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EFFECTS OF DEFORMATION RATE ON THE NECKING OF AN AMORPHOUS COPOLYESTER STUDIED BY MODULATED DSC

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Abstract

The tensile loading-induced necking in notched specimens of an amorphous copolyester (aCOP) was studied by modulated differential scanning calorimetry (MDSC). It was shown that necking occurred by cold drawing since the enthalpy of cold crystallization and that of the subsequent melting agreed fairly with each other. Increasing deformation in the necking zone and increasing deformation rate of the specimens shifted the onset of cold crystallization toward lower temperatures and yielded a slightly higher glass transition temperature (T_g). This was attributed to the molecular orientation caused by mechanical loading. The finding that the melting contained a non-reversing part was considered as appearance of possible microcrystallinity. The T_g range was strongly influenced by the deformation rate and reflects the thermomechanical history of the samples accordingly.

Keywords: amorphous copolyester (aCOP), cold crystallization, cold drawing, glass transition, modulated DSC, necking

Introduction

Recently several papers were devoted to the toughness assessment of amorphous copolyesters (aCOPs) by adopting the essential work of fracture (EWF) approach [1–4]. A striking feature of these studies was that the necked area of the specimens was produced by cold drawing and not by plastic deformation, even when high deformation rates (v) were used. Therefore, the usual 'plastic zone' designation according to the EWF theory is not straightforward in this case. The

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onset of cold drawing was substantiated by shape recovery of the necked region when heated above the glass transition temperature (T_g) [2, 4]. Infrared thermographic (IT) pictures seemed also to support that T_g was not reached in the bulk [1–4] so that no plastic flow might occur. Furthermore, no sign of strain-induced crystallization that should make the deformed region opaque, was detected. Nevertheless, it is well known that amorphous thermoplastic homo- and copolyesters are prone to undergo crystallization between the T_g and melting range (cold crystallization) [5–6].

It was recently shown by modulated differential scanning calorimetry (MDSC) [7], X-ray scattering [8] and microhardness measurements [9] that the β–α transition in β-phase isotactic polypropylene (β-iPP) strongly depends on the local deformation and orientation in the plastic zone of double deeply edge-notched tensile-loaded specimens (DDEN-T). Based on this finding it was assumed that the cold crystallization capability of the aCOP depends also on the local deformation (strain) of similar DDEN-T specimens. A further open question in this respect is whether or not the strain rate affects the cold crystallization behavior. The aim of this study was also the elucidate if the T_g region may reflect the thermal and/or mechanical prehistory of the aCOP samples. The MDSC technique was employed to shed light on all these issues.

Experimentals

Specimens for this study were taken from the necked region of DDEN-T specimens of aCOP which were tensile fractured in EWF tests. Loading of the DDEN-T specimens of ca. 0.5 mm thickness occurred at room temperature (RT) and various crosshead speeds (v), viz v=1, 10 and 100 mm min^{-1}. In respect to the EWF tests the interested reader is addressed to our former works [1–4]. The aCOP studied was supplied by Eastman Chemical Company (Kingsport, TN, USA) and synthesized from dimethyl terephthalate (DMT), and two diols – ethylene glycol (EG) and 1,4-cyclohexane dimethanol (CHDM). The aCOP con-

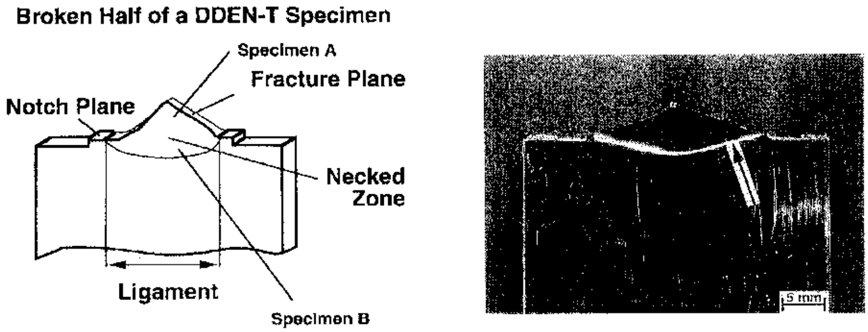

Fig. 1 Necked region of the fractured DDEN-T specimens of aCOP along with indication for the MDSC sampling

tained 68 mole% CHDM and its inherent viscosity (IV) was 0.705 dl g^{-1}. IV was determined in a 0.5 g/100 ml solution of a 60/40 phenol/tetrachloroethane mixture at 25°C. Samples for the MDSC study were taken from the necked region of the DDEN-T specimens as indicated in Fig. 1.

MDSC investigations were performed on a TA Instruments Thermal Analyst 2200 system equipped with a 2920 auto-modulated DSC connected to a liquid nitrogen cooling accessory (LNCA II). DSC scans were taken from 10 to 300°C at a heating rate of 2°C min^{-1} with a modulation amplitude of ±0.5°C min^{-1} and a frequency of 60 s under nitrogen flow. Data were analyzed by the related software package MDSC V(1.1A) of TA Instruments.

Results and discussions

Bulk material

Figure 2 shows the deconvoluted conventional (C), the reversing (R) and non-reversing (NR) DSC traces taken from the bulk of the specimen (i.e. from the non-necked region cf. Fig. 1). On the C curve one can see the exothermic cold crystallization (peak temperature T_{cc}=173.5°C). The enthalpy of this crystallization agrees well with that of the subsequent melting (T_m=226°C). This is the first hint for the initial fully amorphous structure of the aCOP. The small endothermic peak superimposed on the glass transition (T_g) step (T_g=80.9°C) is likely related to the thermomechanical prehistory of the aCOP sample – this will be treated later.

In the R-trace the T_g step is obvious. This is followed by a very broad melting (T_m=219°C), the enthalpy of which is slightly lower than that of the C-trace. This means that part of the melting is a NR process.

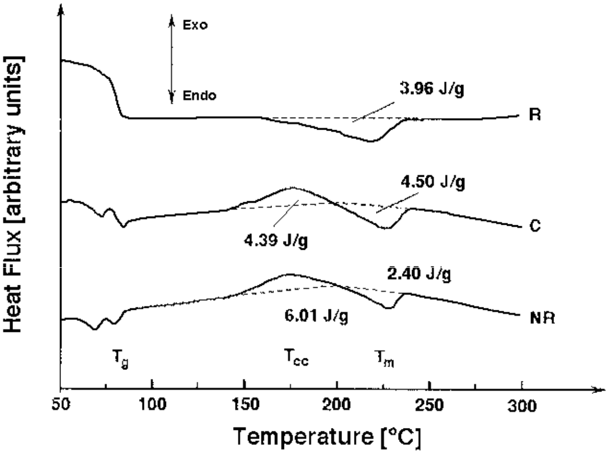

Fig. 2 MDSC curves for the bulk (unstretched) aCOP. Designations: C – conventional, NR – non-reversing and R – reversing components, respectively

Based on the NR trace one can claim that the cold crystallization is fully NR, whereas the melting contains also a small NR component (T_m=229°C). This behavior can likely be explained by some intrinsic microcrystallinity in the aCOP. (Since aCOPs with high CHDM comonomer content are more prone for cold crystallization than with less CHDM – this fact provides us with a checking possibility of the above assumption.) The T_g region of the NR curve will be discussed later.

Effects of local deformation and deformation rate

Comparing the MDSC-traces of samples taken from position B at various v (i.e. v=1 and =10 mm min^{-1}, respectively – see Fig. 3) and from positions A and B at constant v (v=100 mm min^{-1}; Fig. 4), the following observations can be made:

Glass transition

– there is a slight increase in the T_g with v according to the R-traces. This shift toward higher temperatures (ca. 3°C) can be attributed to a strong molecular orientation due to cold drawing

– the T_g region shows a substantial change as a function of v (see R and NR-curves). This aspect will be discussed in a separate section.

Cold crystallization

– the cold crystallization peak in both C and NR-traces is shifted to lower temperatures. This shift is more pronounced at higher local strain rates (cf. response of samples A and B in Fig. 4) and the higher is the overall strain rate (cf. Fig. 3). This shift in the onset of T_{cc} becomes very clear when compared to the bulk material (Table 1)

– the enthalpies of the cold crystallization and that of the melting in the C-trace are similar (cf. Table 1). This suggests that no strain-induced crystallization occurred during the fracture mechanical test.

Melting

– in the R-curves of Figs 3 and 4 neither the melting enthalpy nor the melting peak temperature are changing with v. The related melting enthalpy value is, however, somewhat higher than that of the bulk

– the melting peak of the NR trace shifts to slightly lower temperatures (cf. Table 1). On the other hand, its enthalpy is practically unaffected by v. The fact that there is an NR component of the melting may be an indication for some microcrystallinity. This assumption should be checked next by X-ray scattering techniques.

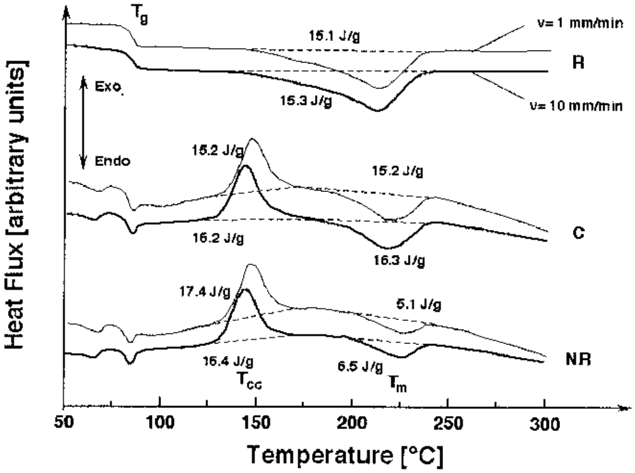

Fig. 3 MDSC curves for samples type B of the necked region of a DDEN-T specimen fractured by v=1 and 10 mm min^{-1}, respectively. For designations cf. Figs 1 and 2

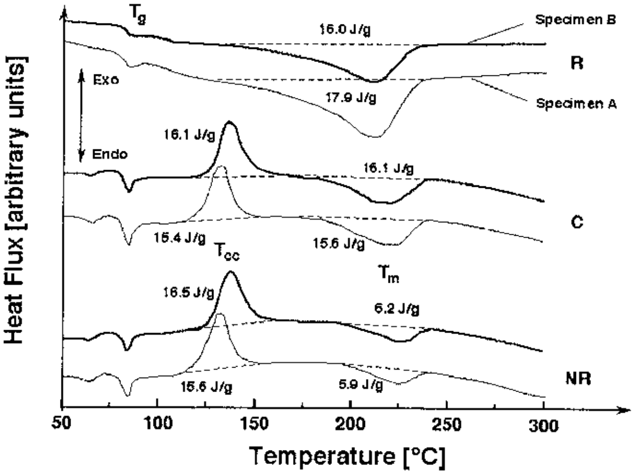

Fig. 4 MDSC curves for samples A and B taken from the necked region of DDEN-T specimens of aCOP fractured at v=100 mm min^{-1}

Glass transition region

The above MDSC results indicate that the T_g region changes considerably with v. Figure 5 shows that the T_g is increased by ca. 3°C due to the necking process associated with molecular orientation, which obviously hampers the mobility of the chains and thus increases T_g.

Table 1 Change in the crystallization (T_{cc}) and melting temperature (T_m) peaks due to cold drawing as a function of the deformation rate (v)

aCOP	Sample type	Conventional (C)		Reversing (R)	Non-reversing (NR)	
		T_{cc}/°C	T_m/°C	T_m/°C	T_{cc}/°C	T_m/°C
Bulk		174	226	218	176	229
Necked region produced by						
v=1 mm min^{-1}	A	139	219	209	139	227
	B	146	216	211	146	225
v=10 mm min^{-1}	A	137	219	210	137	225
	B	143	218	211	143	223
v=100 mm min^{-1}	A	131	220	212	131	223
	B	136	217	211	136	223

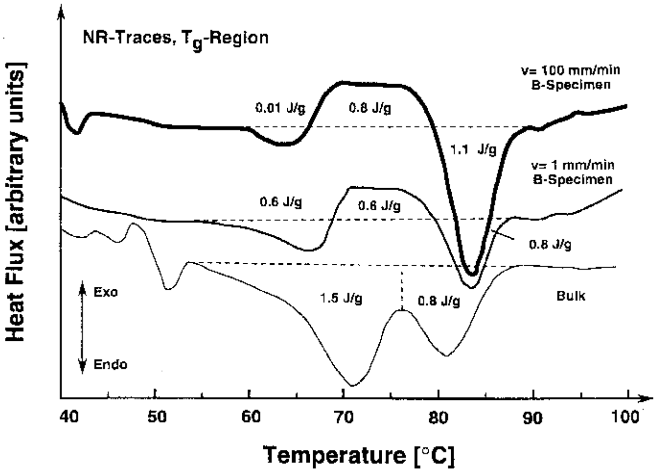

Fig. 5 NR-curves for samples B taken from the bulk and from that necked region of DDEN-T specimens of aCOP fractured at various deformation rates (v)

The earlier presumption that the peak at $T\approx70^{\circ}\mathrm{C}$ is reflecting the thermomechanical ‘prehistory’ of the samples seems to be confirmed. Figure 5 shows how the shape and the enthalpy value of this peak in the NR-trace are changing with increasing v. The most striking effect is that the initial endothermic peak becomes partially exothermic by cold drawing. Further studies by using various techniques and specimens of well-known prehistory are needed to obtain a deeper understanding of this topic.

Conclusions

Based on this MDSC study performed on the necked zone of aCOP specimens tensile loaded in a broad deformation range (v=1...100 mm min^{-1}), the following conclusions can be drawn:

1 – necking in the deeply double edge-notched tensile (DDEN-T) specimens occurred via cold drawing even at the highest deformation rate (v) studied. This was deduced from the C-traces which demonstrated that the cold crystallization and melting enthalpies are practically identical

2 – the local deformation (cf. samples A and B) and the deformation rate strongly affect the onset of cold crystallization. With increasing v the onset of the cold crystallization is shifted toward lower temperatures. This can be explained by the mechanical loading-induced orientation of the molecules that favours the crystallization

3 – the R and NR-traces showed that the melting is mostly a R-process. The physical interpretation is possibly that aCOP can be transformed into its amor-

phous stage by selecting suitable conditions. The fact that the melting has some NR component may be a hint for the presence of some micro- or paracrystallinity

$4-\nu$ strongly affected the T_g region. The T_g value slightly increased with increasing ν which may be explained by the related molecular orientation (R-trace). The T_g preceeding peak in the C- and NR-traces changed with cold drawing. Therefore, this peak was believed to reflect the thermomechanical prehistory of the samples.

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