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A MODULATED DSC STUDY ON THE STRAIN-INDUCED βα-TRANSFORMATION IN A β-FORM ISOTACTIC POLYPROPYLENE

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Abstract

The mechanical strain-induced βα-transition of a β-phase isotactic polypropylene (β-iPP) was studied by modulated differential scanning calorimetry (MDSC). Samples were taken after tensile fracture of a double notched specimen from its process and plastic zones, respectively, and the related calorimetric response was compared to that of the bulk material. In contrast to conventional DSC results, it was found that the βα-transformation was not completed in the process zone. Furthermore, the melting of the α-iPP showed both non-reversing and reversing characteristics, whereas the melting of the β-phase proved to be a reversing process. Therefore, it was recommended to consider the conversion grade of the βα-transformation by the relative change in the melt flux of the reversing β-melting peak.

Keywords: βα-transition, β-PP, damage zone, modulated DSC, polypropylene, strain-induced recrystallization

Introduction

It was shown in several studies, that the β crystalline modification of isotactic polypropolyne (β-iPP) recrystallizes in the α-form during heating (e.g. [1–4]), more exactly if the sample was kept at ambient temperature prior to melting [4]. This βα-transition can also be triggered by mechanical loading [3–7]. Recent studies claimed [5–7] that this βα-transformation is accompanied with a considerable increase in toughness. The toughness improvement proved to depend on both molecular mass of the PP [8] and loading frequency [7, 9]. Based on differential scanning calorimetric (DSC) results it was reported [7] that the βα-conver-

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sion changes locally in the stress whitened damaged zone caused by the mechanical loading. The conversion grade of this βα-transformation cannot be easily estimated by taking conventional DSC traces because of the following overlapping processes: partial melting of the β-iPP, βα-recrystallization and melting of the resulting α-phase [3–4, 7]. Although a curve resolution of the DSC traces sheds some light on this phase transformation, the conversion grade can hardly be determined. From the viewpoint of fractional conversion open question are relied on the normalization value (melting enthalpy of the initial β-iPP or of the resulting α-iPP) and sampling (whether or not the bulk should serve for normalization).

Since the modulated DSC (MDSC) is a proper tool to separate complex, overlapping thermal transitions, our aim was to use this technique in order to gain deeper insight on this strain-induced βα-transformation in β-iPP. A further goal of this study was to find a way for estimating the fractional conversion of this βα-transition within the damage zone.

Experimentals

The manufacturing of 1 mm thick β-iPP sheets was described in an earlier work in details [7]. Object of this study was the stress whitened area of a double deeply edge-notched specimen (DDEN-T) produced in tensile fracture at room temperature (*RT*) and v=1 mm min^{-1} crosshead speed. Figure 1 shows this stress-whitened damaged zone along with its process and plastic constituents, also schematically. It should be noted here, that this designation is in harmony with the work of fracture approach used for ductile polymers (e.g. [6]). In a scanning

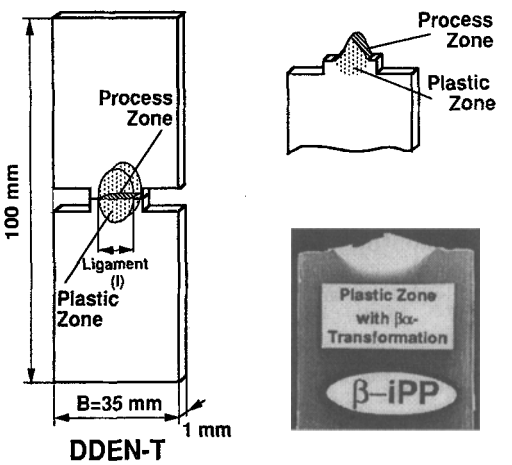

Fig. 1 Process and plastic zones in a fractured DDEN-T specimen of β-iPP schematically and in realty (see macrophotograph)

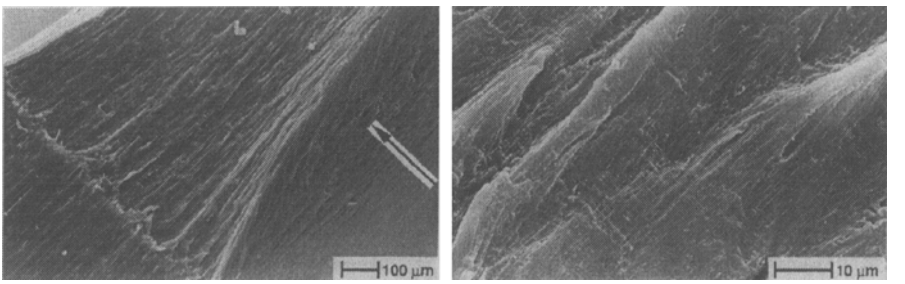

Fig. 2 SEM pictures taken from the fracture surface of a DDEN-T specimen of β-iPP. Notes: the fracture plane represents the process zone; the surface plastic zone of the specimen is indicated by arrow

electron microscope (SEM) the process (fracture plane) and plastic zones are well discernible (Fig. 2). Figure 2 also shows that the βα-transformation is associated with microvoiding. The light scatter among these microvoids within the plastic zone is responsible for the 'whitening' effect, usually termed to 'stress-whitening' (cf. Fig. 1). It is not yet fully understood how far and it what extent this microvoiding is an effect of the βα-transformation. Nevertheless this 'side effect' of the βα-transformation is exploited for the production of microporous films [10–11].

MDSC investigations were performed on a TA Instruments Thermal Analyst 2200 System equipped with a 2920 auto-modulated DSC connecting to a LNCA II. In order to compare to the regular DSC results [7], a heating rate of 2°C min^{-1} was used with a modulation amplitude of ±0.5°C min^{-1} and a frequency of 60s in the presence of nitrogen. All runs were set up from 0 to 200°C. The heating rate might not slow enough to provide a full deconvolution in the melt region, MDSC still can provide some valuable information for all the samples scanned under the same conditions, even, the sample weight was kept constant (10.1 mg). Data were analyzed by the related software package 1.1A of TA Instruments.

Results and discussions

Bulk material

The conventional DSC trace (trace C in Fig. 3) taken from the bulk of the specimen (cf. Fig. 1) shows the onset of melting of the β-iPP (T=100°C), its endothermic melting peak (T=148.9°C; 43.3 J g^{-1}), the exothermic βα-recrystallization peak (T=152.8°C; 7.78 J g^{-1}) and the endothermic melting of the α-phase (T=168.1°C; 62.0 J g^{-1}).

In the non-reversing (NR) component two exotherms (T=147.8 and 152.1°C) and one endothermic peak (T=168.2°C) can be resolved. It is obvious that the

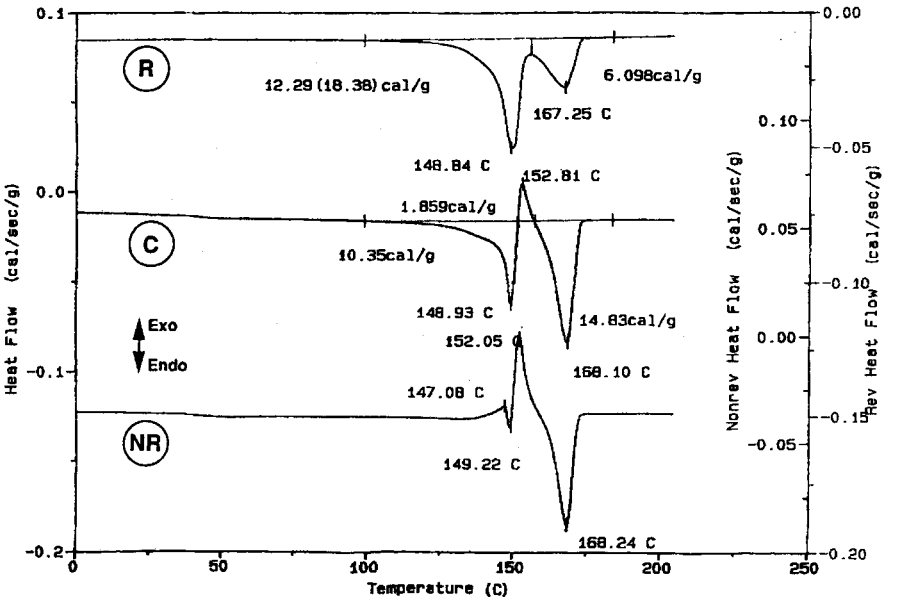

Fig. 3 MDSC curves for the bulk (unstretched) β-iPP. Designations: C – conventional, NR – non-reversing and R – reversing components, respectively

main βα-recrystallization at T=152°C is a non-reversing process. The preceeding small exotherm peak may be attributed to one or more of the following effects: non-isothermal cooling of the specimen (yielding β-crystals with different thermal stability and thus chance for ββ′-recrystallization), frozen-in stress state of the molded plate, efficiency of the β-nucleant. It is likely that the stabilization of the β-phase by multistep recrystallization, recommended by Varga [3–4], would provide with further information on the influence of the aforementioned parameters. The reversing trace (R) illustrates how well the melting processess of the β-(T=149.0°C; 51.4 J g^{-1}) and α-iPP (T=167.3°C; 25.5 J g^{-1}) are separated. Furthermore, it is interesting to note that the melting of α-iPP contains both R and NR components, whereas that of β-iPP seems to be a solely reversing process. The finding that the melting of the β-iPP is a reversing process is quite unexpected. Based on the findings of Varga (e.g. [4, 12]) a reversing process is most likely to occur when the β-iPP was not cooled below a critical temperature of about 100°C. This threshold limit was passed, however, since the specimens were stored and tested at *RT*.

Comparing the melting enthalpy data of α-iPP from the C-(=62.0 J g^{-1}) and R-traces (=25.5 J g^{-1}), the latter proves to be much smaller. The rationale behind this large difference is that the reversing component reflects only the melting of more perfect crystals, which are not involved in partial melting and subsequent recrystallization processes. This is a clear hint that the outcoming α-peak can

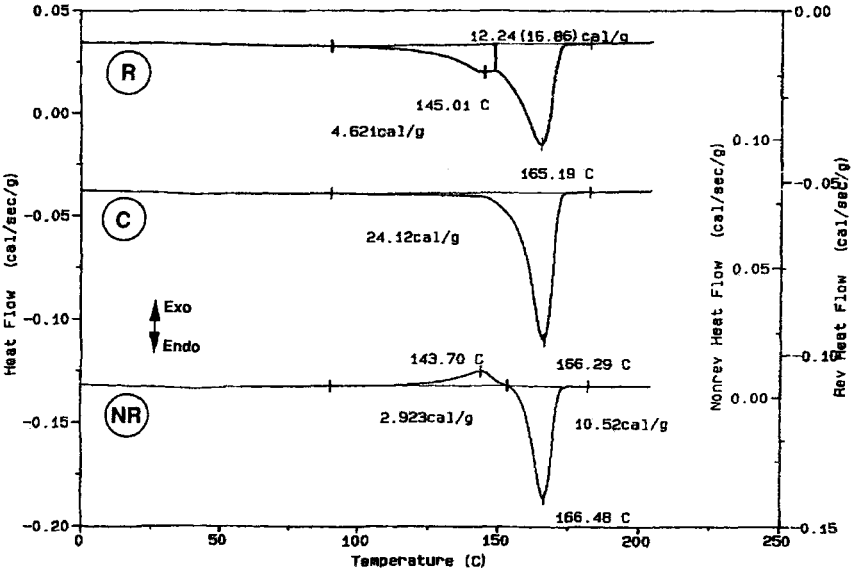

Fig. 4 MDSC curves for the process zone (fracture plane) of the fractured DDEN-T specimen of β-iPP. For designations cf. Fig. 3

hardly represent a normalization value if the determination of the fractional conversion of the βα-transformation is targeted.

Process zone

The C-trace in Fig. 4 demonstrates the melting of the α-phase solely (T=165.2°C; 100.9 J g^{-1}). This is in concert with our previous finding that the βα-transformation in the process zone (i.e. fracture plane) is completed [6–7]. In the NR trace of Fig. 4, on the other hand, a shallow exothermic peak appeared (T=143.7°C, 12.2 J g^{-1}) prior to the α-melting (T=166.6°C; 44.0 J g^{-1}). Since this peak is obviously related to the βα-recrystallization, the βα-transformation during mechanical loading was not completed even in the process zone. The R-curve in Fig. 4 shows again the β- and α-melting peaks at T=145.0°C (19.3 J g^{-1}) and T=165.2°C (51.2 J g^{-1}), respectively. The melting enthalpy values were calculated according to the curve sectioning indicated in the Figures. The R-trace substantiates that the strain-induced βα-recrystallization results in an increased amount of more prefect α-crsytals.

Plastic zone

Comparing the C-traces in Figs 3, 4 and 5, one can recognize that the fractional conversion of βα-transformation in the plastic zone is between that of the

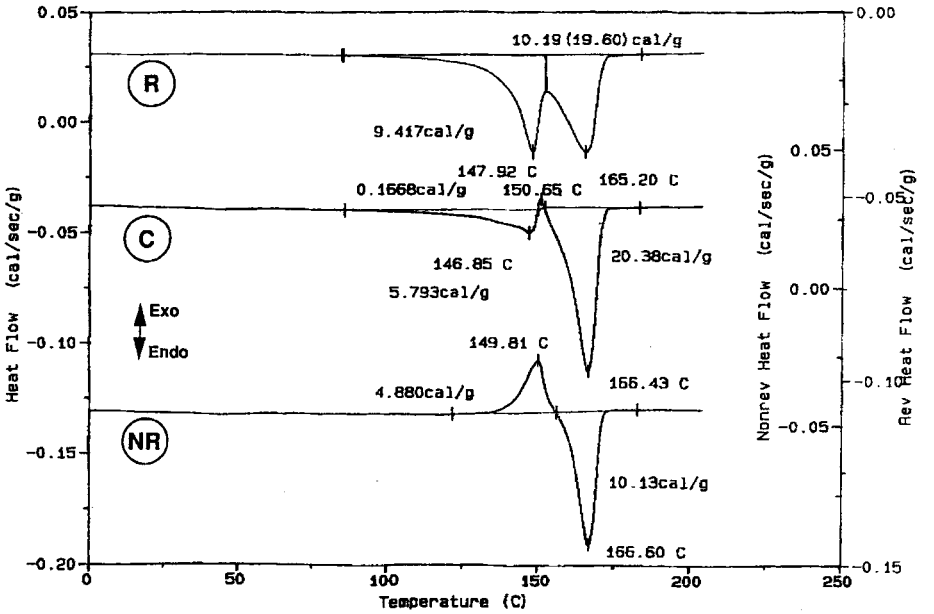

Fig. 5 MDSC curves for a sample taken from the plastic zone of a fractured DDEN-T specimen of β-iPP. For designations cf. Fig. 3

bulk and process zone, as expected. The melting of the remnant β-phase (T=146.9°C, 23.8 J g^{-1}), followed by the βα-recrystallization (T=150.7°C; 0.7 J g^{-1}) and α-melting (T=166.4°C; 85.3 J g^{-1}) are well discernible. In the NR-trace the exothermic βα-recrystallization (T=149.8°C, 20.4 J g^{-1}), preceeding the melting of the α-iPP (T=166.6°C; 42.4 J g^{-1}) are well resolved. In the related R-curve one can distinguish between the melting of the β-iPP (T=147.9°C; 39.4 J g^{-1}) and α-iPP (T=165.2°C; 42.6 J g^{-1}) very clearly. The relative proportion of the β- to α-crystals lays between that of the bulk and process zone, respectively.

βα-*transformation*

The above MDSC results indicate that the βα-transformation is best reflected in the reversing (R) components of the MDSC. Here the melting processess of the β- and α-iPP are well separated, and in addition, this separation is likely not influenced by other parameters such as processing. A simple relation of the reversing β-melting to the overall reversing melting enthalpy does not correlate with results of wide-angle X-ray scattering (WAXS). Recall that a β-iPP of high purity was used in this study [7]. It is therefore recommended to use the normalized (considering the sample mass) ratio of the peak height of the reversing β-melting for estimating the βα-conversion:

$$\text{Fractional } \beta\alpha\text{-conversion} = 1 - \left(\frac{\text{Heat flux}_{\beta,\,\text{specimen}}}{\text{Heat flux}_{\beta,\,\text{bulk}}}\right)_{T = 148^{\circ}\text{C},\ m = \text{const.}}$$

where m is the sample mass.

According to this rough estimation the βα-transformation in the process zone is of about 84%, while in the plastic zone of about 36% – which seem to agree with WAXS results (at least for the plastic zones) more properly. It should be noted here, that the conversion grade in the plastic zone changes locally: its value decreases from the fracture plane toward the boundary between the plastic zone and specimen bulk [7]. This is an effect of the strain field within the plastic zone. Varga [4, 13] has shown by conventional DSC that the βα-transformation is, in fact, strain-dependent.

The main argument for use of the above rough calculation is that a curve resolving of the superimposed melting in the reversing MDSC is still questionable. In order to find a more adequate approach, it is necessary, however, to study the whole plastic zone by WAXS. Scanning the plastic zone by X-rays in several steps from the fracture plane toward the bulk and comparison of the results with those of the MDSC (taken from the same positions of the plastic zone) would contribute to a better understanding of this strain-induced βα-transformation. This study is now in progress.

Conclusions

Based on this calorimetric study performed on the damage zone of a β-iPP where βα-transformation occurs, the following conclusions can be drawn:

1) Modulated DSC (MDSC) is a proper tool to study the βα-transformation initated by mechanical and/or thermal loading in a β-phase isotactic polypropylene (β-iPP)

2) Since the α-phase iPP is generated mostly by the βα-transition, its melting has both non-reversing (NR) and reversing (R) components. By contrast, the melting of the β-iPP is a reversing process, so that it can be used for the estimation of the fractional βα-conversion

3) In contrast to conventional DSC, the MDSC technique revealed that the βα-transformatin is not completed even in the process zone, i.e. in the fracture plane of the specimen.

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