oriented samples. (a) Entire cross-section of the sample; (b) inner layer of the sample; and (c) inner layer of the sample, X-ray beam direction is parallel to the sample plane.

in layers. There is no cylindrical symmetry in their arrangement around the extrusion direction, unlike the arrangement of the axes in the crystalline lattice. From the pictures of small-angle scattering shown in Figure 4, it can be concluded that in the core of the strip lamellae are packed in parallel stacks and are oriented relative to the extrusion direction so that their normals to the surface lie in the plane formed by the extrusion direction and the normal to the plane of the strip. The angle between the normal direction to the lamellae surface and the extrusion direction, as it follows from Figures 3 and 4 is about 30°.

Hence for the core of the studied specimens is typical arrangement of layerlike lamellae and lamellar stacks are arranged as parquet boards, *a* axes of the crystalline lattice of polyethylene being inclined. They form with the surfaces of the lamellae angles up to 30°. Such a structure resembles the texture of the rolled polyethylene.[12] Conditions of crystallization of the polyethylene melt in the core of the strip are evidently close to the conditions causing structural rearrangement caused by rolling. Formation of specific highly oriented *c* texture at the initial stage of crystallization is due to the same factors that occur in the row crystallization model of Keller.[10,11] As was shown, with high shear stresses and rapid cooling, according to this theory, formation of highly oriented *c* texture is possible.[8,9] It is evident that under the extrusion conditions corresponding to formation of *a* texture, crystallization of polymer in bulk occurs in the absence of considerable pressure from the rolls. If a great amount of the melt is fed to the rolls, some of the melt in the core of the strip is squeezed in the opposite direction, therefore, mostly crystallized polymer passes between the rolls. Thus crystallization in the core of the strip with high shear stresses and pressure leads to formation of specific inclined arrangement of the lamellae respective to the extrusion direction. In the surface layer, whose texture due to shear stresses is frozen, structure with rotation of lamellae around the direction of the *b* axes of lattice is formed.

Differences in texture of the surface layers and in the core of the strand studied allows the conclusion to be drawn about the involved differences in mechanical properties of the layers. The three-layer sandwich formed depending upon the extrusion mode, this way or other, reflects properties of every constituent layer. This latter fact evidently enables modifying the properties of such films in the desirable direction.

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