Effect of an Obstacle During Processing on the Weld Line of Injection-Molded Glassy Polystyrene: Microhardness Study

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ABSTRACT: The microhardness (H) technique is used to characterize the quality of the weld line in injection-molded glassy polystyrene by means of a cylindrical obstacle. In particular, the effect of the indentation location (closer or further from the obstacle edge parallel to the injection direction and across the weld line), both on the surface and in the bulk, was examined. Only for surface measurements close to the obstacle (up to 10 mm) a well-pronounced decrease in H (~30%), followed by a sharp increase in a narrow distance (0.20–0.25 mm), was observed. For the bulk measurements on the same location a slight decrease in H was detected. Additional H measurements made up to 60 mm from the obstacle for both cases showed that the weld line remains

INTRODUCTION

The use of microhardness (H) to characterize the changes in microstructure, molecular orientation, and micromechanical properties of injection-molded polymer materials has been the object of increasing interest.¹⁻⁴ In addition, it is known that process variables induce important changes in the microstructure and properties of injection-molded materials.^{5,6} Hardness variations often occur in the surface and across the thickness of the molded samples. As a result, the mechanical properties can be controlled by processing variables such as melt and mold temperature, injection pressure, and mold design, for example.²

Earlier studies⁷ have shown that microhardness may give useful information about the correlation be-

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undetectable. The results obtained reveal that the presence of a cylindrical obstacle causes the formation of a weld line on and near the surface only at distances not exceeding the obstacle diameter. At larger distances, because of the effective mutual interdiffusion of polymer chains, the two parallel fronts coming from the two sides of the obstacle developed a homogeneous material without any weld line according to the microhardness test. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3362–3367, 2004

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tween processing parameters near and at the weld line or knit line, that is, the region at which the separated melt fronts reunite. In practice, this occurs in injection molding (e.g., after a flow obstacle), in the case of multiple gating for melt streams of the same material, or in the case of two-component injection molding for melt streams of different polymer materials.⁸

In a previous study⁹ we reported on the H variation across the weld line, arising when the two opposite flow fronts fill the cavity of the mold using two glassy polymers, polycarbonate (PC) and polystyrene (PS). A large hardness difference between H measured away from the weld line and H measured at z = 0 (H_{min}) was found. For PC this difference was about 20 MPa (\sim 14%), whereas for PS it was larger than 50 MPa $(\sim 30\%)$.⁹ The measurement of H along the injection direction and across the weld line for the PC and PS samples, containing a pigment for better visualization of the flow front, was also performed.⁹ For both polymers, the measured higher H values on the side containing the pigment show the hardening effect of the pigment within the polymer. Such an asymmetry is in contrast to that of the case without using pigment.⁹

In a more recent work we extended the above studies on the same two glassy polymers (PC and PS) processed using a two-component injection-molding system.¹⁰ Specifically, the influence of processing temperature on the H-value across the weld line, arising

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Figure 1 Schematics of an injection-molded plate with an obstacle. The weld line is parallel to the injection direction and the indentation measuring directions are perpendicular to the weld line.

when the two opposite flow fronts meet, coherently filling the cavity of the mold, was examined. It was found¹⁰ that the broadening of the weld line (expressed in the microhardness changes across the line z= 0) depends primarily on opportunities for mutual chain diffusion from the two polymer fronts coming from opposite sides. Such a case is very close to the well-studied phenomenon of physical healing,^{11,12} in which the mutual interdiffusion is determined by chain flexibility and diffusion conditions (temperature, molecular weight, etc.). Furthermore, it was shown¹⁰ that the main factors affecting the quality of the welding at the line z = 0 are the glass-transition temperature (T_g) of the polymer under investigation and the processing conditions: melt temperature, mold temperature, injection speed, and others.

The aim of the present report was to extend the above studies^{9,10} on glassy PS processed by injection molding using a mold with a cylindrical obstacle. In addition, for the sake of comparison, the measurements are carried out on the surface of the molded plate as well as on the "bulk" surface after cutting and polishing at different locations with reference to the obstacle edges across the injection direction.

EXPERIMENTAL

Materials

High molecular weight polystyrene (PS 165 H, T_g = 100°C; BASF AG, Ludwigshafen, Germany) sam-

ples were used in this study. The moldings were prepared in the form of rectangular plates of $100 \times 80 \times 2$ mm with a circular obstacle (diameter of 12 mm). The plates were molded using a melt temperature (T_m) of 240°C and a mold temperature (T_w) of 50°C. The injection rate was 10 cm³/s. From the central part of an injection-molded plate, containing the weld line, six test samples were cut and embedded in a thermoset resin to enhance their fixing during polishing and subsequent measurements.

Techniques

Microhardness was measured across the boundary (weld line) at the surface of every test sample using a microindentation tester with a Vickers diamond indenter. The hardness value (in MPa) was computed from the residual projected diagonal impression, using $H = kP/d^2$, where *P* is the applied force (in N), *k* is a geometrical constant equal to 1.854, and *d* is the length of the projected indentation diagonal (in m). A load of P = 25 mN and a loading cycle of 6 s were used. Indentations were made on a line (designated further as *z*) perpendicular to the injection direction (Fig. 1).

Two types of H measurements were carried out.

1. Measurements on the surface of the plates (Fig. 1)

One indentations series was performed at five different positions (O1 to O5) behind the obstacle (O), and



Figure 2 Schematics of the location of six test samples for microindentation measurements: (a) in the plane perpendicular to the weld line, and (b) test positions with respect of the weld line and edge of the sample.

one indentation series before the obstacle (O-1), as depicted in Figure 1. The location of each series on the weld line is shown in Figure 1. At every series the respective test distance z across the weld line is 2 mm (1 mm from each side).

2. Measurements in the planes perpendicular to the weld line (on the "bulk" surface) (Fig. 2) Six test samples [P1 to P6, Fig. 2(a)] were taken from a

plate in such a way that the cut surfaces [S1 to S6, Fig. 2(a)] are equidistant. On every cut surface two test



Figure 3 Micrograph showing indentation on the surfaces of the injection molded plate near the weld line area (see Fig. 1).

series were performed. The first one was carried out along a line that is parallel to the surface of the sample at a distance of 0.1 mm from the edge and designated further as S1 A. The second test sequence was run through the middle of the gap of the sample and designated further as S1 B. The two test series had a length z = 2 mm across the weld line. This situation is schematically presented in Figure 2(b).

Optical micrographs from the indentation surface (Fig. 1) were taken using a Leitz (Wetzlar, Germany) light microscope in the reflection mode.

RESULTS AND DISCUSSION

Figure 3 illustrates an optical micrograph of several indentations made on the vicinity of the weld line. In contrast to previous measurements,⁹ in which practically only one indentation characterized the steep decrease of H near the weld line, in the present case, according to our recent experience,¹⁰ the same line is defined by at least five indentations, which makes the reported decrease in H more reliable.

Furthermore, the H-values are plotted as a function of the distance z from the weld line for the two types of measurements: on the mold surface (Fig. 1) and on the bulk surface [Fig. 2(b)].

Microindentation hardness on the surface

Figure 4 illustrates the variation in H as a function of *z*, for various indentation series placed at various dis-

tances from the obstacle (up to 60 mm) on the surface of the molding along the injection direction (Fig. 1). For the sake of comparison a measurement before the obstacle (O-1, Fig. 1) was also carried out. The indentation series were performed perpendicular to the weld line as shown in Figure 1, and denoted by O-1 to O5. The (O) point denotes the center of the obstacle, and the (O-1) denotes the indentation series before the obstacle. We denote the position of the weld line as z = 0.

Results show a rather different microhardness behavior depending on the location, before or after the obstacle (O), and particularly how far the test location was from the obstacle (Fig. 1). First of all, one has to stress the fact that, in accordance with expectation, before the obstacle there is no indication for the existence of any weld line (Fig. 4, curve O-1), where rather constant values of H of about 210 MPa are observed.

The situation changes drastically with the first measurement after the obstacle (Fig. 1, O1) being situated closest to the obstacle. Figure 4, curve O1, shows the gradual decrease of H along the z direction, until a



Figure 4 Microhardness H as a function of distance z from the weld line measured on the surface of the molded plate with obstacle for glassy PS. The curves are denoted according to Figure 1.

minimum value at z = 0 is reached. Then, one observes a further increase of H when indenting away from z = 0. The weld line zone containing the H changes is defined within a 0.20–0.25 mm region, which is much smaller than the previously reported one (1 mm) for the same polymer⁹ and about the same in a more recent measurement (0.20–0.30 mm).¹⁰

Most interesting is to note the large hardness difference found between H measured away from the weld line and H measured at z = 0 (H_{min}). This difference is about 70 MPa (~ 30%) (Fig. 4, curve O1). The same difference becomes smaller (35 MPa) for the next measurement series being further away from the obstacle (Fig. 4, curve O2).

The H-values measured at even larger distances from the obstacle (O) (Fig. 1) look completely different, as can be concluded from the other results also presented in Figure 4 (curves O3–O5). There is no decrease in the H-values around the weld line (z = 0)larger than the observed scattering of the experimental points. What is more, the lines observed (Fig. 4, curves O3–O5) as well as the H-values obtained are the same as those for the test before the obstacle (Fig. 4, curve O-1). These results appear to indicate that after some distance from the obstacle (\sim 5–10 mm in the present case, being of order of magnitude of the obstacle diameter), the obstacle does not have any further influence on the melt flow in the sense of formation of a weld line. Similar findings have been reported in the literature (e.g., Mennig¹³).

Microindentation hardness on the bulk surface

The results from evaluation of H performed on the bulk surface after cutting and polishing (Fig. 2) lead to the same conclusion (see Fig. 5).

It should be noted again that measurements of H at a distance of 0.1 and 1 mm from the starting [Fig. 2(a)] sample surface edge [as shown in Fig. 2(b)] were performed. The values obtained are practically identical (compare curves S1A and S1B in Fig. 5).

The H-values from the closest location to the obstacle show, again, a minimum around z = 0 (Fig. 5, curves S1A and S1B) similarly to the case with the measurements on the surface of the injection-molded plates (Fig. 4, curve O1). The main difference between the two cases (Figs. 4 and 5) is the degree of the changes in H. In the last case the decrease in H is only a few percent and indicates only a not very well defined weld line.

Measurements of H at greater distances from the obstacle [Fig. 2(a) samples P2–P6] show that even this small decrease in H (Fig. 5, curves S1A and S1B) is no longer present (Fig. 5, curves S2 to S6) (the data obtained from samples S3 and S5 are not plotted in Fig. 5). From the results of the bulk surface measurements (Fig. 5) one can conclude that very close to the obstacle



Figure 5 Microhardness H as a function of distance z from the weld line measured on the "bulk" surface of the molded plate with obstacle for glassy PS. The curves are denoted according to Figure 2(a).

edge (\sim 5 mm) only a slight indication for the existence of weld line can be detected. For greater distances there are no hints for the existence of such a weld line.

Influence of the temperature

Regarding the influence of the indentation's location, that is, closer or further apart from the obstacle (or, in other words, from the formed hole edge), it should be noted that the differences observed (Figs. 4 and 5) are mostly related to the temperature of the two fronts at the instant they meet. Let us try to get an idea about the temperature difference of the melt closer or further from the obstacle wall.

When the polymer melt comes into contact with the cylindrical obstacle, it splits into two fronts. What is of particular importance for these two fronts is that being in contact with the obstacle (with a temperature T_w = 50°C) they decrease significantly their initial start-

ing temperature of 240°C. For this reason when the two fronts meet immediately after the obstacle there is no mutual chain diffusion resulting in a randomization and homogenization. As a consequence a more or less well developed weld line can be detected at the locations closest to the obstacle.

The reminder of the two melt flows, not in contact with the obstacle, do not experience its cooling effect and for this reason when they meet behind the obstacle they preserve their cavity temperature typical for this part of the mold, which allows their homogenization without formation of any weld line.

This consideration is also supported by the observation that, even for measurement locations being closest to the obstacle but performed on the original sample surface (Fig. 4) or on the "bulk" surface (Fig. 5), the weld line is differently expressed (compare curves O1 and O2 of Fig. 4 with curves S1 A and S1 B of Fig. 5). Because the melt in the middle part of the sample is not in direct contact with the mold cavity walls, their welding conditions are more favorable compared with those on the sample surface.

The above interpretation (effect of melt temperature and location of the microindentations across the welding line, as derived from the H measurements on the surface and in the bulk of glassy PS processed using a mold with a cylindrical obstacle) supports the analogous measurements on PS and PC both processed at two melt temperatures but the same mold temperature on a two-component injection-molding machine. Again, the dominating role of the melt temperature, particularly when the two polymer fronts meet, is stressed. One should note here that the case under discussion is very close to the well-studied phenomenon of physical healing,^{11,12} where the mutual interdiffusion is determined by chain flexibility and diffusion conditions (temperature, molecular weight, etc.).

CONCLUSIONS

1. In agreement with preceding results,^{9,10} microhardness was shown to be an appropriate technique that can accurately define the region across the weld line in injection-molded parts and can furnish information about the local degree of mutual interdiffusion within the weld boundary.

- 2. The broadening of the weld line as well as its appearance and disappearance (expressed in the microhardness changes across the z = 0) depend primarily on the possibility for mutual chain diffusion from the two polymer fronts meeting behind the obstacle.
- 3. It is shown that welding behind the obstacle is more effective in the bulk than on the surface of the injection-molded sample.

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References

- Baltá Calleja, F. J.; Baranowska, J.; Rueda, D. R.; Bayer, R. K. J Mater Sci 1993, 28, 6074.
- Rueda, D. R.; Kubera, L.; Baltá Calleja, F. J.; Bayer, R. K. J Mater Sci Lett 1993, 12, 1140.
- Flores, A.; Bayer, R. K.; Krawietz, K; Baltá Calleja, F. J. J Macromol Sci Phys 2000, B39, 749.
- Ania, F; Dunkel, M; Bayer, R. K.; Baltá Calleja, F. J. J Appl Polym Sci 2002, 85, 1246.
- Birley, A. W.; Hawort, B.; Batchelor, J. Physics of Plastics: Processing, Properties and Materials Engineering; Hanser: Munich, 1992.
- Eder, G.; Janeschitz-Kriegl, H.; Liedauer, S. Prog Polym Sci 1990, 15, 629
- 7. Heck, S.; Poellet, P. VDI-Bericht 1989, 731, 167.
- Nguyen-Chung, T.; Plichta, C.; Mennig, G. Rheol Acta 1998, 37, 299.
- Garcia Gutiérrez, M. C.; Rueda, D. R.; Baltá Calleja, F. J.; Kuehnert, I.; Mennig, G. J Mater Sci Lett 1999, 18, 1237.
- Boyanova, M.; Baltá Calleja, F. J.; Fakirov, S.; Kuehnert, I.; Mennig, G. Adv Polym Technol, to appear.
- 11. Kausch, H. H. Polymer Fracture; Springer: Heidelberg/New York, 1987.
- 12. Wool, R. P. Polymer Interfaces; Hanser: Munich/New York, 1996.
- 13. Mennig, G. Angew Makromol Chem 1991, 185/186, 179.