Fracture Behaviour of β-Polypropylene as a Function of Processing Conditions

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Summary: The commercial grade of isotactic polypropylene (iPP) homopolymer (Mosten 58.412) was doped with different amount of β-nucleant (NJ Star NU-100). The fracture behavior of the β-iPP was examined on injection- and compression moulded specimens under dynamic load. The fracture toughness K_{Id} and J_{Id}, respectively, were used to describe the fracture behavior. The influence of processing conditions (the mould temperature and injection velocity) and the distance from the gate were also taken into the consideration. Structural changes during processing were characterized by DSC analysis. It was found that: (i) the amount of 0.03 % of β-nucleant gives the highest toughness (ii) the toughness of the β-iPP depends on the distance from the moulding gate and on the processing conditions (iii) the degree of crystallinity correlates with the fracture parameters.

Introduction

Isotactic polypropylene (iPP) is widely used as a raw material mainly for injection moulding of various technical parts. Generally, polypropylene is characterized by poor low temperature impact behavior because of its relatively high glass transition temperature. The incorporation of elastomer particles offers a classical solution to this problem. Heterophase PP blends with increased toughness were first prepared by melt compounding PP with different polyolefines or prefabricated ethylene-propylene copolymers [1,2)]. Enhancement of toughness results, however, in considerable reduction of stiffness and strength. Another possibility of toughness enhancement is phase transformation. The principle of "phase transformation toughening" is widely used in metals and ceramics technologies. Application of this principle to polymers, mainly PP, became a topic of investigation in recent years [1-5)]. Commercial grades of isotactic polypropylene crystallize essential into α-modification (α-iPP) with a sporadic occurrence of β-phase (β-iPP). For preparation of samples rich in β-modification the introduction of selective β-nucleants is the most reliable method [6)]. For estimation of the change in the toughness of β-iPP the standard test (Izod, Charpy and Dynstat) were originally used [7)]. Concepts of fracture mechanics (linear elastic fracture mechanics-LEFM or elastic-plastic

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fracture mechanics-EPFM) determine an inherent material parameter, which is independent of testing configuration [8].

The aim of this paper is to clarify the effect of processing conditions and the amount of β-nucleant on the fracture mechanics characteristics. Attention is also focused on the correlation of fracture and structure characteristics.

Experimental

The material used in this investigation was commercial isotactic polypropylene homopolymer Mosten 58.412 supplied by Czech company Chemopetrol Litvinov (MFI at 230°C and 21.2 N: 3 g/10 min, density: 909 kg/m^3). As a β-nucleant NJ Star NU-100 supplied by Rika International (GB) was used. Chemical structure of this nucleant is similar to N', N'-dicyclohexil-2. 6-naphtalene dicarboxamide. Samples of β-iPP with various wt. contents of β-nucleant were prepared by extrusion compounding of matrix with this nucleant. Two processing procedures were used: (i) injection moulding (ii) compression moulding. For injection moulding a Battenfeld BA750/200 machine with multicavity mould (according to the previously Czech standard) was used. The injection moulding conditions are summarized in Table 1.

Table 1. Processing conditions.

Heating zone temperatures	200/210/220/230 °C
Mould temperature (MT)	40 °C, 60 °C and 85 °C
Injection pressure	433 bar
Holding pressure	361 bar
Moulding rate (MR)	40 % (of the maximum) and 80 %
Holding pressure time	80 s
Cooling time	20 s

For compression moulding we used two procedures: (i) according to ISO 293/c (T=210°C and cooling rate 10 ± 2°C/min) (ii) a modified method according to N. Brown [9].

To study in detail the fracture behavior under dynamic load we used instrumented Charpy impact test and procedure described in [10]. The specimens were:

1. Bars (120x10x4 mm) cut into three specimens (marked with L-left, M-in the middle part of the bar, R-right).
2. Specimens (120x10x4 mm) cut from compression-moulded plaque.

Single-edge-notch specimens for three-point bending impact (length L = 60 mm, width W = 10 mm, thickness B = 4 mm) were notched with fresh razor blade up to a_0 = 2 mm. The test conditions were temperature 23°C; pendulum hammer speed 1.5 m/s and support span s = 40 mm. The dynamic fracture parameters K_{Id} and J_{Id} were estimated according to equations in [10]. Structural changes were characterized by DSC analysis. The samples (4mg) were taken from the innermost part of the bars (marked L, M, R). The analysis was carried out on Perkin-Elmer DSC using the scanning rate of 20°C/min. The DSC thermograms and standard Peak-Fit software were used for evaluating (i) fusion temperature of β- and α components ($T_{m\alpha}$, $T_{m\beta}$); (ii) fusion heat (H_α, H_β); (iii) crystallinity (X); (iv) crystallinity of α- and β phases (X_α, X_β) and percentage of β phase (ϕ_β).

Results and discussion

The instrumented Charpy impact test was carried out with a set of materials including the concentrations 0.01, 0.03, 0.05, 0.07, 0.1 and 0.13 wt. % of β-nucleant. The specimens were taken from three different distances with respect to the moulding gate (marked L, M, R). Toughness characteristics (K_d - dynamic fracture toughness, J_d – dynamic J-integral value) as a function of the content of β-nucleant are shown in Fig. 1 - 2.

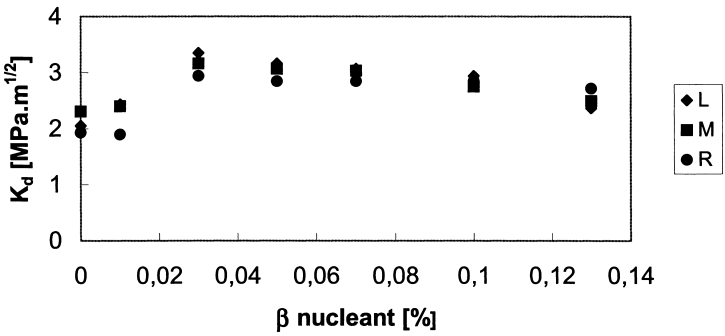

Figure 1: Influence of β-nucleant and distance of the moulding gate on fracture toughness. Moulding conditions: MT = 60 °C, MR = 40 %.

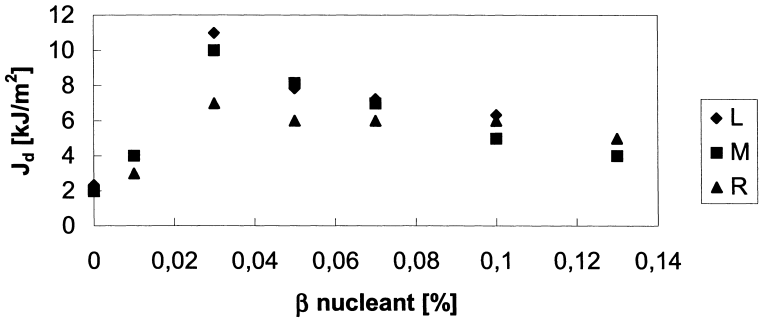

Figure 2: Influence of β-nucleant and distance of the moulding gate on fracture parameter - J_d. Moulding conditions: MT = 60°C, MR = 40 %.

The fracture toughness reached its maximum value at 0.03 wt. % of β-nucleant and for the specimens taken near the moulding gate. Considerable difference in this trend is for J_d values (Fig. 2) than for K_d (Fig. 1). The fracture parameter K_d is derived only from stress state near the crack tip in contrast to J_d parameter, which includes stress - strain state near the crack tip. The influence of moulding conditions on the fracture toughness is illustrated in Fig. 3 for neat matrix and for material with 0.05 % of β-nucleant.

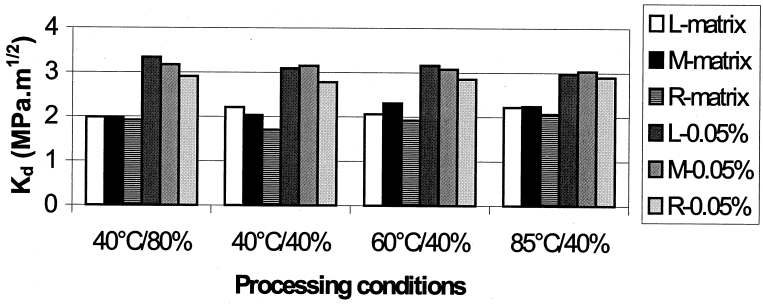

Figure 3: Influence of moulding conditions and the distance of moulding gate (L-left, M- in the middle, R-right) on fracture toughness.

Compression moulded plaques were cut into specimens of dimension 60x10x4 mm and provided with the notch up to the depth of 2 mm. The notch was prepared in the same way as for injection-moulded specimens. For the fracture test we have selected only the basic set of materials (matrix, 0.05, 0.07, 0.1 and 0.13 wt. % of β-nucleant) because the widespread use of this technology is not expected. The fracture parameters (K_d and J_d) were estimated under the

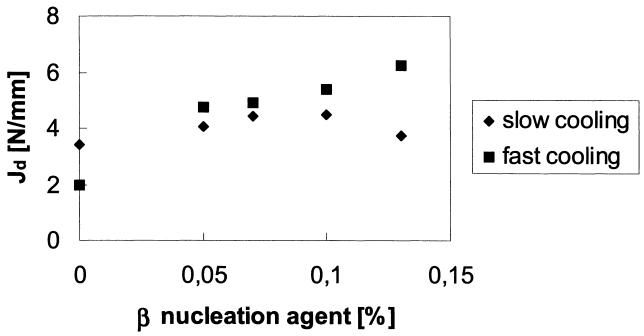

Figure 4: Influence of β-nucleant and compression moulding conditions on fracture parameter J_d.

same conditions as for instrumented Charpy impact test. The value of the J_d parameter for two compression-moulding conditions is shown in Fig. 4.J_d values for specimens prepared according to the modified method (slow cooling) have similar trend as has the J_d values for injection-moulded specimens (Fig. 2 and 4). The maximum value of J_d moves to the higher content of β-nucleant (Fig. 4). There is a monotone rise in J_d values (Fig.4) for specimens prepared according to the ISO standard (fast cooling). We do not know the exact explanation of this behavior but the different cooling rate builds up different conditions for recrystalization of β to α phase [11]. The structural changes due to different amount of β-nucleant are shown in Fig. 5.

The structural parameters were evaluated by means of DSC records and Peak-Fit software for all samples and moulding conditions with respect to distance for the moulding gate. The results are summarized in Table 2 for material with 0.05 wt. % of β-nucleant.

The average values of the crystallinity (X) and the crystallinity of α phase (X_α) are shown in Table 3 for all materials under study.

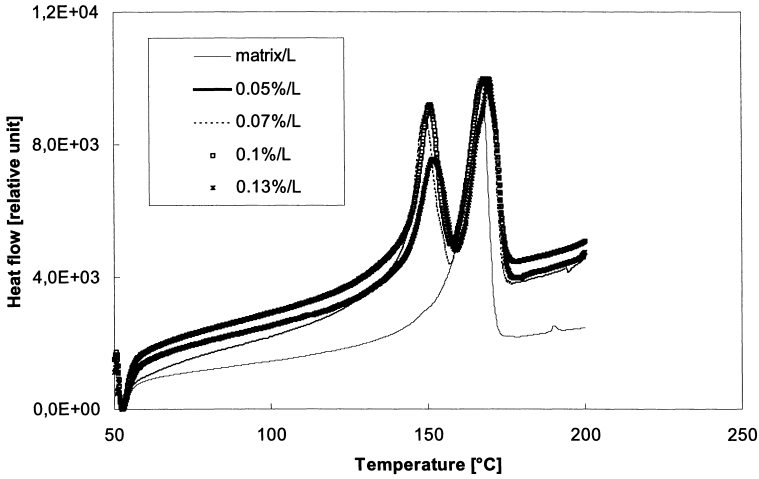

Figure 5: DSC records for all tested samples. The specimens were taken near the moulding gate. Processing conditions: MR = 40 %, TF = 40 °C.

Table 2. Structural parameters - matrix material with 0.05 wt. % of β-nucleant.

Position	Proces. condit.	$T_{m\alpha}$	$T_{m\beta}$	H_α	H_β	X_α	X_β	X	ϕ_β
	°C / %	°C	°C	J/g	J/g	%	%	%	%
L	40/40	169.0	150.1	52.7	53.6	29.6	31.5	61.2	32.6
M		170.0	150.3	50.1	51.3	28.2	30.2	58.3	31.3
R		170.6	151.1	49.9	53.8	28.0	30.5	58.5	31.6
L	40/80	168.5	148.9	50.3	54.8	28.2	32.2	60.5	33.4
M		168.8	150.2	43.4	64.0	24.4	37.6	65.0	39.2
R		170.6	150.7	48.2	55.9	27.1	32.9	59.9	34.1
L	60/40	170.4	151.6	40.6	66.3	22.8	39.0	61.8	40.7
M		167.4	148.5	42.7	62.6	24.0	36.9	60.9	38.4
R		169.7	150.6	36.7	68.1	20.6	40.1	60.7	42.0
L	85/40	167.3	151.0	37.3	69.9	21.0	41.1	62.1	43.1
M		169.1	151.6	32.2	78.4	18.1	46.1	64.2	48.7
R		170.3	154.3	30.5	75.8	17.1	44.6	61.7	47.2

Table 3. The average values of crystallinity.

Material	X / %	X_α / %
Matrix (M)	59.25	59.25
M + 0.05 % β-nucleant	61.20	24.09
M + 0.07 % β-nucleant	60.70	25.43
M + 0.10 % β-nucleant	61.30	25.18
M + 0.13 % β-nucleant	61.60	25.74

The matrix material (Fig. 5) contains only α phase in comparison with matrix doped with β-nucleant. The percentage of β phase (ϕ_β) depends on processing conditions and the distance of moulding gate (Tab. 2).

The specimens prepared from compression-moulded plaque under slow and fast cooling regime were also analyzed by DSC method. The DSC records for matrix material are shown in Fig. 6. There is a considerable difference between slow and fast cooling regime. The fusion temperature for matrix under fast cooling moves to the higher temperature, higher enthalpy of fusion and crystallinity in comparison with slow cooling regime. These results are in agreement on lower value of fracture toughness.

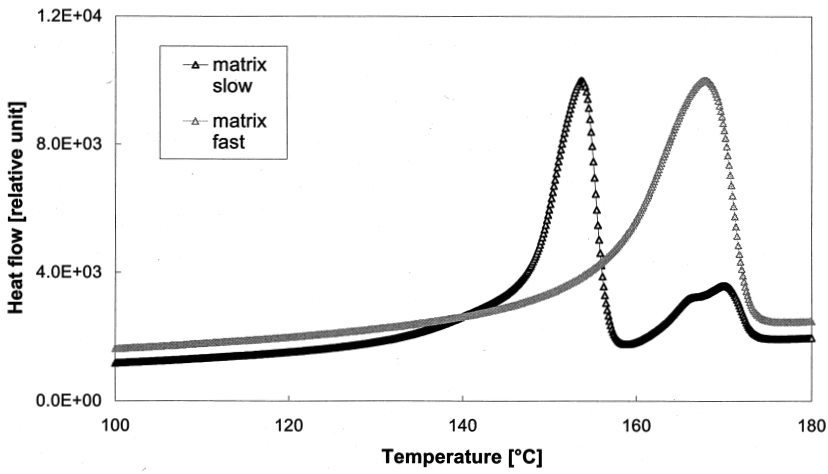

Figure 6: DSC records for matrix material.

The crystallinity (X) and the crystallinity of α and β phase (see Tab. 3) seem to be the most sensitive structural parameters. The results obtained from the fracture test using injection-moulded specimens were correlated with these structural parameters (Fig. 7).

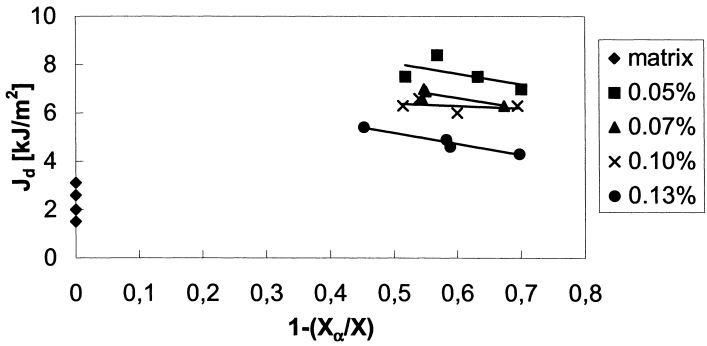

Figure 7: Correlation between J - integral and the relative crystallinity.

There is a good correlation between fracture property and crystallinity (Fig. 7). The higher the values of the relative crystallinity are the lower the toughness of material. The crystallinity changes with moulding conditions.

Conclusions

- Adding β-nucleant enhances the dynamic toughness of iPP matrix.
- Processing conditions (injection moulding versus compression moulding) influence substantially the dependence of dynamic toughness on the amount of β-nucleant.
- The maximum value of dynamic toughness is achieved at 0.03 wt. % of β-nucleant for injection-moulded specimens. This value depends on injection moulding conditions and on the distance of moulding gate.
- The change of dynamic toughness is reflected in the change of structural parameters, mainly in the crystallinity.
- There is a good correlation between the crystallinity and fracture characteristics for injection-moulded specimens.

Acknowledgements

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