Toughness Profile in Injection-Molded Polypropylene: The Effect of the β-Modification

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ABSTRACT: Fracture toughness characterized by the J-integral method has been evaluated along injection-molded bars of isotactic polypropylene. A significant increase in toughness with decreasing distance from the specimen gate has been observed with maximum steepness of the dependence in the central part of the specimen length. Parallel analysis of wide-angle X-ray diffraction patterns has shown a similar dependence of the crystalline β-phase concentration. It is suggested that polypropylene with β-crystallites has better structural continuity in the amorphous phase and, consequently, higher inherent ductility and superior macroscopic toughness than the related material containing only α-crystallites. Consequences of β-phase gradients for practical toughness testing are also discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2255–2259, 1998

Key words: polypropylene; injection molding; fracture toughness; morphology; polymorphism; crystallinity; X-ray diffraction

INTRODUCTION

Injection molding is the most common way of processing polymers. It is used for the production of a wide range of part sizes, starting from tiny microswitches up to large parts in the automotive industry. Therefore, quite logically, standard test pieces for the assessment of mechanical properties are also frequently prepared by injection molding. The obtained results allow a direct view of the behavior of real injection-molded parts; at the same time, they reflect specific structural features of injection-molded material, such as shell-core effects, orientation gradients, and possible polymorphism in some crystallizing polymers. These structural features, in turn, influence the material's properties. In particular, the favorable effect of the crystalline β-phase on the toughness of isotactic polypropylene has been reported by several authors.[1–5] A dramatic increase in toughness in comparison to conventional moldings was also achieved by shear-controlled orientation and ascribed to molecular alignment.[6]

In this article, an investigation of fracture toughness of injection-molded isotactic polypropylene is presented for notches located at different distances from the specimen gate. At the same time, the crystalline structure has been monitored at the same locations by wide-angle X-ray diffraction (WAXD). Thus, the relation between fracture toughness and the crystalline structure of the material was established.

EXPERIMENTAL

Material

The material used in this study was isotactic polypropylene homopolymer Mosten 58.412 supplied

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by CHEMOPETROL Litvínov, Czech Republic. The manufacturer characterizes the material by a melt flow index of 3 g/10 min (21.2 N, 230°C) and a weight-average molecular weight M_w of about 170,000. From the pellets of this polymer, standard impact testing bars ($4 \times 10 \times 120$ mm) were injection-molded at the Polymer Institute, Brno. A Battenfeld BA 750/200 injection molding machine was used for the production of the bars. The injection-molding conditions are summarized in Table I.

Test Pieces

Single-edge-notch specimens for three-point bending impact testing (length L, 60 mm; width W, 10 mm; thickness B, 4 mm) were prepared from the injection-molded bars of the original length of 120 mm. The notches were introduced by a razor blade and had a depth of 2 mm and a tip radius of 0.2 μm. The location of notches along the edge of the original moldings varied, as shown in Figure 1. Seven various locations of the notch in the original moldings were selected with the distance d from the molding gate being 30, 40, 50, 60, 70, 80, and 90 mm. The test pieces were then cut to the length of 60 mm with the notch located in the center. (The geometrical arrangement of the given impact tester did not allow us to evaluate shorter specimens and, thus, to locate the notch closer to or farther from the molding gate.)

Fracture Toughness Measurements

An instrumented Charpy impact tester PSW 0.4 with 4J work capacity was used for the measurements. Experimental parameters were notch depth a = 2 mm (a/W = 0.2); support span s = 40 mm ($s/W = 4$); pendulum hammer speed $v_H = 1.5$ ms^{-1}. The hammer hit the specimen always in the center

Table I Processing Conditions for the Moldings Used for Impact Testing

Heating zone temperatures	210, 222, and 230°C
Die temperature	240°C
Mold temperature	60°C
Screw compression ratio	2.3
Screw back pressure	5 bar
Injection pressure	627 bar
Holding pressure	627 bar
Holding pressure time	30 s
Freezing time	15 s
Cycle time	60 s

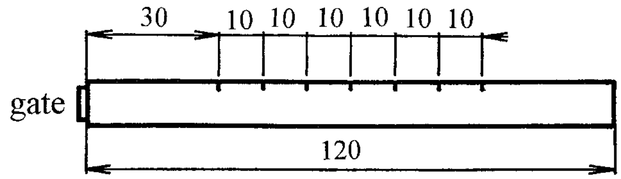

Figure 1 Location of notches in bar moldings for fracture toughness measurements.

of the specimen length and opposite to the notch. The tests were repeated under identical conditions 10 times for the 2 extreme notch locations (d = 30 and 90 mm) and 3 times for the other locations (d = 40–80 mm). An average value and standard deviation of the J-integral were calculated from the individual test results. The experimental procedure is described in more detail elsewhere.[7–9]

During impact tests the load (F)–deflection (f) diagrams were recorded. The total deformation energy up to the maximum impact load (A_G) was divided into elastic (A_{el}) and plastic (A_{pl}) parts. The values of the J-integral were determined by the following eq. (1), proposed by Sumpter and Turner:[10]

$$J_{Id}^{\mathrm{STEA}} = \eta_{el}\frac{A_{el}}{B(W-a)} + \eta_{pl}\frac{A_{pl}}{B(W-a)}\cdot\frac{W-a_{eff}}{W-a} \quad (1)$$

where

$$\eta_{el} = 0.5 + 5.5(a/W) - 5(a/W)^2 \quad (2)$$

$$\eta_{pl} = 2 - \frac{(1-a/W)\cdot(0.892 - 4.476\,a/W)}{1.125 + 0.892(a/W) - 2.238\,(a/W)^2} \quad (3)$$

and a_{eff} is the crack length at the onset of unstable crack propagation.

The specimen size criteria of J_{Id} value are given by[8,9]

$$B;\, a;\, (W-a) \geq \varepsilon\,\frac{J_{Id}}{\sigma_d} \quad (4)$$

where

$$\varepsilon = 224 J_{Id}^{-0,94} (J \text{ in N mm}^{-1}). \quad (5)$$

X-ray Diffraction Measurements

The crystalline structure at varying distances from the molding gate (corresponding to the notch locations) was characterized by WAXD. Diffraction patterns were measured in the interval of diffraction angles 2θ from 5 to 40°. A wide-angle powder diffractometer HZG (Präzisionsmechanik Freiberg) using CuK_α radiation monochromatized with a β-filter was used for the measurements. Profile analysis was applied to the obtained diffraction patterns using the published program.[11] The relative amount of the β-form in the crystalline phase was characterized by the ratio K. The value of K was assessed from intensities of crystalline reflections of α- and β-phase using the following relation:[4]

$$K = I_\beta/(I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3} + I_\beta)$$

where I_β is the integral intensity of 300 reflection of the β-phase, and $I_{\alpha 1}$, $I_{\alpha 2}$ and $I_{\alpha 3}$ are the integral intensities of the 110, 040, and 130 reflections of the α-phase, respectively. These intensity values were obtained with help of profile analysis.

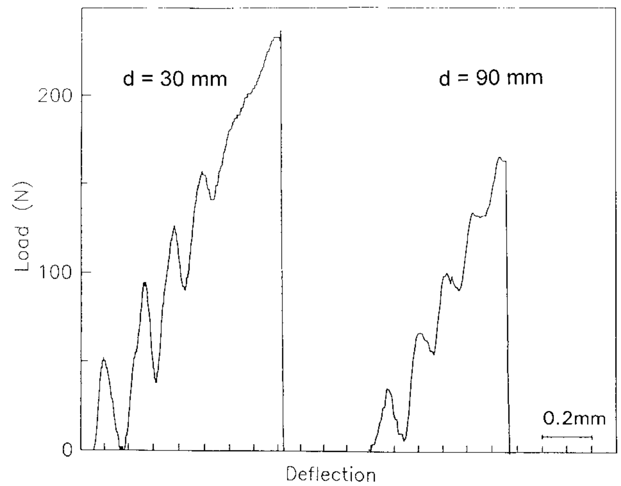

Figure 3 Typical load–deflection diagrams for a notch located at a distance 30 mm (left) and 90 mm (right) from the gate.

RESULTS

The experimental dependence of the J-integral calculated according to eq. (1) on the gate-notch distance is plotted in Figure 2, together with the estimated standard deviation values. A marked decrease in the J-integral fracture toughness with increasing distance can be seen with the steepest decrease in the central part of the bar (gate-notch distance 60 mm). The J-integral values for the 2 extreme notch locations differ by a factor of 1.75. Comparison of the corresponding typical load–deflection diagrams in Figure 3 shows that the decrease of the toughness with the increase of the gate-notch distance from 30 to 90 mm reflects a simultaneous decrease of both load and deflection values. The dynamic modulus of elasticity and the dynamic yield strength also decrease. Nevertheless, it is the fracture energy that appears to be the single key parameter describing this type of behavior.

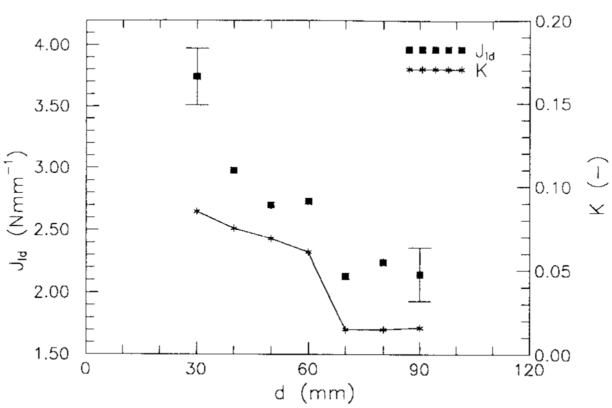

Figure 2 Dependence of fracture toughness expressed by the J-integral and relative β-phase concentration K as a function of distance from the molding gate.

Characteristic parts of X-ray diffraction (XRD) patterns (angular interval 2θ from 15 to 18°) at varying distances from the specimen gate are presented in Figure 4. It can be seen that the 300 diffraction maximum of β-phase decreases and finally vanishes as the distance from the molding gate increases. Along the distance of 60 mm between the nearest and farthest notches from the gate, the β-phase concentration K decreased from 8.5 to 1.5%. In Figure 2, the ratio K is plotted together with the J-integral values as a function of the distance from the molding gate. A similar trend of the 2 dependences is obvious. Thus, we suggest that the observed toughness profile along the length of the molded bars reflects a corresponding gradient in the β-phase concentration.

It is interesting to compare our results with data published elsewhere. Tjong et al.[5] reported a relatively small increment in G_c due to the β-phase crystalline structure (5.3 and 6.7 kJ/m^2 for α- and β-polypropylene, respectively) for an injection-molding polypropylene grade. On the other hand, Karger-Kocsis et al.[3] obtained twice higher values of fracture energy G_c for β-polypropylene prepared with a β-nucleation agent than for a ref-

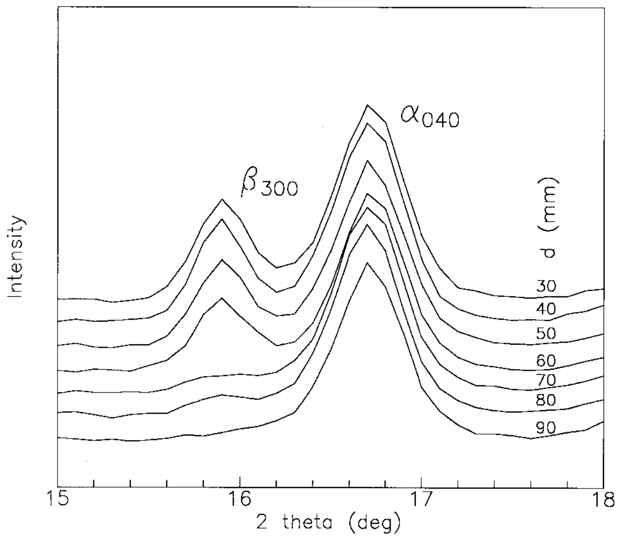

Figure 4 The X-ray diffraction patterns recorded at various distances (indicated at the curves) from a molding gate of an injection-molded bar. For better resolution, the individual diffractograms are shifted along the vertical axis.

erence α-modification.[3] In the present study, a relatively small fraction of the β-modification caused a marked increase in the material toughness; in fact, in the vicinity of the specimen gate, the effect approached that reached by an efficient β-nucleant.[3] This observation seems to indicate a possible long-distance influence of the β-crystalline phase on the material structure in the bulk. This notion should be incorporated in a structural model.

STRUCTURAL MODELS

So far, no unambiguous structural mechanism has been generally accepted to explain the observed effect of the β-phase on the toughness of isotactic polypropylene. Karger-Kocsis has recently suggested[2] that phase transformation toughening, which improves toughness of zirconia-containing ceramics, can also work in polypropylene. He proposed that a stress-induced transformation from less dense (hexagonal β-phase) to more dense (monoclinic α-phase) crystalline structure at the root of a growing crack results in crack blunting and toughness enhancement. Indeed, a pronounced strain dependence of the β-α transformation has been indicated by Varga[1] and, more recently, comprehensively discussed.[3] Nevertheless, it is difficult to characterize these structural changes directly on the fracture surface and assess their energy contribution. Besides, the phase transformation in polypropylene is associated with a volume decrease in contrast to the volume increase in zirconia ceramics.

Therefore, it seems more likely that the higher ductility and toughness as compared to the α-modification is an inherent property of the β-phase itself. It might reflect a distinct structural arrangement, for example, the sheaf-like spherulitic structure, as suggested by Tjong et al.[5] The structural model of Elyashevich and coworkers[12,13] offers another possibility. It is based on the notion that the hexagonal β-phase consists basically of extended-chain crystallites; consequently, the amorphous portion of the material contains a high amount of connecting chains. The difference between polypropylene structure with α- and β-crystallites according to this model is schematically illustrated in Figure 5. It is evident that a structure with extended chains in the crystalline regions interconnected by many continuous chains can better transfer mechanical force, can be drawn to a higher extent, and will show higher modulus and strength after drawing as compared to a morphology with folded-chain lamellae.

Evidently, a real polypropylene material can contain both structural arrangements. The proposed model, however, suggests not only a particular structure in the crystalline phase but also higher continuity in the amorphous portion of the material. Then a relatively small fraction of the β-phase can produce a long-range effect in the amorphous matrix of the material, thus influencing important end-use properties, toughness, in particular. Typically, toughness is a matrix-controlled property, not only in polymer composites but also in semicrystalline polymers.

CONCLUSIONS

Parallel assessment of the J-integral and crystalline structure along injection-molded bars of isotactic polypropylene has suggested that the observed gradient in fracture toughness can be ascribed to a varying β-phase concentration. A structural model derived from the Elyashevich theory[12,13] has been offered to explain this observation. It is based on a notion of extended chain crystallites interconnected by continuous chains. Moreover, the results obtained in this study have important consequences for practical mechanical

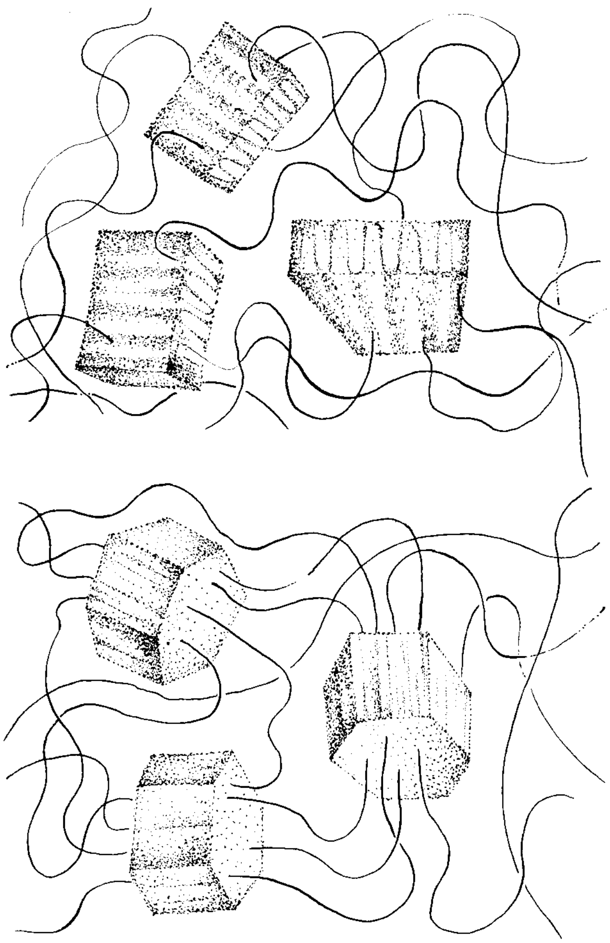

Figure 5 A schematic model of supermolecular structure of α (top) and β (bottom) isotactic polypropylene. It is suggested that the β-phase consists predominantly of extended-chain crystallites with a high amount of continuous chains interconnecting the amorphous and crystalline regions. A real polypropylene material can contain both structural arrangements.

testing. Indeed, notches in injection-molded specimens for impact tests are normally introduced in the middle of the specimen length. This is exactly the region where both crystalline structure and toughness show the largest gradients. Thus, experimental scatter observed in mechanical data and differences in results reported by various authors may reflect real structural differences between individual test pieces arising from molding conditions or they may reflect notch location in different portions or layers of a given test piece. Therefore, the effects of the β-phase should be considered not only in structural studies but routinely in standard mechanical testing and characterization of physical aging of isotactic polypropylene.

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