SHEAR BANDS AND FRACTURE IN CRYSTALLINE POLYMERS

K. Friedrich

Institut für Werkstoffe, Ruhr-Universität Bochum,
Postfach 10 21 48
4630 Bochum, Germany (West)

ABSTRACT

In analogy to the well known shear bands which form in amorphous
Polystyrene, discrete shear bands are also found in crystalline,
spherulitic Polypropylene as well as in Polybutene-1 under compression
at temperatures lower than $0,75$ T_G. They have propagated along spheru-
lite boundaries as well as through the crystalline arrangements inside
the spherulites. The band initiation stress σ_{BI} increases, respective-
ly the strain at fracture ε_F decreases with decreasing temperature
and increasing stiffness of the tested polymer. In addition, in the
semicrystalline polymers both properties are influenced by molecular
and morphological parameters.

The higher the degree of crystallinity, which was varied by the
atactic content in PP or by thermal treatments, the higher is σ_{BI},
while the strain at fracture ε_F decreases with crystallinity. From
the mechanical data obtained in the compression tests a mode II-frac-
ture toughness K^*_{IIC} is calculated to give information on the re-
sistance of each polymer to crack propagation and fracture under
shear stress conditions. It indicates a higher sensitivity to cracks
in amorphous PS as compared to the semicrystalline PP and PB-1. In
the last mentioned polymers shear band fracture can be favored by the
existance of soft spherulite boundaries containing voids and im-
purities.

KEYWORDS

shear bands; crystalline polymers; morphology; crack formation;
fracture toughness; Polystyrene; Polypropylene; Polybutene-1.

INTRODUCTION

The macroscopically brittle fracture is one of various modes of fail-
ure in loaded thermoplastic polymers. It is often preceded by the
formation of localized stable defects, their structure, shape and
density being determined by strain rate, temperature and loading con-

ditions (Kausch, 1976; Wendorff, 1978). The most important of these micromechanical deformation zones preceding crack formation, are crazes. The process of craze formation which mainly occurs under tension, and its influence on crack propagation and fracture of amorphous as well as semicrystalline polymers have been elaborated to a large extend in recent years (Kambour, 1973; Olf and Peterlin,1974; Opfermann, 1978). But there are very few studies which consider in detail the very closely related phenomenon, the formation of shear bands. It is well known that when crazing is suppressed, amorphous polymers such as Polystyrene, deform by localized shear with the appearance of coarse shear bands and/or a diffuse shear zone, consisting of many fine shear bands (Whitney, 1963; Wu and Li, 1976).

Two sets of individual coarse shear bands appear in high speed deformation, especially when the ambient temperature is much lower than the glass transition temperature of the tested polymer. The importance of the shear band intersections on crack formation was pointed out recently by Chau and Li (1979). Furthermore Friedrich and Schäfer (1979 a,b) have discussed the shear fracture processes. Coarse bands lead to shear fracture without much plasticity while a broad shear zone leads to ductile failure after considerable plastic strain.

More recently it was shown, that shear band formation can occur in some semicrystalline thermoplastics as well, especially when comparable testing conditions as in amorphous Polystyrene are chosen (Friedrich, 1980; Williams and Mayer, 1979). In these cases the number of elements influencing the deformation processes is enhanced by microstructural parameters, i.e. molecular structure, crystallinity and morphology. This contribution reports in detail the conditions under which shear bands in spherulitic Polypropylene and Polybutene - 1 are formed. In addition the influence of morphology of these polymers on crack formation and shear band fracture shall be discussed.

EXPERIMENTAL

The experiments described here have been carried out with two types of crystalline spherulitic Polypropylene with the same molecular weight, but with various atactic contents: PP 1120, 5% atactic, and PP 1320, 20% atactic, both obtained from the BASF, A.G. Ludwigshafen, Germany. For additional tests Polybutene - 1 (PB - 1, Vestolen BT 8000, CWH, Marl-Hüls, Germany) was used. The individual test pieces were subjected to different heat-treatments which are described elsewhere (Friedrich, 1978, Friedrich, 1979 c). Thus different morphologies could be produced.

Notched specimens with following dimensions: 10 mm x 10 mm x 20 mm were loaded under compression with a strain rate of $\dot{\varepsilon} = 4.10^{-4} s^{-1}$ in a temperature range between -40°C and -196°C. The meassured values of band initiation stress σ_{BI} and nominal fracture strain ε_{F} were compared with recently obtained results of amorphous Polystyrene (PS).

STRUCTURE OF SHEAR ZONE UNDER VARIOUS TESTING CONDITIONS

In analogy to the well-known observations in amorphous Polystyrene

two sets of coarse shear bands, not exactly perpendicular to each other, are also found in crystalline polymers, when the deformation is performed at temperatures enough below the glass transition temperatures of these polymers (Fig. 1a). The bands have propagated under angles between 35 and 42°C to the compressive axis, directly through the crystalline arrangements inside the spherulites as well as along spherulite boundaries.
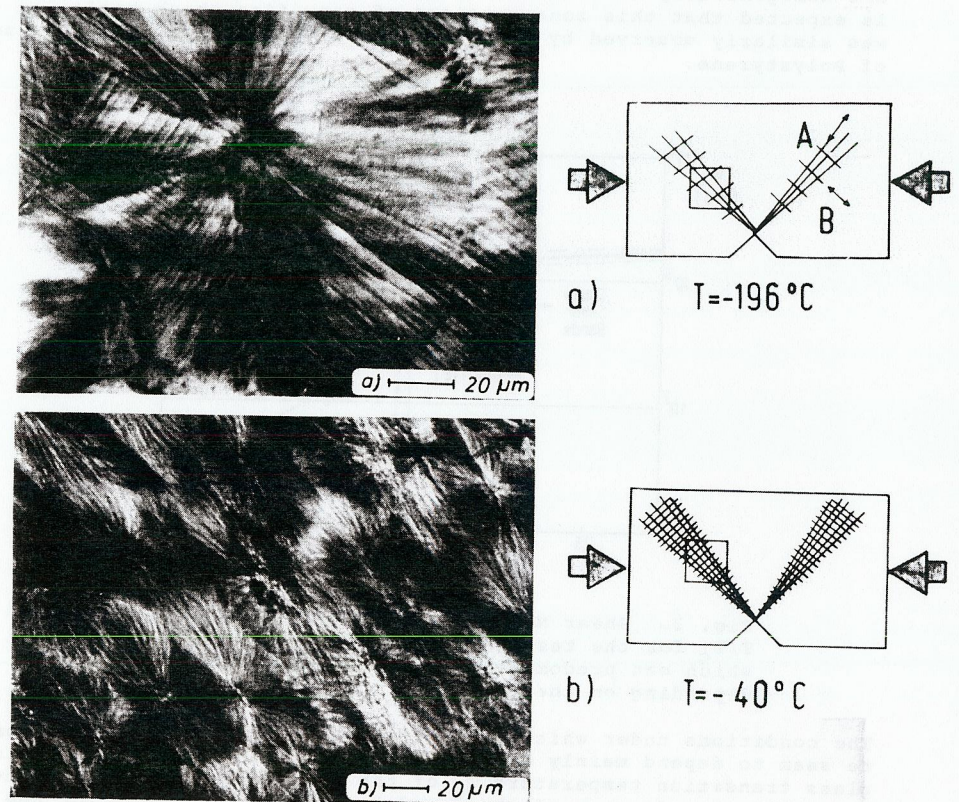

Fig. 1. Structure of the shear zone at various temperatures in Polypropylene :
a) T = -196°C, two sets of discrete shear bands A and B
b) T = -40°C, diffuse shear zone with homogeneous deformation of spherulites

Estimating the band thickness d ($\simeq 1$ μm) and the amount of displacement x at intersections of shear bands with each other or with certain morphological elements, i.e. spherulite boundaries, the degree of local plastic deformation inside the band, ε_i, can be calculated as $\varepsilon_i = x/d$. Its value is one or two magnitudes higher than the external strain before fracture, ε_a. The exact ratio depends on

the testing temperature, similar to the obtained results with Polystyrene (Friedrich and Schäfer, 1979 b). The higher the temperature, the lower was the ratio $\varepsilon_i/\varepsilon_a$; on the other hand the density of coarse shear bands increased with increasing temperature.

Finally, when the testing temperature is near the glass transition temperature a broad shear zone instead of discrete coarse shear bands develops at an angle of 45° to the direction of the external stress (Fig. 1b). Inside this zone the spherulites are homogeneously deformed in direction to the main shear stress. It is expected that this zone consists of many fine shear bands, as was similarly observed by Wu and Li (1976) in the diffuse shear zone of Polystyrene.
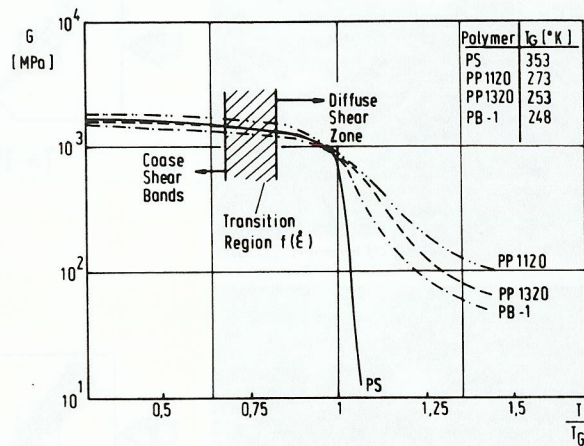

Fig. 2. Shear Modulus G vs. ratio of undercooling T/T_G for the tested polymers. The modes of deformation, which can predominate under compression, are indicated depending on the ratio T/T_G.

The conditions under which the different deformation modes predominate seem to depend mainly on the ratio of ambient temperature T to the glass transition temperature T_G of the material. This fact can be deduced from a diagram of shear modulus G vs. ratio T/T_G for the tested polymers (Fig. 2). The amorphous Polystyrene as well as the semicrystalline polymers Polypropylene and Polybutene exhibit a tendency to the formation of coarse shear bands when a ration of $T/T_G = 0{,}75$ is distinctly undercut.

There exists a transition region in the neighbourhood of $T/T_G = 0{,}75$, where both phenomena, coarse shear bands and/or a homogeneous shear zone, can occur according to the strain rate $\dot{\varepsilon}$. But at elevated temperature, i.e. near $T/T_G = 1$ or above, the formation of a diffuse shear zone under shear stress conditions becomes more and more probable.

INFLUENCE OF MOLECULAR STRUCTURE AND MORPHOLOGY ON BAND INITIATION AND FRACTURE

Figure 3 indicates the influence of the polymeric material on the band initiation stress σ_{BI} and ball thrust hardness H_K (DIN 56456) for various testing temperatures. For all materials (amorphous PS, semicrystalline PP and PB - 1 with fine spherulitic morphology) both mechanical properties increase with decreasing temperatures. The dotted line in Fig. 3 indicates the fact for PB - 1.
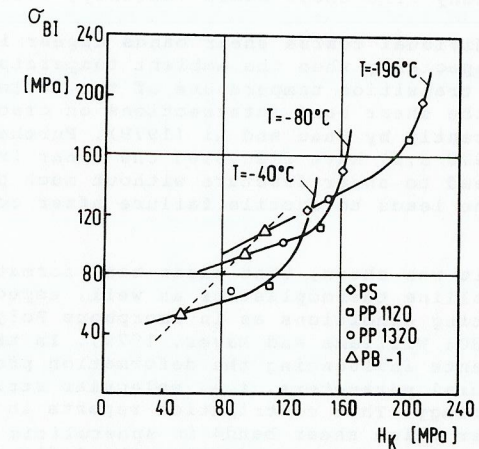

Fig. 3. Correlation between shear band initiation stress σ_{BI} and ball thrust hardness H_K for various polymers at different temperatures.

On the other hand, there exists an increase of σ_{BI} and H_K with the polymer in the sequence PB - 1 → PP 1320 → PP 1120 → PS. Both effects must be related to changes in the material, which are combined with more or less flexibility of molecular chains and/or whole morphological regions. Flexibility shall be understood as the capacity of individual molecular segments or crystalline blocks to localized slipping and slip-tilting during plastic deformation. In particular these properties are given when the shear modulus G is low, indicated in the lower σ_{BI} - values for PB - 1 and PP 1320 as compared to the stiffer materials PP 1120 and PS. In the last, amorphous polymer slipping of molecular segments is strongly hindered by the spread benzene rings along the chains. In the other polymers the flexibility is mainly influenced by the degree of crystallinity as a meassure for a locally higher bonding between the chains due to shorter distances in the crystalline order. The higher amount of crystallinity in PP 1120 (X_c = 60%, determined by density meassurements) as compared to PP 1320 (X_c = 43%) and PB - 1 (X_c = 40%) provides more stiffness and less ductility of the microstructural elements.
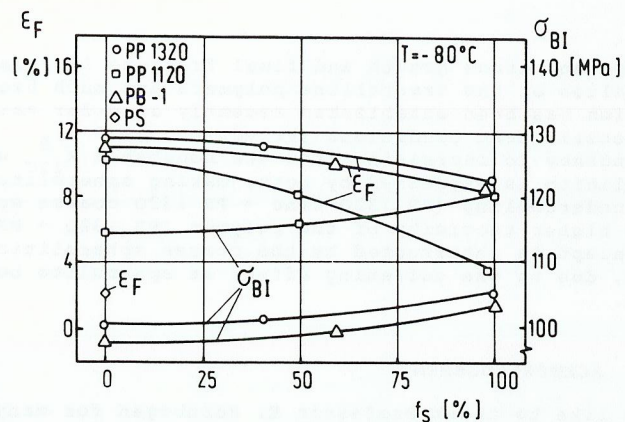
Fig. 4. Influence of morphology (f_S = content of coarse spheru-
lites) on band initiation stress σ_{BI} and strain at fracture ε_F

This tendency becomes also clear in a comparison of the mechanical
data σ_{BI} for fine and coarse spherulitic morphologies of the three
polymers (Fig. 4). Due to the slower crystallization process the
coarse spherulitic structures possess higher crystallinity and thus
higher values of σ_{BI}. On the other hand, a decrease in fracture
strain ε_F is observed with crystallinity.
This seems to be due to the fact, that once a shear band has formed
in a high crystalline structure it is easier to concentrate further
deformation in this band than to form new ones in the highly stiff
environment. Thus fewer bands are formed in the material with higher
crystallinity and fracture occurs at lower values of ε_F. Before
fracture crack formation develops by the interaction of shear bands
with each other (Fig. 5a) and with certain morphological elements,
i.e. spherulite boundaries.

This effect is especially distinct for the highly isotactic PP 1120.
In this polymer a softening of spherulite boundaries occurs during
the slow cooling process due to the concentration of low molecular
weight components, impurities and the formation of voids (Friedrich,
1979 d). When these zones are situated in the plane of growing shear
bands or cracks, they are preferred for further propagation (Fig. 5b).
In addition, these defects can give rise for secondary crack
formation.

CALCULATION OF A MODE II-FRACTURE TOUGHNESS

Finally it shall be attempted to calculate the fracture toughness of
the various polymers and morphologies under mode II-conditions.
According to former calculations of the mode I-fracture toughness K_{IC}
from tensile test properties by Hahn and Rosenfield (1968), the
mechanical data obtained in the compression test shall be used to
determine a mode II-fracture toughness K_{IIC}^{*}. It can be regarded as a
measure for the resistance of each material and morphology against
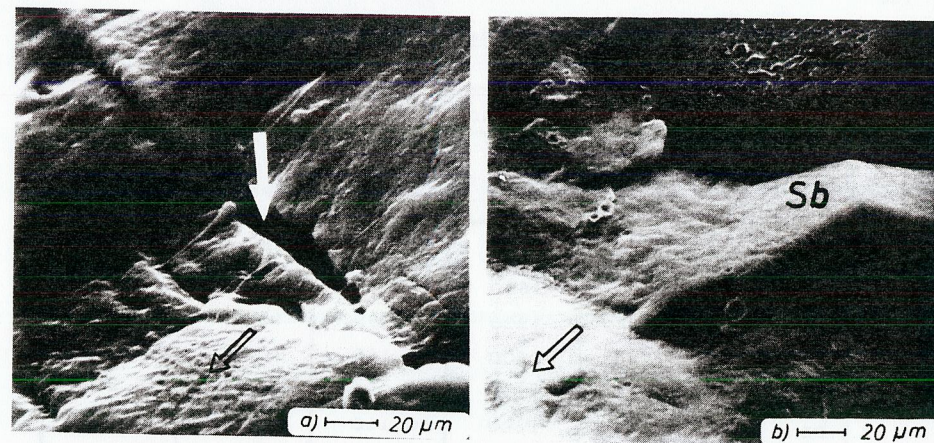crack propagation and final fracture under shear stress conditions.

Fig. 5. Structure of the shear fracture surface:
a) Secondary crack formation in one of the shear bands
   "B" (arrow) in fine spherulitic PP 1120

b) Preferred fracture in spherulite boundaries Sb of
   coarse spherulitic PP 1120. The open arrows indicate
   the sliding direction of the counterpart before fracture.

The following equation shall be used for calculation:

$$K_{IIC}^{*} = (\tau_{BI} \cdot \varepsilon_F \cdot G \cdot n^2 \cdot L)^{1/2}$$

with

K_{IIC}^{*}	-	mode II-fracture toughness
τ_{BI}	-	shear stress for band initiation ($\tau_{BI} = \frac{1}{2} \sigma_{BI} \cdot \sin 2\phi; \phi \approx 45°$)
ε_F	-	strain at fracture
G	-	shear modulus
n	-	work hardening exponent
L	-	empirical constant with the dimension of a length ($L \approx 1m$)

Using the data listed in Table 1 K_{IIC}^{*}- values are received being a
little bit higher than measured values of these polymers under mode
I-conditions. The factor n^2 was estimated as $5 \cdot 10^{-4}$, that means the
work hardening exponent n is near zero. This assumption is based on
the fact that in the shear bands separation takes place by viscous
flow of the material. A temperature rise in the bands seems to be
very likely, considering the criteria of Argon (1973) for unstable
deformation, which dealt with the occurrence of localized shear
instability from strain softening or adiabatic heating. His adiabatic
term θ is high, that means adiabatic effects are favoured, when the
material yields a high plastic resistance and low thermal conducti-
vity and when high deformation rates and low testing temperatures
predominate. Indeed, scanning electron microscopy of the fracture
surface showed drawn fibrils, which appeared to have melted.

TABLE 1   Calculated Shear Fracture Toughness K_{IIC}^*

| Polymer | Morphology | Mechanical Data at T = -80°C | | | |
		G MPa	ε_F	σ_{BI} MPa	K_{IIC}^* MPa·m$^{1/2}$
PS	amorphous	1600	0,022	155	3,7
PP 1120	fine sph.	1600	0,105	120	7,1
PP 1120	coarse sph.	1900	0,035	122	4,5
PP 1320	fine sph.	1400	0,115	100	6,4
PP 1320	coarse sph.	1750	0,090	105	6,5
PB - 1	fine sph.	1200	0,110	95	5,6
PB - 1	coarse sph.	1400	0,095	95	5,7

Finally, the K_{IIC}^*- values are compared with the band initiation stress σ_{BI} (Fig. 6). Such a diagram can give informations about polymers with optimal strength, defined after Hornbogen (1977) as the property of a material with high resistance to plastic deformation (σ_y) as well as high resistance to crack propagation and fracture (K_{IC}^y). Only a significant combination of both mechanical properties guarantees a certain security in a structural element.
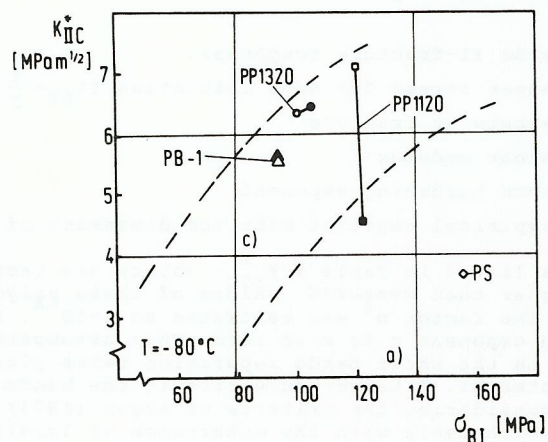

Fig. 6. K_{IIC}^* vs. σ_{BI} for the tested polymers at T=-80°C.
(a) amorphous polymers expected,
c) crystalline polymers.)

In particular, this diagram contains the following informations:
1. Inspite of a high band initiation stress σ_{BI} the resistance of PS

to subsequent crack growth and final fracture is relatively low. The K_{IIC}^*- values of the crystalline polymers are much higher. A similar connection has been established recently also for various polymers under tensile test conditions (Friedrich, 1979 e).
2. A tendency to increasing fracture toughness K_{IIC}^* with increasing crystallinity is expressed by both, making spherulites coarser by slower undercooling (PP 1320 fine → PP 1320 coarse spherulitic), as well as higher tacticity of the polymer (PP 1320 → PP 1120). However, this concept is interrupted by the coarse spherulitic morphology of PP 1120, due to the softening effect at spherulite boundaries in this polymer.

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