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MORPHOLOGY AND ORIENTATION OF PP-STRUCTURAL FOAM MOLDINGS

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ABSTRACT

An experimental study was conducted to investigate the interaction between the macrostructure and morphology of PP-structural foam moldings made by gas-counter pressure process by egression of foamed melt from the core of the molding. The structural foam moldings, center-gated cylindrical plate "disc" (diameter 1800 mm. high 11 mm) were produced on an in-line injection molding machine KuASY 800/250, varying the shot weight and melt temperature. The polymer used was isotactic polypropylene "Buplen" 7523 with 1 wt% chemical blowing agent (azodicarbonamide) added. The morphology, orientation, and processes of non isothermal phase transition have been studied using polarized optical microscopy, SALS, DSC and birefringence. Samples were cut from the discs at different distances from the gate. The presence of a two-layered structure was observed in the solid skin: an outer smectic layer and an inner particular crystalline layer. The thickness of the smectic layer and size of spherulites from skin to the foamed core were determined. The orientation in radical and tangential direction of the flow and perpendicular to the disc surface were studied in mold filling and egression stage. The fixed orientation in final moldings is a complex picture of bubble growth, bubble orientation and shear flow. It was found that the radical orientation decreases with the

distance from the gate. Maximum orientation is located in the solid skin, and minimum in the foamed core, and was shown by means of a birefringence profile.

INTRODUCTION

From a macroscopic point of view, the injection molded structural foams exhibit a sandwichlike architecture consisting of a cellular core surrounded by a relatively solid integral skin. The formation of such a structure depends on the processing conditions and techniques used. The gas-counter pressure process by egression of foamed melt from the core of the molding is an attractive method for manufacturing structural foams. Characteristically for this process, is the two-directional motion and foaming of the gas-containing polymer melt during the mold filling and egression stage. Furthermore, the gas-counter pressure controls the skin thickness, density, and structure of the cellular core affected by the quantity of the egressed polymer melt [1-3]. From a microscopic point of view, an injected-molded polypropylene shows a multi-layered structure of skin and core in cross section. There are many systematic works reported in the literature dealing with details of the layered structure by means of optical microscopy, electron microscopy, X-ray methods (WAXS and SAXS), birefringence [4-8]. On the contrary, the literature data on microstructure of the structural foams are comparatively scarce [9, 10]. Hornsby *et al.* reported on the formation of structural foam cell wall spherulites, and on the dimensions and shape of the spherulites.

The aim of the study is to investigate the interaction between the macro-structure, morphology, and orientation of polypropylene structural foam moldings.

EXPERIMENTAL

The polymer used was commercial isotactic polypropylene "Buplen" 7523, a Bulgarian product, (density $\rho = 0.901$ g/cm^3 and MFI (230/2,16) = 3.5 g/10 min). The chemical blowing agent was azodicarbonamide "Genitron"EPA, which generates nitrogen in the temperature range of decomposition from 170 to 210°C. The polymer in pellets form was mixed with 1.0 wt% blowing agent powder by dry tumbling

The object of investigation was a center-gated cylindrical plate "disc" (diameter 180 mm, height 11 mm), The structural foam samples were molded on a on-line injection molding machine KuASY 800/250 fitted with a hydraulic shut-off

nozzle to prevent the leakage of gas-containing polymer melt before the injection. They were prepared by the following operations: injection of gas-containing polymer melt into a tempered and pressurized with nitrogen, mold cavity, and foaming by egression of foamed melt from the core of the molded part back towards an accumulator.

The melt temperature T_m was varied from 200 to 260°C, and the shot weight from maximum shot ("full shot") to minimum shot ("short shot") below which the production of good quality parts is not impossible. The other processing conditions were constant: mold temperature T_f - 20°C, cooling time t - 5 minutes, gas-counter pressure P_g - 1.0 MPa.. Samples were cut from the discs at different distances from the gate (20, 40, 60, 80 mm) parallel and perpendicular to the direction of the flow.

The morphology, orientation, and processes of nonisothermal melting and crystallization have been studied using polarized optical microscopy, small angle light scattering (SALS), birefringence, and differential scanning calorimetry (DSC). Samples were cut from the discs at different distances from the gate (20, 40, 60, 80 mm) from the gate parallel and perpendicular to the direction of the flow (Figure 1). The microtomed sections (50 μm thick) were mounted between microscope slides using Canada balsam.

Optical microscopic observation were made with a MIN-8 polarizing light microscope. The H_v-pattern of SALS were obtained by He-Ne laser equipment.

The orientation in radial $(\Delta N)_r$ and tangential $(\mu N)_t$ direction of the flow and perpendicular to the disc surface $(\Delta N)_p$ were studied by birefringence in filling and egression stage using a polarizing light microscope with a Berek compensator.

Calorimetric measurements were made with Perkin Elmer DSC-7 equipment with a heating and cooling rate of 10°C/min.

RESULTS AND DISCUSSION

Cellular Structure

The formation of cellular structure by gas-counterpressure process by egression of foamed melt from the core of the moldings has been discussed in detail in our previous studies [2, 3]. Here, we shall describe briefly two basic stages of this process: mold filling and egression. The mold filling with gas-containing PP-melt runs at relatively high injection pressure and shear rate, rapid cooling of the melt in the mold walls, and under continuous influence of gas-counterpressure on the advancing meltfront. The viscosity of the gas-containing PP-melt is mainly a

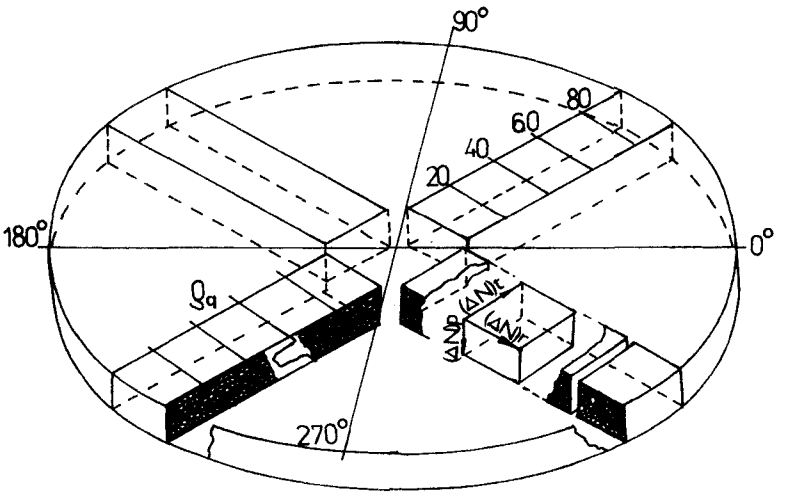

Figure 1. Center-gated structural foam specimen and the position of microtomed section from the gate.

function of the melt temperature. After mold filling with maximum shot weight, under conditions of limited foaming, the bubble growth compensates the shrinkage as a result of crystallization of the PP-melt. The real foaming of gas-containing PP-melt begins in the egression stage. The combined bubble growth gives rise to an axial pressure gradient in mold cavity, which drives the foamed melt with low shear rate from the melt towards an accumulator. A similar phenomena is observed in mold filling with minimum shot weight, but in this case, the axial pressure gradient drives the foamed melt to fill the mold cavity. The viscosity of the foamed PP-melt is mainly a function of the expansion grade.

Figure 2 illustrates the bubble morphology and corresponding diagrams of density distribution across structural foam moldings in filling and egression stage. The diagrams were obtained by measuring the amount of light transmitted through X-ray photographs on cross section of the prism cut off from the test specimens. It is seen that the skin thickness and the core density decrease after egression of foamed melt from the moldings. Obviously, due to changing pressure, shear rate and shear stress fields, the bubbles change their orientation, but it is always in the direction of the motion of the melt. It is well known that for uniform flow the shear stress is zero at the centerline of the flow, and maximum at the boundary. Therefore, the bubbles close to the skin are elliptical in configuration and oriented in direction of

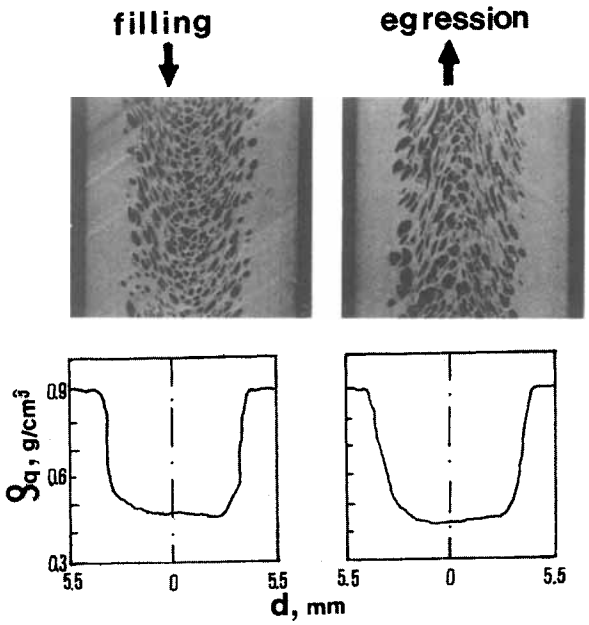

Figure 2. Photomicrographs of bubble morphology in mold filling and egression stage and corresponding density distribution across the PP-structural foam molding with overall density $\rho = 0.63$ g/cm^3 (distance from the gate 60 mm; melt temperature 220°C; "short shot").

shear. The fixed bubble orientation in the final moldings is in the direction of egression that is in accordance with Thron's earlier investigations [11].

Spherulite Morphology

Two layers are observed in the unfoamed skin by the optical microscopy: an outer smectic (amorphous) layer and an inner particular crystalline layer. The thickness of the smectic layer varies from 60 to 100 μm with increasing of the melt temperature from 200 to 240°C (Figures 3a and 3b) This thickness depends on the melt temperature, heat conductivity, and temperature gradient. An increase of the size of the spherulites from the skin to the foamed core is observed, as is shown in the series of optical micrographs on Figure 3 (b-e) and Figure 4 (b-e). This difference in size is due to the different conditions of crystallization in the bulk of the samples. The spherulites in the foamed core are the largest (Table 1). Most probably, the reasons for that are as follows: on the one hand, the surface of the cells is not a nucleus-former, on the other hand, the low heat conductivity, due to the

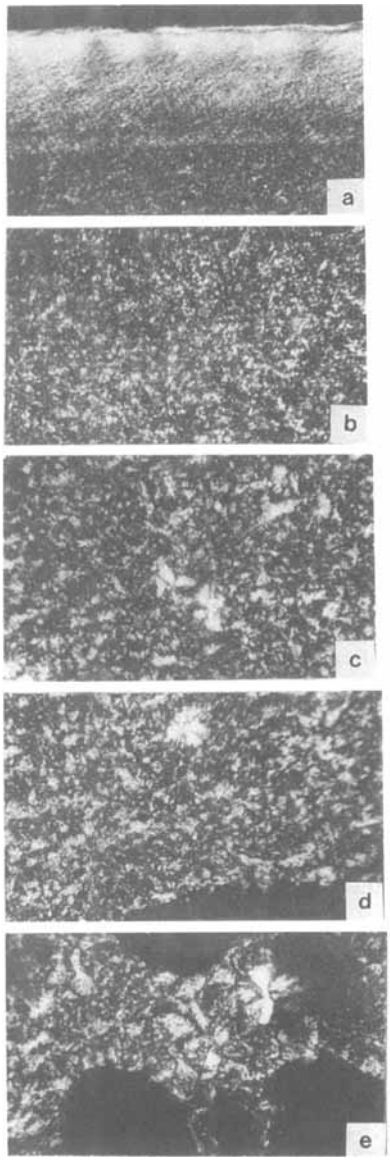

Figure 3. Optical micrographs of cross-sections of PP -structural foam molding at melt temperature 200°C x45.

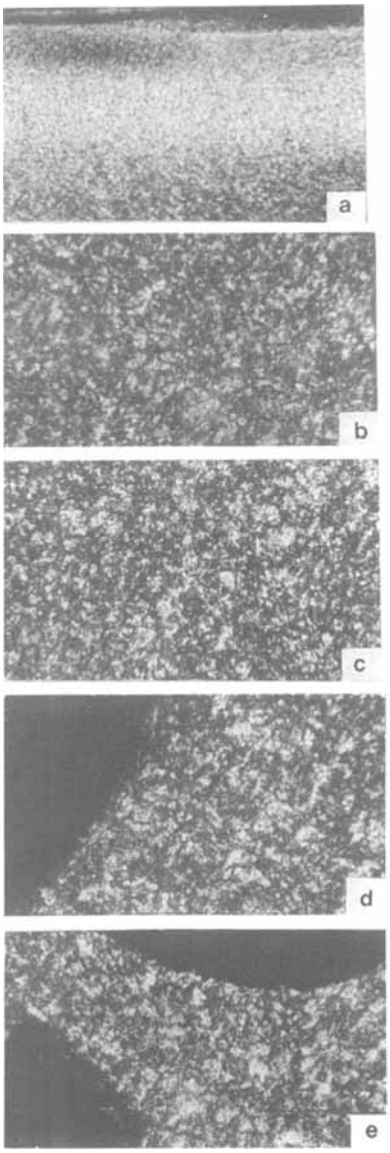

Figure 4. Optical micrographs of cross-sections of PP-structural foam molding at melt temperature 240°C x45.

TABLE 1. Spherulite Size and Parameters of Phase Transition

	Spherulite size [μm]		Melting temperature [K]		Enthalpy of melting [cal/g]	
	skin	core	skin	core	skin	core
200°C	22	35	434,8	431,9	16,01	17,06
240°C	13	37	438,4	4371	16,09	16,71

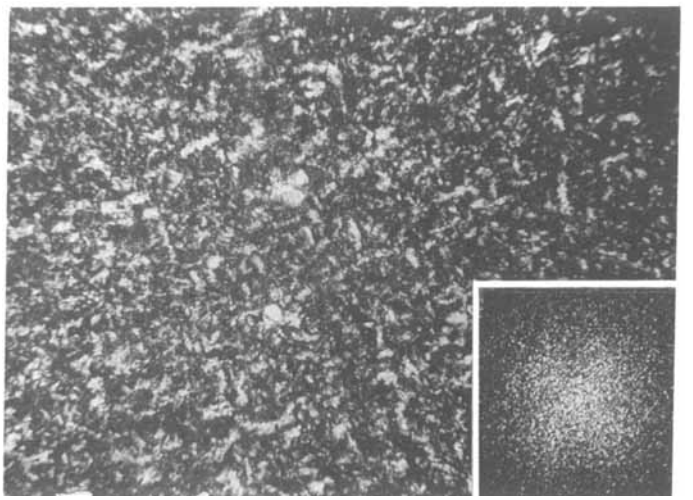

Figure 5. Optical micropraphs and corresponding H_V-pattern in the skin of PP-structural foam molding.

gas-phase, keeps the temperature long enough for the growth of the formed spherulites.

The measured spherulite size in the unfoamed skin is in accordance with the average spherulite diameter, calculating from H_V-pattem of SA1 S. From the H_V-pattern of the crystalline part, it can be seen that the spherulites are not flattened (Figure 5). The influence of the surrounding birefringence of amorphous areas on the spherulite H_V-patterns is observed .

The temperature and enthalpy of the phase transitions are determined by DSC curves, presented in Figure 6, at two melt temperature in the skin and in the core (Table 1). The melting curve for the skin, besides the main peak, has another, slightly expressed peak, due to reorganization and the following melting of the

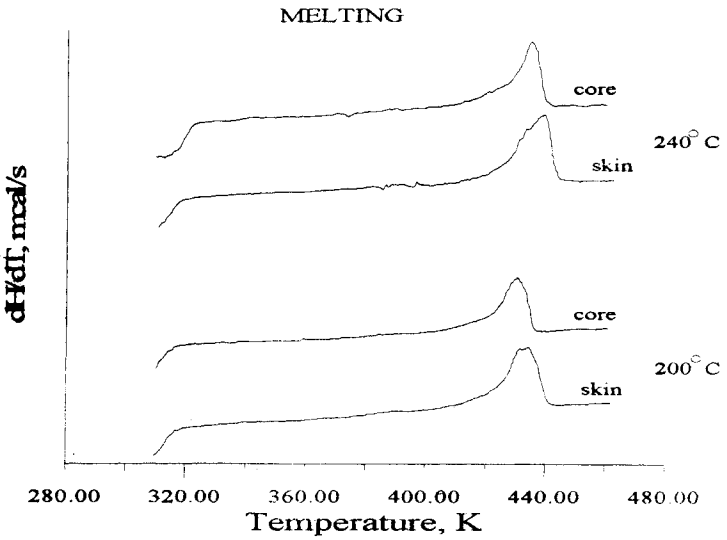

Figure 6. DSC-curves of melting of PP-structural foam molding.

smectic layer. It is established that the spherulites in the skin melt higher temperature. Moreover, the melting peak of both samples at different melt temperature is removed from each other in a few degrees. According to us, the reasons are the higher orientation in the skin, and the imperfection of the spherulites in the foamed core.

Orientation

Figure 7 shows the birefringence, related to the orientation in radial direction of the flow, vs. the distance from the gate in solid unfoamed skin of PP-structural foam molding. As expected, the radial orientation in mold filling with "short shot" decreases with increasing the distance from the gate. The reason is the decrease of the velocity of the advancing melt front with increasing of the distance into the mold. The radial orientation visibly decreases near the gate in egression stage due to the back flow of foamed melt. In the furthest areas there is no back flow and the nucleated bubbles grow at the place. In this case, the molecular relaxation is the process which reduces the orientation. The data confirm our assumption that reorientation caused by motion of foamed melt from the interior of the moldings appears near the gate. It is established that the radial orientation increases with increasing of the shot weight. The higher values of radial orientation are due to the orientation in mold filling with "full shot" caused by higher injection pressure and

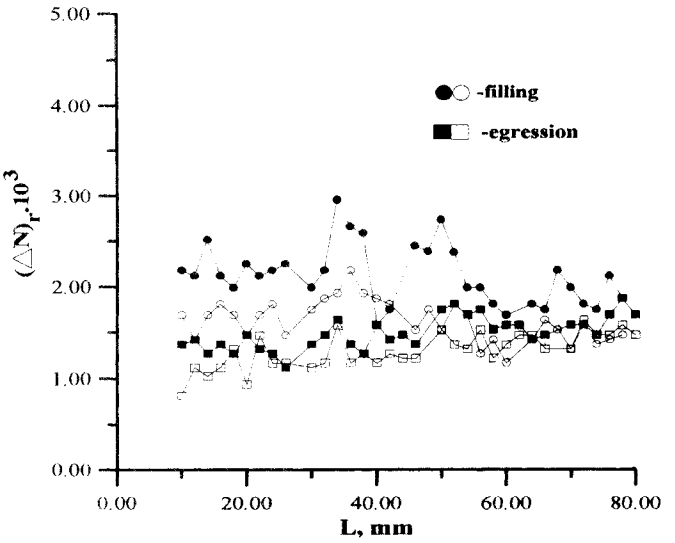

Figure 7. Birefringence vs. the distance from the gate in different layers (●■ - 0. 3 mm; ○□ 1.4 mm from the surface; melt temperature 220°C; "short shot").

the lower contribution of the back flow in egression stage to the reorientation. The presented results are in accordance with our investigations on macrostructure parameters (local density, distribution across the section, bubble orientation and bubble morphology.

The birefringence profile across the section of PP-structural foam molding at the distance 40 mm from the gate are given in Figure 8. At first glance, it is seen that maximum orientation is located in the skin. The radial orientation is at maximum closeness to the surface of the skin in mold filling (curve 1) and egression (curve 2) stage and decreases with the distance to the centerline. The tangential orientation in mold filling (curve 1) is maximum at the superficial layer of the skin. The described dependencies are in accordance with the Tadmors model [12], which attributes the radical orientation to the shear forces and the tangential orientation to the elongation forces fountain like flow. The decrease of radial orientation is more strongly expressed on the boundary between the solid skin and foamed core (transitional layer) in egression stage because of the shear forces in back flow between the frozen skin layers. In the foamed core, which cools slowly, the macromolecules have sufficient time to relax and the orientation is very low. During that time large spherulites reformed.

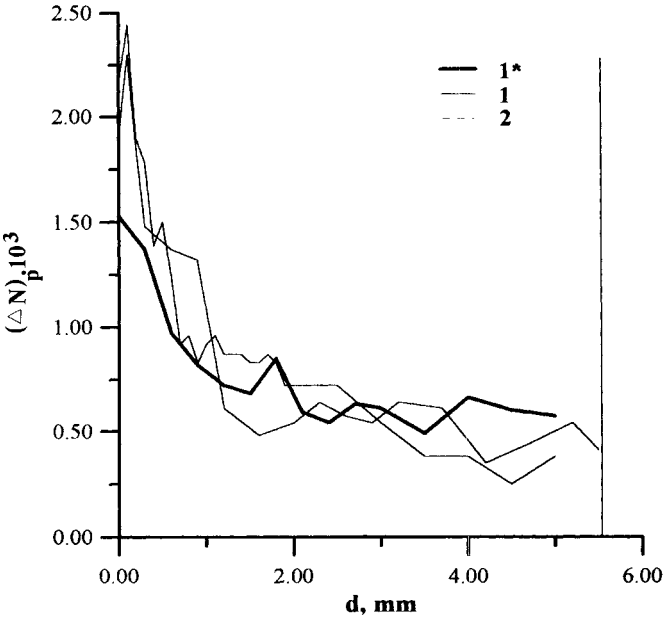

Figure 8. Birefringence profile across the section of PP-structural foam molding (distance from the gate 40 mm; melt temperature 220°C; "short shot").

CONCLUSION

The presence of two layers is found in the solid skin by optical microscopy: an outer smectic layer, and an inner particular crystalline layer. Large spherulites are presented in the foamed core. The structure and the size of the both layers and of spherulites have been clarified by measurements of SALS and melting behavior.

The fixed orientation in final PP-structural foam moldings is a complex picture of bubble growth, bubble orientation and shear flow in two directional expansion process. The birefringence profile across section show, that maximal orientation is located in the solid skin. It has been proved that the two directional expansion process causes reorientation in the transitional layer in the areas near the gate. The orientation is minimum in the foamed core because of low cooling rate. l he distribution of the orientation in the structural foam moldings is in accordance with the macrostructural parameters.

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