

FROM CRYSTALLINE BLOCK SLIPS TO DOMINANCE OF NETWORK STRETCHING

— MECHANISMS OF TENSILE DEFORMATION IN SEMI-CRYSTALLINE POLYMERS

Y. Men* and G. Strobl*

Fakultaet fuer Physik, Albert-Ludwigs-Universitaet, 79104 Freiburg, Germany

Abstract The mechanism of tensile deformation in semi-crystalline polymers was studied based on true stress-strain curves obtained with the aid of a video-controlled tensile set-up. The deformation is affected by both the crystalline and the amorphous phases. However, the relative weights of the two portions change with the deformation stage. At low deformations the coupling and coarse slips of the crystalline blocks dominate the mechanical properties, which allows the system to maintain a homogeneous strain distribution in the sample. As the stretching increases, at a critical strain the force generated from entangled fluid portions reaches a critical value to destroy the crystallites. The dominant deformation mechanism then changes into a disaggregation – recrystallization process.

Keywords Semi-crystalline polymer, Deformation mechanism, Network, Mechanical property

INTRODUCTION

The deformation mechanisms of semi-crystalline polymers have been widely investigated due to their primary importance for their daily use. Due to the fact that semi-crystalline polymers are made up of two interpenetrating networks, one built up by the entangled fluid part and the other by the crystallites, for many years studies on the deformation of semi-crystalline polymers generally concerned two separate aspects. On the one hand, the deformation of the semi-crystalline polymers can be regarded as the stretching of a network under a high inner viscosity due to the existence of the entanglements and the crystallites. This view can be proved by the observation that the drawn samples show an almost complete retraction to their original length on heating up to the melting point^[1, 2], and by the modeling of the stress-strain behaviour of semi-crystalline polymers, which is often equivalent to the extension curve of an ideal rubber with viscous elements superposed^[3, 4]. On the other hand, the deformation of semi-crystalline polymers always shows a plasticity which denotes an irreversible change in the crystalline phase. Many efforts thus have been made to study the underlying mechanism. Two general but different mechanisms have been suggested. Firstly, the deformation process of a semi-crystalline polymer can be described by a partial melting and recrystallization^[5], secondly, it can be related to slips of crystallites. Two slip processes, an interlamellar sliding and an intralamellar slip have been discovered^[6, 7, 8, 9]. The intralamellar slip can be accomplished by a homogeneous shearing of layer-like crystallites or by relative displacement of blocks^[10, 11]. The discussion of different deformation mechanisms indicates that basic structural features of semi-crystalline polymers are also under discussion.

In recent years, the development of modern techniques, especially atomic force microscopy (AFM), provided a direct view on the crystallites which clearly show a block-like substructure^[12, 13]. The block-type substructure of lamellae initiated novel views^[14] which suggest that the crystallization of an entangled polymer melt might always be a multi-step process passing over intermediate states. Prior to the formation of lamellar

* Corresponding authors: Y. Men and G. Strobl; E-mails: men@frs106.physik.uni-freiburg.de, strobl@uni-freiburg.de
Received August 24, 2001; Revised November 16, 2001; Accepted November 20, 2001

crystallites the system always creates a mesomorphic layer, which then solidifies through a cooperative structural transition to produce a granular crystalline layer. This finally transforms into the homogeneous lamellar crystallites, which are built up of blocks with a thin boundary in between.

The mechanical properties of semi-crystalline polymers are therefore thought to be closely related to the unique block-type substructure of crystalline lamellae. We have performed extensive experimental work on the uniaxial drawing of polyethylene (PE) and syndiotactic polypropylene (sPP) and found a general description for the deformation process^[15–17]. Along a true stress-strain curve, one always finds critical strains (A, B and C) where the differential compliance and the recovery property change. The critical strains remain constant under the variation of the crystallinity^[15], the deformation temperature, the strain rate^[16] and the crystalline lamellar thickness^[17], which may lead to a large change in the stresses at each critical strain. Obviously, the system can easily react to the external stress in a well-defined way. This seems possible only when block slips are generally activated during the deformation process. The block slip processes provide sufficient degrees of freedom to accomplish the system rearrangement in the way needed.

Because of the interpenetrating networks built up by both crystallites and the entangled fluid the reaction of the semi-crystalline polymers upon stretching is influenced by both portions. The relative weight changes with the deformation stage. From this point of view, the different critical strains could reflect different properties of the two portions. It is thus the purpose of this paper to illustrate the physical background of the critical strains by analyzing the temperature dependence of the elastic modulus and the yield stress and the crystallinity dependence of the maximum elasticity for a series of PEs. Along a stretching run, as described in the following sections, at low deformation below yield the force is transmitted via the crystallites; as the strain increases, the force generated from the entangled fluid becomes more and more important. There exists a continuous transition from the slips of crystalline block to a dominance of network stretching.

EXPERIMENTAL

Samples

Materials used in this work were three polyethylenes: A linear polyethylene (Hoechst AG, Frankfurt) with 76% crystallinity (PE27), a branched polyethylene (BASF AG, Ludwigshafen) with 33 CH₃ per 1000 C atoms and 46% crystallinity (LDPE33) and a polyethylene-vinyl acetate copolymer (Exxon Chemical Europe, Machelen, Belgium) with 17.5% VA content and a crystallinity of 26% (PEVA18). Samples for mechanical testing were prepared by pressing the pellets at 160°C into a sheet form with a thickness in the range of 0.3–0.5 mm. The melt sheets were kept at this temperature for 20–30 min for completing the polymer chain relaxation. Crystallization occurred during a controlled slow cooling of the pressure plates down to room temperature. The temperature dependent crystallinity was determined by the measurements of the differential scanning calorimetry (DSC), which follows at each temperature from the remaining heat of fusion. DSC experiments were performed in a Perkin-Elmer DSC-4 at a heating rate of 10 K/min. DSC samples and the “dog bone” specimens for the tensile tests were cut from the same melt pressed sheets.

True Stress-True Strain Measurement

In the great majority of the known results of the studies of the tensile deformation of semi-crystalline polymers, an engineering load-extension curve was registered under a condition of constant cross-head speed. In Fig. 1, the left curve gives a typical nominal stress-strain relationship for a high density polyethylene (PE27) sample. Here, the nominal stress σ_{nom} , and the nominal strain ε_{nom} are defined as

$$\sigma_{\text{nom}} = \frac{F}{A_0} \quad (1)$$

and

$$\varepsilon_{\text{nom}} = \frac{\Delta L}{L_0} \quad (2)$$

where F is the load applied, A_0 and L_0 are the original cross-section area and length and ΔL is the change in length. This nominal stress-strain curve does not give much valuable information due to the inhomogeneity of the deformation process, *i.e.* the formation of the neck.

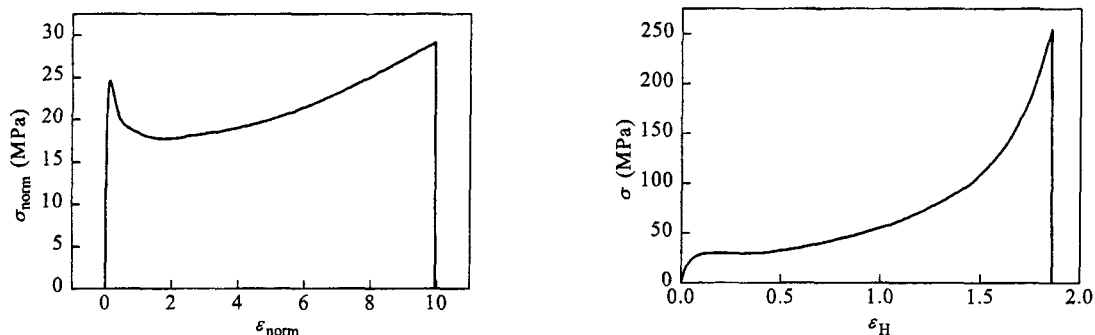


Fig. 1 PE27: nominal stress-strain curve (left) obtained under a constant cross-head speed of 1.95 mm/min, corresponding to a initial strain rate of $5 \times 10^{-3} \text{ s}^{-1}$. True stress-strain curve (right) obtained under a constant strain rate of $5 \times 10^{-3} \text{ s}^{-1}$.

For an insight study of the mechanism of the deformations in semi-crystalline polymers, we thus need a true stress-strain curve which is recorded under a constant strain rate. This is achieved via a video-controlled uniaxial tensile set-up. It was built up several years ago under the continuous efforts first by Rainer Hiss^[18] then by Sven Hobeika^[19] in our group. It comes close to the device developed and used by G'Sell and his co-workers^[20, 21]. The basic units of this setup are a Instron 4301 tensile testing machine, a CCD camera and a computer controlling system. When a neck begins to form during a stretching run, its profile is registered with the aid of a CCD camera. Assuming a constant sample volume during the deformation, the local strain in the center of the neck can be derived from the minimum diameter. The related local stress can be calculated simultaneously. In a stretching run, the true values of stress and strain are continuously registered with the aid of the video camera connected to a computer via a frame grabber. The results are used to adjust the cross-head speed in such a way that a constant local strain rate is maintained in the center of the neck. In our experiments, the Hencky measure of strain ε_H is used as a basic true strain quantity. It is defined as

$$\varepsilon_H = \int_{L_0}^L \frac{dL}{L} = \ln \frac{L}{L_0} = \ln(1 + \varepsilon_{\text{nom}}) \quad (3)$$

where dL is the infinitesimal change of length and L is the current value of the length. The right curve in Fig. 1, shows a typical result of a stretching run. The same sample as used in the left curve was stretched at constant Hencky strain rate of $5 \times 10^{-3} \text{ s}^{-1}$. Comparing it with the left curve, the first observation is that the stress maximum in the engineering stress-strain curve, which is characteristic for a necking sample, has disappeared. The true stress-true strain curve represents a result without the effect of neck. It is possible to compare the deformation behaviour between different samples based on this technique.

Step-Cycle Test

For the study of the recovery properties, a step-cycle test was performed. In this measurement, the sample is extended step-by-step with a constant Hencky strain rate as shown in Fig. 2. After each step, the sample's speed of extension is inverted and used to contract the sample until a stress of zero is achieved. Thereupon, the sample is extended again, at this given speed, until it re-reaches the point at which it left the regulated curve. This experiment leads to a decomposition of the total strain ε_H into a base (plastic) $\varepsilon_{H, b}$ and a cyclic (elastic) $\varepsilon_{H, c}$ part.

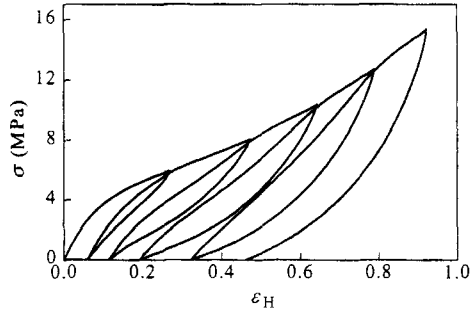


Fig. 2 Example of a step-cycle test
The total strain of each step ϵ_H is split into two parts. The base part $\epsilon_{H,b}$ represents the irreversible strain, and the cyclic part $\epsilon_{H,c} = \epsilon_H - \epsilon_{H,b}$ represents the strain recovered after each loop.

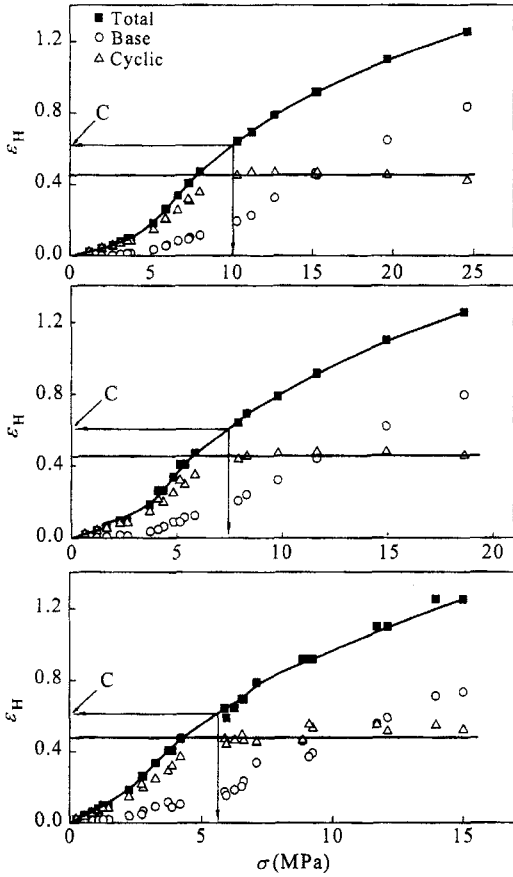


Fig. 3 Total strain, base part and cyclic strain component as a function of imposed stress, derived for PEVA18 from step-cycle tests at different temperatures: 23°C (top), 38°C (center) and 50°C (bottom)

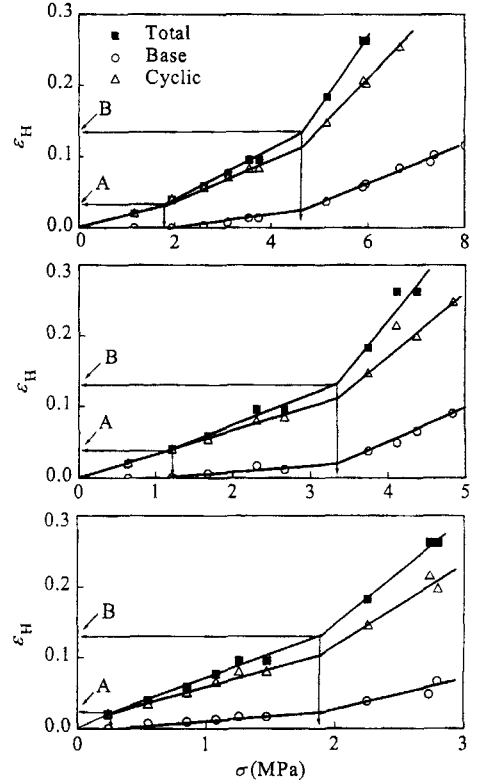


Fig. 4 PEVA18 at different temperatures: 23°C (top), 38°C (center) and 50°C (bottom)
Partitioning of the total strain into the cyclic and the base component for small strain values (enlarged view from Fig. 3)

RESULTS AND DISCUSSIONS

The Critical Strain Law

We start with some typical results of the step-cycle measurements on a polyethylene-vinyl acetate copolymer (PEVA18). Figure 3 shows the changes with temperature of the total strain, the base, and the cyclic component. At first, both base and cyclic parts increase with the total imposed strain. However, the increase for the cyclic part is limited. When the total strain reaches a critical value ($\varepsilon_H(C) = 0.6$) the elastic cyclic strain arrives at a plateau. Further stretching only leads to a more pronounced plasticity. At this transition point stresses vary with the deformation temperature but the strains keep constant. A closer look at the low deformation region (Fig. 4) shows the same temperature independence for the two other transition points A and B. At A, for the first time the irreversible strain $\varepsilon_{H, b}$ arises. Then at point B, a strong increase in the differential compliance is observed. The same results are also obtained for other polyethylene samples with different crystallinity when they were deformed at different temperature and strain rate^[15, 16, 22]. Critical strains A, B and C always appear at the same value of about 0.03, 0.12 and 0.6, respectively. Accompanying changes of the crystalline texture were found by the simultaneous 2D wide angle X-ray scattering measurements^[15]. These critical strains were understood as: (1) the onset of isolated slip processes (point A), (2) a change into a collective activity of slips (point B), and (3) the beginning of fibril formation after a fragmentation of the lamellar crystals (point C). Besides the three critical points, for polyethylenes with moderate molecular weights another transition point, D, shows up before fracture. Only when the imposed deformation is larger than D the truly plastic strain appears. Below D, all deformations can be totally recovered upon heating samples to their melting point. Point D depends on the molecular weight^[22], molecular chain structure and deformation temperature^[16, 22].

The Elastic Modulus and the Yield Stress

Studies mostly concerned the mechanical properties at room temperature. The few attempts to interpret the variations with temperature were not too successful. In one paper, Crist *et al.*^[23] calculated the temperature dependence of the yield stress based on a screw dislocation model. Comparison with the experimental results was not very satisfactory. The effect of temperature on Young's modulus and yield stress is huge as shown in Fig. 5. The lines in both plots just depict the empirical law^[23] that, in a semilogarithmic plot, the room temperature values of the yield stress and the Young's modulus of polyethylene are linearly dependent on the crystallinity. Looking at the data of PE27 as an example we find large drops in both the yield stress and the Young's modulus when the crystallinity does not change much, but the drawing temperature is increased. Hence, we find an explicit temperature effect as a major property in the mechanics and have to ask about its origin. In a global view, deformation of a semi-crystalline polymer may be understood as the stretching of two interpenetrating networks, one built up by the entangled fluid parts and the other by the crystallites. Entropic forces generated from the entangled fluid portions increase linearly with the drawing temperature which would lead to an increase of the elastic modulus with temperature. Obviously, according to our results (Fig. 5) this is not seen in the drawing of a

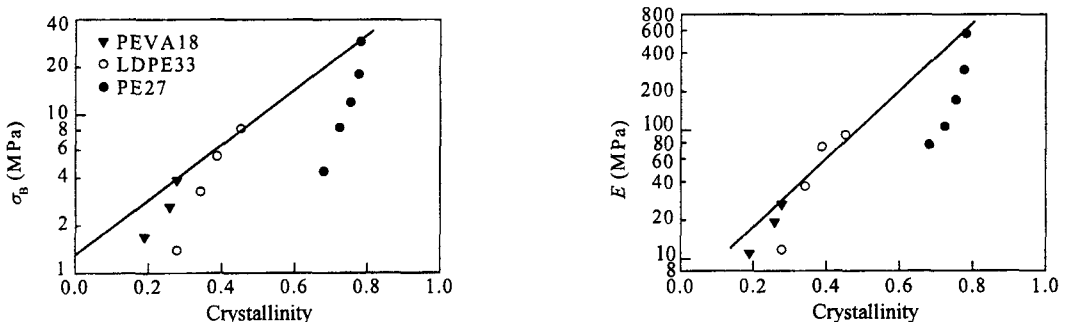


Fig. 5 Yield stress and Young's modulus in dependence on the crystallinity of PE27, LDPE33 and PEVA18. The line denotes the room temperature relationship. Data taken from Refs. [16, 22] from measurements obtained at different temperatures.

semi-crystalline polymer. It can be thus concluded that at low deformations below the yield point the force is mainly transmitted via the crystallites. The elastic modulus and also the yield stress then are determined by their coupling. In view of the blocky substructure of the crystalline lamellae it is clear that the coupling of the blocks is of primary importance. Increasing the temperature may lead to a successive decoupling of blocks, which would reduce the number of routes of force transmission and thus the stiffness.

If we acknowledge that the Young's modulus is determined by the coupling of blocks, then the yield stress is the stress which causes a collective activity of the block slips. Both quantities are related to the blocky lamellar substructure of semi-crystalline polymers. It is thus reasonable to ask about the relationship between them. Approximately, the yield stress and strain are related by

$$\sigma_y \cong E \epsilon_y \tag{4}$$

It is clear that as soon as the slip process occurs the structure is starting to be changed and thus the Young's modulus. This happens at point A. However, as we have shown in the last section the yield strain B remains small and constant for all testing condition. This gives $\epsilon_y = \text{Constant}$, and from Eq. (4) we have $\sigma_y \sim E$. It is thus reasonable to use Eq. (4) to study the relationship between σ_y and E . If Eq. (4) holds, we would expect that a plot of σ_y versus E follows a line. Figures 6 gives the result, which confirms the expectation.

As we have discussed that the same deformation mechanism was found for all PEs under all testing conditions, we thus expect that Eq. (4) holds for all PEs. This is indeed the case, as indicted in Fig. 6. Data from three distinctly different polyethylenes and testing temperatures follow a same line. The crystallinity changes the number of blocks on the one side and, the temperature changes the viscosity of the block-slip process on the other side. And both are strongly related with the mechanical properties. However, as demonstrated in Fig. 6, both factors affect the relation between the Young's modulus and yield stress in the same way. This is clearly demonstrated in Fig. 6 when we look for example at the data of PE27. The shift of the data points to lower values is mainly due to the change of the temperature. Within the testing temperature range, crystallinity changes only by a small amount. At high testing temperatures data points are at the same positions as the data from low crystallinity samples taken at low testing temperatures.

The Role of the Amorphous Network

As was demonstrated in last section, the total strain is composed of an elastic and a plastic component which were derived via the step-cycle test. Both components increase with increasing total strain. However, when a critical strain $\epsilon_H = 0.6$ is reached, the elastic part arrives at a maximum value. An elastic strain plateau is thus formed. In Fig. 7, this plateau elastic strain is plotted as a function of the crystallinity for all PEs studied in our group^[15, 16, 22].

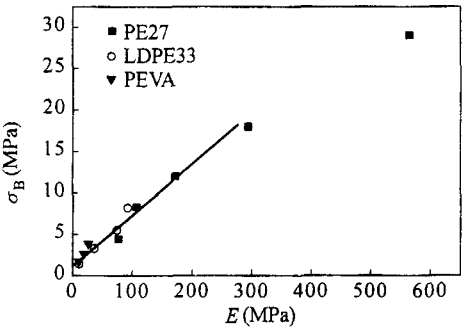


Fig. 6 The relationship between the yield stress σ and the Young's modulus E of PE27, LDPE33 and PEVA18
Data from Fig. 5

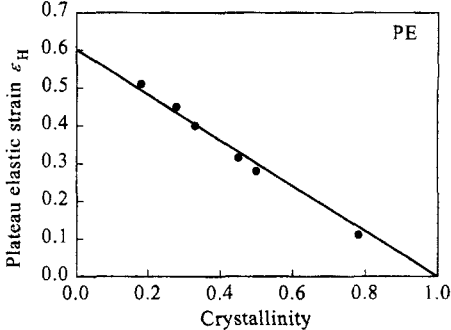


Fig. 7 Crystallinity dependence of the plateau elastic strains as derived from data of Refs. [15, 16, 22]

The linear dependence of the plateau elastic strain $\varepsilon_{H, P}$ on the crystallinity α_c is described by the relation $\varepsilon_{H, P} = 0.6 \times (1 - \alpha_c)$. Apart from this linear dependence, two more important items of information can be obtained from the limiting situations of the samples. Considering a sample with 100% crystallinity, one may conclude that it has no elasticity at all which means that the slip of blocks is irreversible due to the absence of the amorphous entangled fluid, which generally provides the restoring network force. Decreasing the crystallinity results in a linear increase of the elastic plateau. This increase, however, is limited as the crystallinity tends to zero. Then the maximum plateau elastic strain becomes identical with the critical strain at C, $\varepsilon_{H, P} = \varepsilon_H(C) = 0.6$. This finding leads us to the conclusion that the critical strain C is a property of the entangled fluid portion only. For a better understanding we carry out a "Gedankenexperiment". Let us consider a set of semicrystalline PE's with different crystallinity. Two special samples are needed: On the one hand, a fully crystallized PE still with the blocky substructure presents the ideal solid behaviour; on the other hand, we imagine a sample without crystallinity but still keeping the structural feature of lamellae. In the latter case, the lamellar feature can be regarded as a certain number of zero thickness sheets, which are still forming a percolation network. The sheets react to the imposed strain exactly in the same way as the real lamellae. They can be divided into smaller pieces at small strain, and slip out of each other while they are stretched further, and become fragmented like the blocks in the real case when the imposed strain reaches the critical strain at point C. The only difference will be that in the ideal sample the sheet-like lamellae exist without any volume fraction. The assumption makes our ideal sample different from a real polymer melt and an ideal rubber. How would such an ideal sample react on the imposed strain? Figure 8 gives the answer. Following a step-cycle test, we split the total strain into a cyclic (elastic) $\varepsilon_{H, c}$ part and a base (plastic) $\varepsilon_{H, b}$ part. We plot the cyclic and the base strain as a function of the total strain.

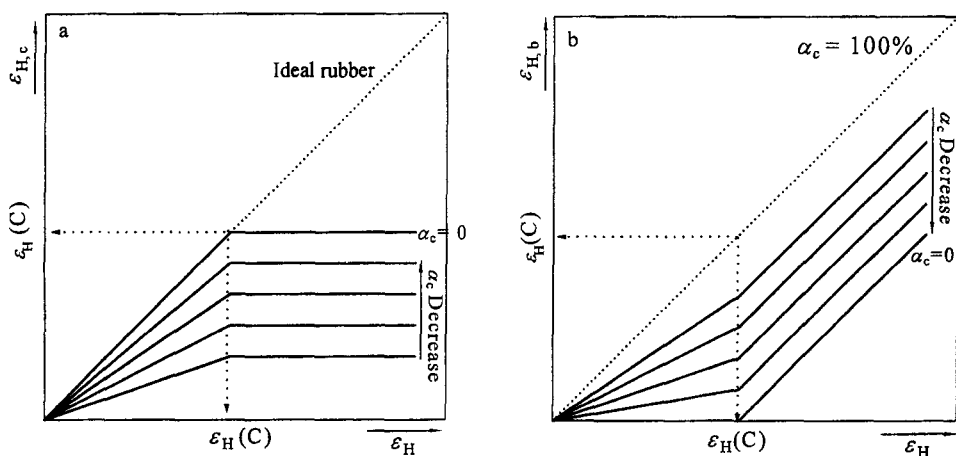


Fig. 8 Results of ideal step-cycle tests for samples with different crystallinity: (a) cyclic strain $\varepsilon_{H, c}$ as a function of total strain ε_H ; (b) the base strain $\varepsilon_{H, b}$ as a function of total strain ε_H

Figure 8(a) presents the dependence of cyclic strains on imposed total strains, and Fig. 8(b) gives the behaviour of the base part correspondingly. It can be seen that the cyclic and base strains show a general tendency on stretching. The critical strain is observed at $\varepsilon_H(C)$ where the elastic plateau appears and, the plastic strain increases in a more pronounced manner correspondingly. First, let us consider the base strain of the fully crystallized sample in Fig. 8(b). Due to the absence of amorphous entangled fluid, this sample loses the critical strain behaviour. Generally we get $\varepsilon_{H, b} = \varepsilon_H$ in this case. No elasticity should be expected because we assumed that this ideal sample deforms via a block slip process only. The samples with a certain crystallinity react as in the real case. As the crystallinity decreases to the other limiting situation, $\alpha_c = 0$, a unique behaviour of the ideal sample shows up. In Fig. 8(a), the ideal sample reacts like an ideal rubber, if the total strain is less than the critical strain $\varepsilon_H(C)$. When the total strain is larger than $\varepsilon_H(C)$, it shows a maximum elasticity, *i.e.* the plateau of

the cyclic strain, which is accompanied by the linear increase of the base part from $\varepsilon_H(C)$ on (Fig. 8b). For a better understanding of this special behaviour we make a simple calculation. From the finding of a critical strain law governing the deformation process, we may conclude that a homogeneous strain situation is always obtained when a semi-crystalline polymer is deformed. We have

$$\varepsilon_H(\text{Cry.}) = \varepsilon_H(\text{Amor.}) = \varepsilon_H \quad (5)$$

where $\varepsilon_H(\text{Cry.})$, $\varepsilon_H(\text{Amor.})$ and ε_H denote the strain in the crystalline region, amorphous region and for the sample as a whole respectively. We denote the length of the whole sample, and the fold length of the trajectories through crystalline and amorphous phases as L , L_C and L_A . It follows from the definition of Hencky strain and equation 5 that

$$\ln \frac{L_C + \Delta L_C}{L_C} = \ln \frac{L_A + \Delta L_A}{L_A} = \ln \frac{L + \Delta L_C + \Delta L_A}{L} \quad (6)$$

where ΔL_C and ΔL_A are the extensions of the crystalline and the amorphous phase trajectories respectively. The deformation of the crystalline phase is accomplished by the slip process and thus irreversible. Hence, the elasticity of the sample is given by the deformed amorphous part ΔL_A . In the step-cycle experiment we have the cyclic strain as

$$\varepsilon_{H,c} = \ln \frac{L + \Delta L_C + \Delta L_A}{L + \Delta L_C} = \ln \left(1 + \frac{\Delta L_A}{L + \Delta L_C} \right) \quad (7)$$

and the base part as

$$\varepsilon_{H,b} = \ln \frac{L + \Delta L_C}{L} \quad (8)$$

According to Eq. (6) we have

$$\Delta L_C = \Delta L_A \frac{L_C}{L_A} \quad (9)$$

It follows from Eqs. (7) and (9) that

$$\varepsilon_{H,c} = \ln \left(1 + \frac{\Delta L_A}{L + \Delta L_A \frac{L_C}{L_A}} \right) = \ln \left(1 + \frac{1}{\frac{L}{\Delta L_A} + \frac{L_C}{L_A}} \right) \quad (10)$$

Equation (10) gives the relationship between the cyclic strain of the sample and the deformation of amorphous part. It keeps true only if the strain is homogeneously distributed, *i.e.* Eq. (6) holds. In general, the cyclic strain $\varepsilon_{H,c}$ increases with increasing deformation of amorphous ΔL_A as well as the total imposed strain according to Eq. (6). The value of $\varepsilon_{H,c}$ changes with the crystallinity through the ratio $\frac{L_C}{L_A}$. In the two limiting

cases $L_C = 0$ and $L_C = L$ we have

$$\varepsilon_{H,c} = \ln \frac{L + \Delta L_A}{L} = \varepsilon_H \quad (11)$$

and

$$\varepsilon_{H,c} = \ln \left(1 + \frac{1}{\frac{L}{\Delta L_A} + \infty} \right) = 0 \quad (12)$$

respectively. The above two equations correctly describe the behaviour of the two ideal samples shown in Fig. 8

in the range of $\varepsilon_H \leq \varepsilon_H(C)$. Equation (10) no longer makes sense when the imposed strain is larger than $\varepsilon_H(C)$ which means that the homogeneous strain situation is becoming lost.

How can this special behaviour be understood? It has been discovered for the PEs and s-PP by the measurements of the wide angle X-ray scattering patterns that at C the crystallites begin to be destroyed and new crystallites, namely fibrils, start to be formed^[15, 19]. The physical background of critical point C could be interpreted based on these results. Along a stretching process, one can find first isolated slips being activated at the end of a Hookean elasticity region (A), followed by a collective activity of the slips (B), then the fragmentation of crystallites accompanied by the formation of fibrils (C), and finally, before fracture a chain disentanglement (D). All these transitions show up in step-cycle tests in changes of recovery properties. However, as we mentioned above, for an ideal sample with zero crystallinity neither point A nor point B shows up in the recovery properties. It reacts like an ideal rubber for strains below $\varepsilon_H(C)$ (Fig. 8). From $\varepsilon_H(C)$ on, the ideal sample no longer follows the behaviour of the ideal rubber, but shows an irreversible deformation. How can this be true? The answer is the formation of fibrils. For this formation process, the destruction of crystallites, by a strain induced melting process, is necessary. This view is supported by the experimental observations that the crystalline thickness of semi-crystalline polymer deformed at elevated temperatures is only related with the deformation temperature. The higher the deformation temperature is the thicker are the crystalline thickness. It is thus necessary to melt the previously existing crystalline lamellae before the formation of fibrils.

In general, a critical stress is needed to destroy a crystal. The existence of the critical strain C means that a critical stress is always generated when the sample is stretched to a strain of $\varepsilon_H(C)$. In principle, this stress is created by the orientation of the amorphous part according to the stress-optical rule (see Ref. [24] chapter 7). It follows from the stress-optical rule that

$$\sigma \sim S \quad (13)$$

where S is the orientational order parameter of chains in the amorphous portion. The orientation of the chains under a certain strain is determined by the entanglement density. The denser the entanglements the higher is the orientation. In this sense we arrive at the conclusion that the entanglement density is the same for all samples we studied since they all show the same critical strain C. It should be mentioned that the fibrils form not only out of the previously existing lamellae but may also include deformed amorphous parts. The fibrils provide also the irreversible deformation in the ideal sample. A stretching above C leads to an increase of the amount of fibrils only, and the elasticity does not change any more. The process may also lead to a reorganization of the network within the sample.

CONCLUSIONS

The mechanism of the tensile deformation in semi-crystalline polymers was studied based on true stress-strain measurements obtained via a video-controlled tensile set-up. Analyzing the temperature dependence of elastic modulus and yield stress and the crystallinity dependence of the maximum elasticity of samples shows clear evidence for a transition from the crystalline block slips to the dominance of network stretching. The roles of the crystalline and the amorphous phases change with the deformation stage. Low deformation behavior is controlled by the crystalline block coupling and coarse slips. When the samples are stretched to a critical strain, the force generated from the entangled fluid portion reaches the critical value leading to destruction of the crystallites. The dominant deformation mechanism is thus changed into a disaggregation – recrystallization process.

Acknowledgement Support of this work by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 428 and Graduiertenkolleg "Strukturbildung in Makromolekularen Systemen") is gratefully acknowledged.

REFERENCES

- 1 Capaccio, G. and Ward, I.M., *Colloid Polym. Sci.*, 1982, 260: 46
- 2 Pakula, T. and Trznadel, M., *Polymer*, 1985, 26: 1011
- 3 Haward, R. and Thackray, G., *Proc. Roy. Soc. A*, 1968, 302: 453
- 4 Haward, R., *Macromolecules*, 1993, 26: 5860
- 5 Flory, P.J. and Yoon, D.Y., *Nature*, 1978, 272: 226
- 6 Cowking, A. and Rider, J., *J. Mater. Sci.*, 1969, 4: 1051
- 7 Keller, A. and Pope, D., *J. Mater. Sci.*, 1971, 6: 453
- 8 Young, R., Bowden, P., Ritchie, J. and Rider, J., *J. Mater. Sci.*, 1973, 8: 23
- 9 Bowden, P. and Young, R., *J. Mater. Sci.*, 1974, 9: 2034
- 10 Gerrits, N. and Tervoort, Y., *J. Mater. Sci.*, 1992, 27: 1385
- 11 Seguela, R. and Rietsch, F., *J. Mater. Sci. Lett.*, 1990, (9): 4
- 12 Hugel, T., Strobl, G. and Thomann, R., *Acta Polym.*, 1999, 50: 214
- 13 Loos, J. Thuene, P.C. Lemstra, P.J. and Niemantsverdriet, J.W., *Macromolecules*, 1999, 32: 8910
- 14 Strobl, G., *Eur. Phys. J. -E*, 2000, (3): 165
- 15 Hiss, R., Hobeika, S., Lynn, C. and Strobl, G., *Macromolecules*, 1999, 32: 4390
- 16 Hobeika, S., Men, Y. and Strobl, G., *Macromolecules*, 2000, 33: 1827
- 17 Men, Y. and Strobl, G., *J. Macromol. Sci. Phys.*, 2001, B40: 775
- 18 Hiss, R., Ph.D. Thesis, University of Freiburg, 1996
- 19 Hobeika, S., Ph.D. Thesis, University of Freiburg, 1999
- 20 G'Sell, C. and Jonas, J., *J. Mater. Sci.*, 1979, 14: 583
- 21 G'Sell, C., Hiver, J., Dahoun, A. and Souahi, A., *J. Mater. Sci.*, 1992, 27: 5031
- 22 Men, Y., Ph.D. thesis, University of Freiburg, 2001
- 23 Crist, B. Fisher, C.J. and Howard, P.R., *Macromolecules*, 1989, 22: 1709
- 24 Strobl, G., "The Physics of Polymers", Springer, Berlin, 1997