On the Deformation and Fracture Behavior Semicrystalline Polybutene-1

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1. Introduction

Polybutene-1 crystallizes in the tetragonal form II (11_3-helix) upon cooling from the melt. This form is unstable and slowly transforms into the stable hexagonal form I (3_1-helix) (1). The rate of this crystal-crystal transformation can be considerably increased by applying uniaxial tensile stresses to the sample. This property has been used to study the uniaxial stress-strain behavior of polybutene-1.

2. Results and Discussion

Fig. 1 shows the temperature dependence of the complex shear modulus of both modifications I and II (frequency 1 sec^{-1}). The relaxation range at - 20°C is the glass transition, and the relaxation process at about - 150°C can be explained by segmental motions of methylene groups in the main chain (γ-process). Fig. 2 shows the dependence of the yield stress and fracture stress on temperature. The modulus of modification II as well as the yield stress is less then that of form I except at temperatures below the γ-process, where the mechanial properties of both crystalline forms are nearly the same.

The stress-strain behavior can be divided into the following different regions (see Fig. 2):

a) At temperatures below the γ-process (- 150°C) no crystalline transformation can be observed. The fracture stress does not depend on temperature ("ideal" brittle fracture) and is practically equal for both crystalline forms. From this it can be concluded that fracture occurs within the amorphous regions (rupture of tie-molecules) and not within the crystals.

b) There is also a brittle-like fracture at higher temperatures between - 150°C and - 70°C. In this region, the fracture stress depends on temperature. Outside the fracture surface no transformation from modification II to modification I can be observed. On the fracture surface itself, however, a partially crystalline transformation has taken place during fracture. This can be considered as evidence for a microscopic ductile fracture process. Consequently the brittle to ductile transition is not at - 70°C but at about - 150°C, where the γ-process is frozen in.

c) Above - 70°C up to - 20°C necking occurs during stretching. Before reaching the yield point practically no II to I-transformation occurs. The very moment, however, the yield stress is reached a remarkable crystalline transformation sets in (Fig. 3). Within the neck, at least at lower temperatures, an almost quantitative transformation II to I is achieved.

d) Above the glass transition up to about 70°C the samples are deformed homogeneously without necking. Again the crystalline transformation sets in when the yield point is reached.

From the experimental results it can be seen that there is a threshold stress below which no II to I-transformation takes place during uniaxial tension. This threshold stress seems to be the yield stress. Normally, yielding occurs when the maximum shear stress is equal to the shear strength of the sample. From this one might at first conclud that the transformation II to I is induced by shear rather than by tensile stresses. In order to check this, the influence of shear or tensile stresses on the crystalline transformation have been investigated by measuring the amount of transformed material around a hole of a foil loaded in tension (Fig. 4). The stress fields associated with a hole for tensile specimens are known (2). In the upper part of Fig. 4 the normalized principal stresses σ_1/σ and

σ_2/σ as well as the normalized maximum shear stress τ/σ (σ = tensile stress) are shown which are acting along the line 1. Along this line (and other lines) the II to I-transformation of a streched sample has been measured by means of infrared spectroscopy. Some results can be seen in the lower part of Fig. 4. The ratio R = Ext 920 cm^{-1}/ Ext 900 cm^{-1} which is a measure of the amount of the transformed material, shows a maximum at the same distance from the hole where σ_1 itself has a maximum. From this it can be concluded that in tensile tests the II to I-transformation is induced by a tensile deformation of the crystals and not a shear deformation. The role of the shear stresses (at yield) can be understood as turning the crystals into "tensile-positions", so that a direct tensile deformation and combined II to I-transformation can take place.

Summarizing the results, the following mechanism of the deformation and fracture behavior is proposed: At stresses below the yield point mainly the amorphous regions are deformed. At the yield point itself the crystals are partially turned out from their statistical positions by shear in such a way that presumably the 11_3-helices are oriented parallel to the streching direction.

Due to the partial crystalline character, there is a cooperative link between the helix to helix transition and the segmental mobility within the amorphous ranges. Below the glass transition, where segmental mobility is frozen in, the phase transition is also frozen in (3). The segmental mobility is increased by application of mechanical stress. This leads to a II to I-transformation when the yield point is reached, even at temperatures below the glass transition. Furthermore, it follows that considerable deformation of the crystals sets in only at the yield point. At very low temperatures, especially below the γ-process, the segmental mobility is frozen in in such a manner that local yielding becomes impossible under the acting state of stress.

Probably, there is a direct rupture of tie-molecules before a II to I-transformation can take place during streching.

References

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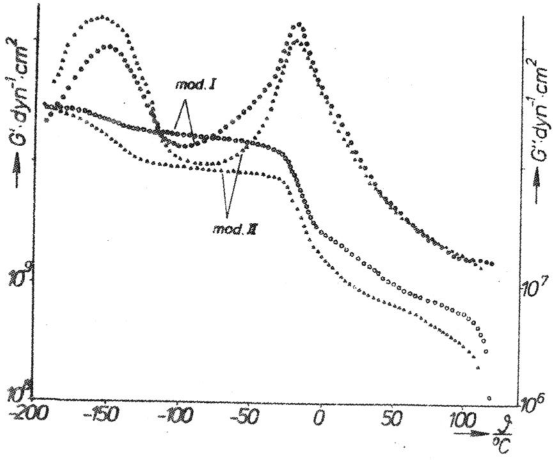

Fig. 1

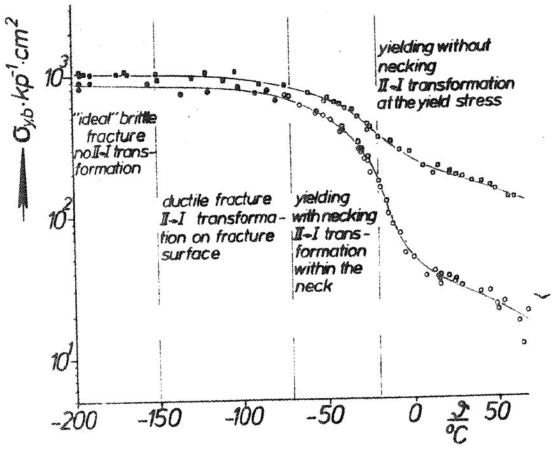

Fig. 2

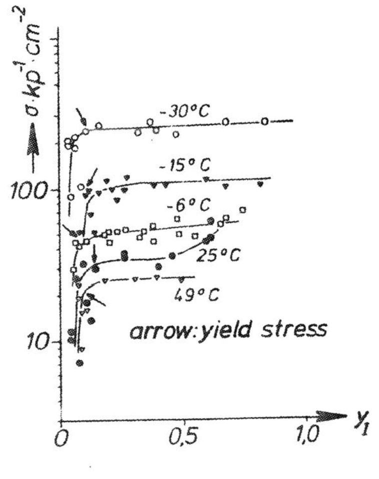

Fig. 3

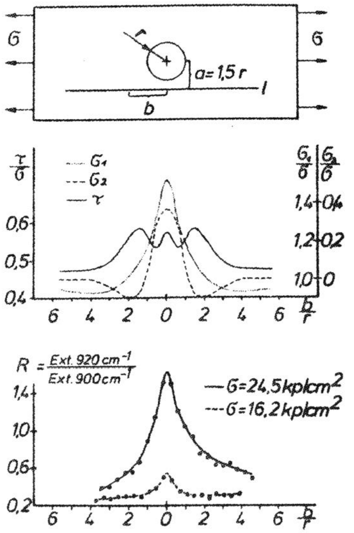

Fig. 4