

The Structural Changes of Polyethylene Film during Punch Deformation

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An experimental results concerning changes of supermolecular structure of polyethylene membrane during punch deformation process is presented. Disc-shaped specimens from low-density polyethylene film (LDPE) processed by extrusion blowing method were cut out and loaded by steel spherical punch. The scanning electron microscopy (SEM) and X-ray diffraction methods were used in order to investigate polyethylene structure. Changes of crystalline formation are presented in polyethylene membrane in different zones of formed polymeric shell. The dimensions of supermolecular formations and peculiarities of their changes after punch deformation of LDPE film were determined.

Keywords: polyethylene, supermolecular structure, membrane, punch deformation, scanning electron microscopy, X-ray diffraction method.

INTRODUCTION

The earlier investigations of low-density polyethylene (LDPE) film behavior during punch deformation showed, that a thin-walled shell with three typical zones such as top, neck and edge is formed after specimen loading perpendicularly to clamping by punch [1]. The size of formed different zones depends on the friction between punch and membrane [2] and on both the size and location of the local defects in specimen [3]. Naturally, the testing conditions have influence on the parameters of the typical punch deformation curve “force – deflection”. It is also known, that the deformation of polymer body causes the changes of its supermolecular structure. For example, polymer yielding (necking) is accompanied by essential fracture phenomenon of structure elements in the various forms of secondary structure [4 – 9].

The aim of this work was to determine the changes of supermolecular formations of LDPE film in the different zones of polymeric punch-formed shell.

METHODS

The subject of the investigations was LDPE film processed by an extrusion blowing method and thickness of which was $\delta = 0.15 \pm 0.01$ mm.

The punch deformation tests were performed at ambient air conditions using a special device [1, 2]. Disc-shaped specimens ($R = 39.9$ mm) were loaded by steel spherical punch ($r = 30.0$ mm) up to rupture. Deformation rate was $v = \text{const} = 100$ mm/min. The friction between specimen and punch was changed using the interlayer of talcum. The samples for the structure investigations were taken from the typical zones of polymeric shell (Fig. 1), i.e. from the edge, neck (zones 2 and 3) and top (zone 1).

Scanning electron microscopy (SEM) was performed by apparatus JEOL JSM 5600 and X-ray diffraction method (diffractometer DRON-6, wave length $\lambda = 1.537$ nm) were used to investigate polyethylene structure.

The samples before SEM analysis were coated by Cu (copper) layer. Samples in the clamps of diffractometer were fixed in two ways, i.e. extrusion axis of LDPE film was oriented in vertical direction and, in the second way, extrusion axis of the film was perpendicular to the specimen clamping (vertical) direction. In this way, two typical X-ray diffraction patterns were recorded for the same sample.

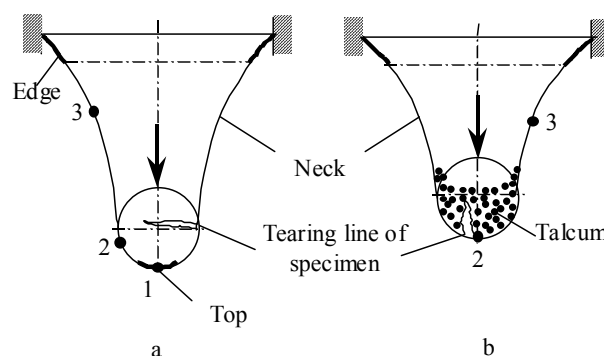


Fig. 1. The schemes of specimen punch deformation and the zones of sample taking: “dry” deformation (a); deformation with interlayer of talcum (b)

The intensities of LDPE characteristic reflexes and their ratio, crystallinity and crystal sizes were defined on the basis of the known method [10].

RESULTS AND DISCUSSION

Polyethylene is a crystalline polymer. During formation of LDPE film by an extrusion blowing method (by method of sleeve extension by compressed air) it is biaxially extended. Such technological processing has influence on the structure of LDPE film.

The macroscopic investigations of LDPE film surface show formation of the striations on the surface of the samples cut in the film machine direction. Microscopically increased strias resemble to the scuffmarks of different depth and the width of the range of 5 – 20 μm . According to this, it can be stated, that LDPE film processed by this kind of industrial method has an oriented structure.

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Table 1. The results of X-ray spectra analysis for LDPE film (thickness $\delta = 0.15 \pm 0.01$ mm)

Sample marking	Sample characterization	Reflex (110) intensity	Sample thickness δ , mm	Intensities ratio I^{110}/I^{200}
0	control	4500	0.15	14.86:1
1*	top	4500	0.15	13.2:1
2*	neck on punch	2690 and 2000	0.03	1.36:1
3*	neck below punch	2700	0.03	–
OT	control heated	6500	0.19	6.2:1
3T*	neck heated	4300	0.13	5.1:1

Notes: * samples taken from neck points (Fig. 1); $L = 30.7$ nm (initial film); Crystallinity – 69.4 %.

Usually, fibril structure, commonly of all supermolecular formations, is observed in the oriented crystalline polymers. The fibril length is several times larger its diameter. Besides, a fibril is a formation of a complicated structure for which crystalline and amorphous phases are characteristic. In non-orientated structures, i.e. in polymers processed by a hot moulding, a fibril is a constituent of the larger crystalline forms such as crystallites or spherulites.

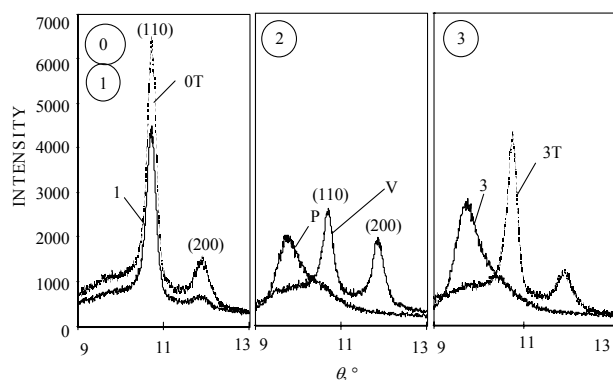


Fig. 2. X-ray diffraction patterns for the control shell zones (see Fig. 1 and Table 1); V – vertical orientation of film extrusion direction in respect to specimen clamping in diffractometer; P – perpendicular orientation of film extrusion direction in diffractometer

The analysis of X-ray results (Table 1, Fig. 2) revealed that the essential changes of LDPE film structure occurred in the neck zone of the shell. The film structure in the top zone of the shell remains almost unchanged compared to that one of the control sample. X-ray diffraction patterns of the samples taken from the shell neck zone differ essentially as compared to those ones of undeformed sample. These differences depend on the sample location in the neck zone in respect to the punch. X-ray diffraction spectra (Fig. 2) of the sample taken from the shell zone (Fig. 1, 2) lying on the punch surface depend on the orientation of the film extrusion direction in respect to sample clamping in diffractometer direction. The appeared creases near the specimen tearing line influence the shape of X-ray diffraction spectra. For this reason, the two different X-ray diffraction spectra were recorded. When LDPE film extrusion direction was parallel to sample clamping in diffractometer (vertical) direction (V in Fig. 2), the X-ray spectra had two typical reflex (110) and (200). After rotation of sample at a 90° angle, the width of the X-ray spectra increased (Fig. 2, P) and their typical

shapes changed compared to those ones in the case of the vertical orientation of film extrusion direction (Fig. 2). Following these results, it can be stated that the polymer film in the neck zone becomes more amorphous as compared to those of undeformed.

X-ray diffraction spectra of the samples from the neck zone located below the punch (Fig. 1, 3) were uniform in shapes, but were flared out (Fig. 2, 3). It shows that essential changes of LDPE film structure occurred in the shell neck zone located below the punch, i.e. in the zone, which is deformed without additional friction.

The essential changes of both geometrical parameters and X-ray spectra were observed after film heating up to the melt point and after latest slow cooling of it. After the thermal operation the initial thickness of the film increased and varied from 0.15 mm to 0.19 mm. Thickness of the samples from the shell neck zone 2, 3 varied from 0.03 mm to 0.13 mm. After heating X-ray spectra showed the increase of typical reflex (110) for undeformed sample OT. The X-ray spectrum of the sample from the neck zone (sample 3T*) is similar to those of the control sample (0). There are different only the ratios of typical reflex intensities (Table 1). Besides, the obtained results of X-ray diffraction showed that the size of crystalline formation is equal to about 30.7 nm and crystallinity is about 69.4 %. The investigations were also performed to determine the kind of crystalline formation. Samples taken from the typical shell zones (Fig. 1) were investigated. Two types of samples were carried out: undeformed (initial) film or top of shell, the thickness of which is close to thickness of initial film, and the samples from the deformed film from neck zone, thickness of which was approximately equal to 20% of initial film thickness.

For the film deformed up to yielding point the fragments of surface roughness (striations) are characteristic (Fig. 3, a). On the line of neck “born” the sharp contrast is seen (Fig. 3, b). The separating line divides the zone of initial film (shell top zone) with very smooth surface (Fig. 3, b) from the neck zone with the significant changes of film structure, where the formations similar to yarns are seen. Threadlike structure of supermolecular formations is seen only in the some area of the investigated surface of film because of difference of film thickness of 5 times on the line which separates top zone from the neck zone (Fig. 3, b).

Film surface in the neck zone, which is remote from the shell top zone (Fig. 4), is smoother and optically more transparent. The texture of the one formation type is seen in the total area of film surface.

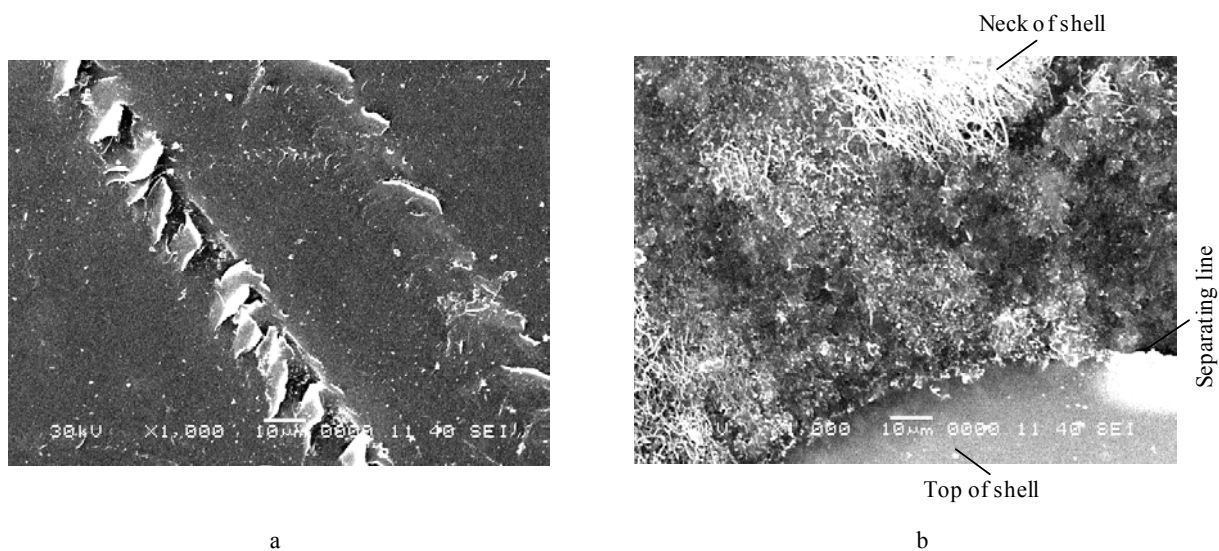


Fig. 3. The fragment of striation of LDPE film surface: for the control sample (0) (a) and strip of neck “born” near the top of shell: for sample taken from the top zone of shell (1) (b) (see Fig. 1 and Table 1), bar length – 10 µm

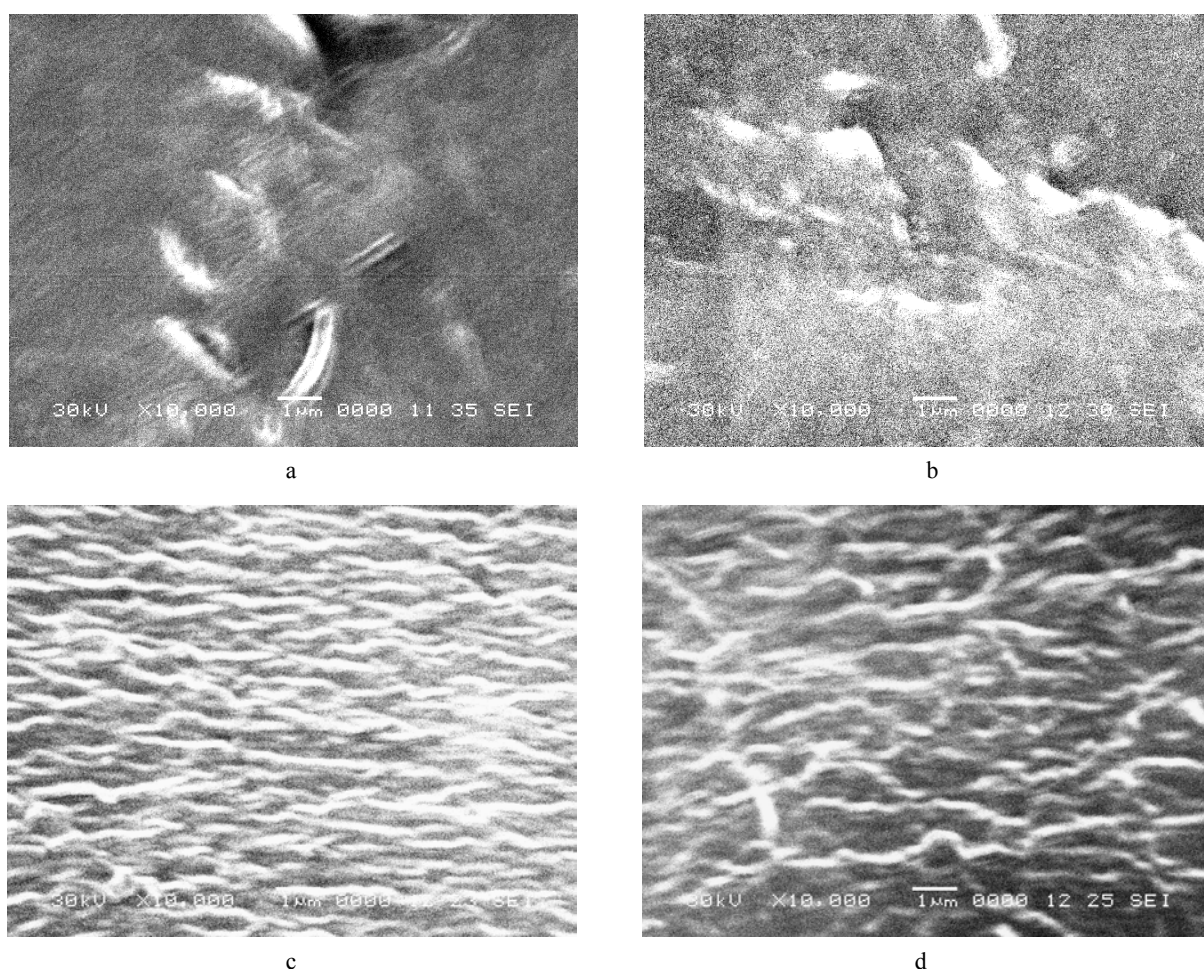


Fig. 4. The SEM microphotographs of LDPE film surface in control zones of shell: undeformed film (0) (a), in the top of shell (1) (b), in the neck lying on the punch (2) (c) and in the neck below punch (3) (d), bar length – 1 µm

The texture is similar to yarn or threadlike structure, which is oriented to the machine direction and, presumably, composed from fibrils (Fig. 4, c and d).

The comparison of the obtained microphotographs have shown, that the shape and linear dimensions of

crystalline formations remain unchanged independently on sample taking location, but only slight differences of compactness were seen. It can be seen (Fig. 4) that fibrils locate more densely in the neck zone lying on the punch surface (Fig. 4, c) compare to those ones in the neck zone,

which is below the punch (Fig. 4, d). In the lower part of neck the fibrils seems located sparsely, i.e. the crystallinity of the LDPE decreases.

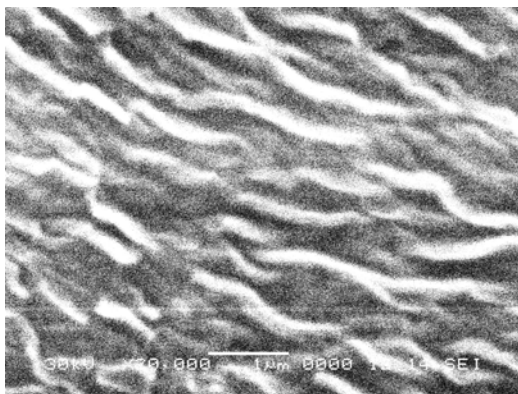


Fig. 5. The arrangement of structure formations in the neck zone of shell in point 3 (Fig. 1), bar length – 1 μm

The dimensions of the structure elements were specified for the samples obtained from the neck zone (Fig. 5): the diameter varied in the range of 200 – 250 nm and length was equal to several micrometers.

Additional information about changes of LDPE supermolecular structures wasn't obtained after heat-treatment of specimens. After heating the film surface became smooth and investigations of deeper layers of film surface using scanning microscope without the additional treatment of them was unsuitable. Only presumption can be made that after film heating fibrils can be lied more densely without formation of new supermolecular structures.

CONCLUSIONS

1. The dimensions of supermolecular formations and peculiarities of their changes after punch deformation of LDPE film processed by extrusion blowing method were determined.
2. The main unit of supermolecular structure of LDPE film is fibril, which is oriented in the machine (extrusion) direction. The average value of its

diameter is in the range of 200 – 250 nm and length is equal to several micrometers.

3. After punch deformation the essential changes of structure formations were obtained in the neck zone of shell.
4. The fibril structure of LDPE film is enough stable. After both punch deformation and heating of film, fibrils lies more densely (or rarely), but they didn't fracture and didn't create larger formations.

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