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Plasticity of semi-crystalline polymers: crystal slip versus melting-recrystallization

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Abstract: Semi-crystalline polymers can be drawn up to very high draw ratios that involve a complete molecular rearrangement of the chain-folded lamellar morphology into a more or less chain-unfolded fibrillar microstructure. This metamorphosis is likely to take place through an intermediate state of high molecular disorder at a local scale. This is the reason why some authors talk of a strain-induced melting-recrystallization process. In contrast, several structural features occurring at moderate plastic strains are relevant to strictly crystallographic processes. A critical discussion of experimental findings and theoretical approaches is made for pointing out the strength or the deficiency of the different author argumentations. No doubt that both phenomena can occur: crystallographic processes are active at all strain levels whereas melting-recrystallization is restricted to the post-yield stage accompanied with chain unfolding. Melting-recrystallization is rather a corollary of chain unfolding than a basic mechanism of the plastic deformation. Besides, it may concern only a part of the crystalline phase and can be inhibited under adequate deformation conditions.

Introduction

The plastic behaviour of semi-crystalline polymers was formerly approached by scientists from the domain of materials science. The relevant concepts of solid state physics consist of crystallographic slip processes involving thermal activation of dislocations [1-10]. Plastic glide, in a polymeric crystal lattice, necessarily occurs in crystallographic planes containing the chains stems in order to avoid cutting of intra-chain covalent bonds. Both longitudinal slip and transverse slip can be activated, parallel or normal to the chain axis [11], as sketched in Fig. 1. In contrast to growth dislocations that have been experimentally often observed, deformation dislocations in polymeric crystals have mainly been studied from a theoretical standpoint. Energetic considerations showed that screw dislocations parallel to the chain axis are more favorable than edge dislocations [3, 9].

The pioneer works by Peterlin and coworkers on the large scale plastic deformation of semi-crystalline polymers have led to the elaboration of a micro-structural model describing the metamorphosis of the original chain-folded lamellar morphology into the partly unfolded-chain fibrillar structure. In that so-called fibrillar transition model, the plastic yielding is ascribed to the shearing of the crystalline lamellae followed by fragmentation into crystal blocks [12], as shown in the sketch of Fig. 2. The crystal blocks are further realigned into microfibrils, like strings of pearls with regular spacing between the blocks. This process should not involve significant change of the crystal block thickness, in comparison to the mother lamellae. However, the commonly reported observation that the long fibril period of various semi-crystalline polymers plastically drawn far beyond the yield point only depends on the draw temperature

[13-15] led a number of authors to conclude that the crystalline phase undergoes a strain-induced melting and subsequently recrystallizes during the drawing process. The former mentioning of melting-recrystallization upon drawing of semi-crystalline polymers by Flory and Yoon [16], more from intuition than from experimental facts, is regularly taken as testimony for the phenomenon certainty.

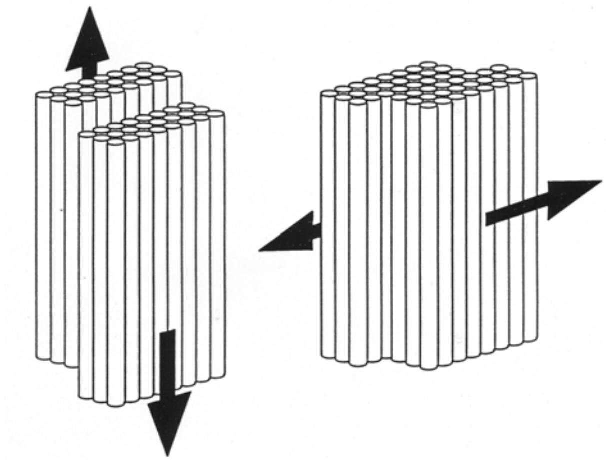


Fig. 1. Schematic crystal slip processes in polymeric materials: (a) longitudinal slip and (b) transverse slip (the cylinders hold for the chain stems) (reproduced from ref. 54 with permission of Elsevier, Copyright 1994).

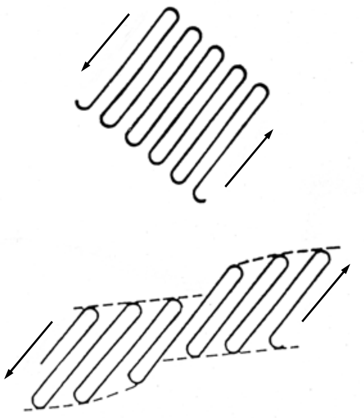


Fig. 2. Peterlin's molecular model for the homogeneous shear and fragmentation of a crystalline lamella (reproduced from ref.12 with permission of the American Institute of Physics, Copyright 1977).

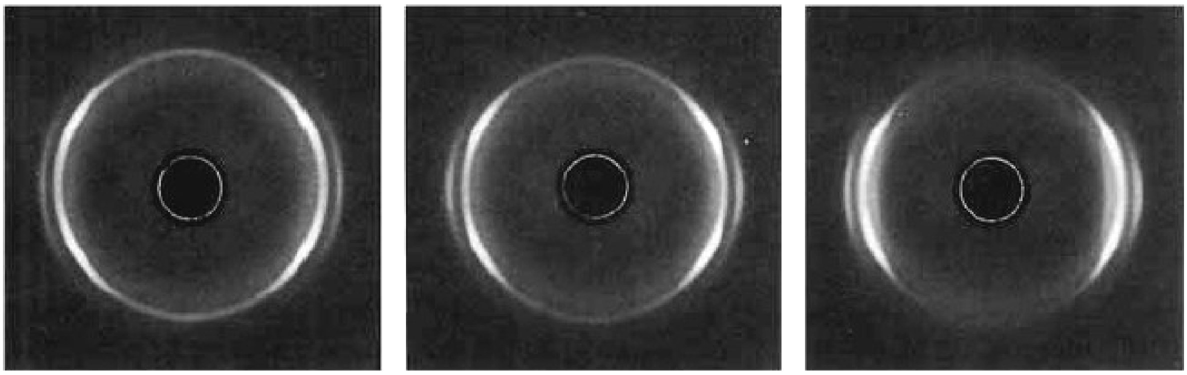
Borrowing from a meticulous transmission electron microscopy study of drawn polyethylene (PE) thin films, Adams et al. [17] proposed a modified fibrillar transition model that includes the melting of a part of the crystalline phase that recrystallizes into thinner crystal blocks than the original lamellae. These new crystal blocks are suggested to grow in alternation between the crystal fragments issued from the broken lamellae, along the draw direction. Although Adams' model could be viewed as a reconciliation of the two points of view, the problem still persists, and many authors continue to privilege one the two processes without evidence that the other one is not valid. The goal of the present paper is to review the various experimental data and hypotheses that have been put forward in that controversial context, in order to separate the actual physical evidences from the subjective arguments.

The crystallographic approach

Crystal slip and texturing

Wide-angle X-ray scattering (WAXS) has been long used for studying the orientation of chains during the melt spinning, film blowing or solid state plastic drawing of semi-crystalline polymers. This is a very convenient means for measuring the degree of chain alignment that is the basis of the self-reinforcement of fibers and films. Small-angle X-ray scattering (SAXS) was also used to evaluate the texturing of the crystalline phase that contributes to the mechanical performances.

Regarding the mechanisms of plastic deformation, combination of SAXS and WAXS proved to be one of the most powerful tools for probing the crystal slip processes. Much attention in this field has been focused at PE which is quite simple from the standpoint of crystalline structure and exhibits a very large panel of chemical architectures. During the plastic instability regime that precedes the fibrillar texturing upon tensile drawing, specific crystallographic orientations develop [18-25]. Fig. 3 reports an example of such typical orientation behaviour of PE under tensile drawing: the outer (200) reflection quickly gathers about the equator while the inner (110) reflection displays a steady quadrant position before to gradually shift to the equator.



$\varepsilon_z=0.2$ $\varepsilon_z=0.4$ $\varepsilon_z=1.0$

Fig. 3. WAXS patterns at three local strains for the tensile drawing of high density PE at room temperature (reproduced from ref. 25 with permission of John Wiley & Sons, Copyright 1996).

This means that the chain axis takes an oblique orientation with respect to the draw axis, before it takes a parallel orientation. Considering that crystal slip necessarily occurs in (hk0) planes containing the chain stems, this finding reveals that the crystallites are tilted towards a preferred direction that is consistent with a Tresca plasticity criterion: plastic glide will be activated when the resolved shear stress in the slip plane, τ, will reach a critical value τ_C. Fig. 4 shows the resolved shear stress construction for uniaxial tensile drawing [26] which obeys the following relation

$$\tau = \sigma \cos\chi \cos\lambda$$

where χ and λ are respectively the angles of the slip plane normal and the slip direction with respect to the draw stress σ. Yielding starts when the resolved shear stress is reached in a dense crystallographic plane family having low τ_C. This condition can be fulfilled by either increasing the draw stress or decreasing the Schmid factor, $\cos\chi \cos\lambda$, by plane tilting with respect to the main stress. Therefore, oblique orientation of the chains with respect to the principal stress gives evidence of crystallite rotation in order to achieve plastic yielding at the lower energy cost. Investigations of single-crystal-textured PE samples have afforded a better insight into the mechanisms of crystal slip [4, 5, 7, 10]. Borrowing from this kind of investigation, Argon and coworkers [27-30] have analyzed the crystalline slip processes involved during texturing of PE, under various deformation modes, using transmission electron microscopy (TEM) together with WAXS and SAXS.

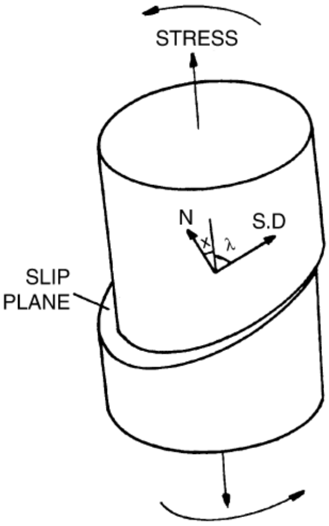


Fig. 4. Resolved shear stress construction for plastic deformation in uniaxial tensile test (reproduced from ref.26 with permission of Elsevier, Copyright 2003).

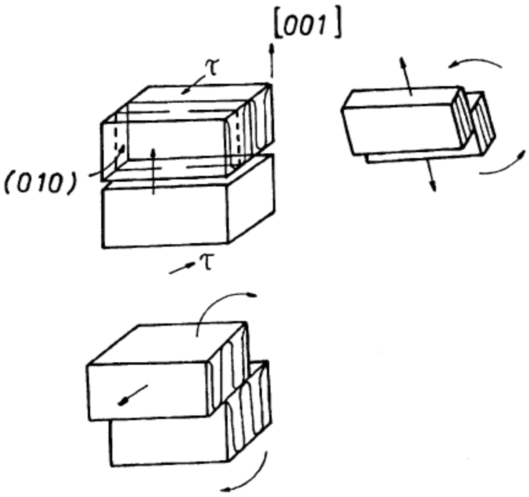


Fig. 5. Schematic of the rotation about the *a* axis and shear along the (010)[001] slip system of a PE crystallite leading to the *b* axis orientation (reproduced from ref.29 with permission of The American Chemical Society, Copyright 1992).

The faster tilting of the *a* crystallographic axis toward the equator under tensile testing reveals a rotation of the lamellae about the *b* axis. This has been taken as evidence of a preferred (100)[001] slip activation [29], in consideration that the critical shear stress of this slip system is the lower one in PE. Crystallite rotation about the *a* axis accompanied with shear of the (010)[001] slip system can also contribute to the plastic behaviour of PE leading to *b* axis orientation, as illustrated in Fig. 5.

Argon and coworkers have also studied isotropic and single-crystal-textured samples of various semi-crystalline polymers such as polyamide 6 [31, 32] and poly(ethylene-terephthalate) [33]. As in the case of PE, these authors have reported detailed analyzes of the plastic processes in terms of crystallographic slip, together with useful data of critical shear stresses and pressure sensitivity factors [31].

Strain-induced phase transition

Twinning and phase transition have been shown to occur in the early stage of plastic deformation of PE [1, 4, 34-37]. Such structural changes, often observed during the solid state forming of metals, are typically shear-driven phenomena that can only be accounted for on crystallographic grounds. Fig. 6 shows the martensitic-like orthorhombic-monoclinic phase change in PE under uniaxial compression [34]. The shearing responsible for the transition is indicated in the median plane of the figure.

Worth mentioning is the more recent *in situ* experimental studies of texture evolution during plastic drawing by combined WAXS and SAXS, thanks to the emergence of high flux synchrotron facilities. Butler et al. [38-41] have revisited the mechanisms of plastic deformation in PE already established from *post mortem* experiments. These authors noticeably corroborated the occurrence of homogeneous and localized crystal slip. Besides, an interesting finding from Butler *et al.* is that the martensitic phase transition in PE is a companion effect of cavitation [38]. Although the authors did not discuss the physical meaning of that coincidence, it is highly likely that heterogeneous crystal slip and crystal fragmentation could concomitantly nucleate cavities between the crystal blocks and strain-induced stacking faults at the fracture surface of these blocks [42].

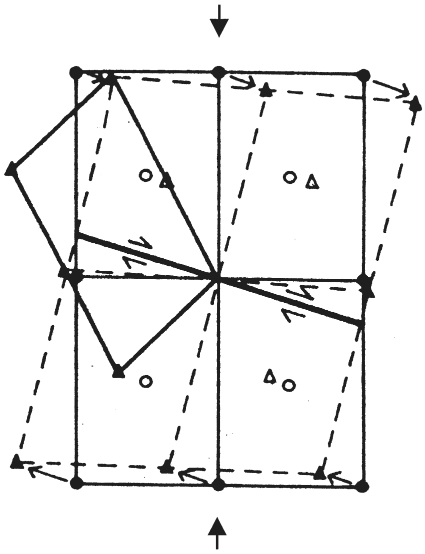


Fig. 6. Martensitic phase transition in the orthorhombic unit cell of PE in compressive testing (reproduced from ref.4 with permission of John Wiley & Sons, Copyright 1970).

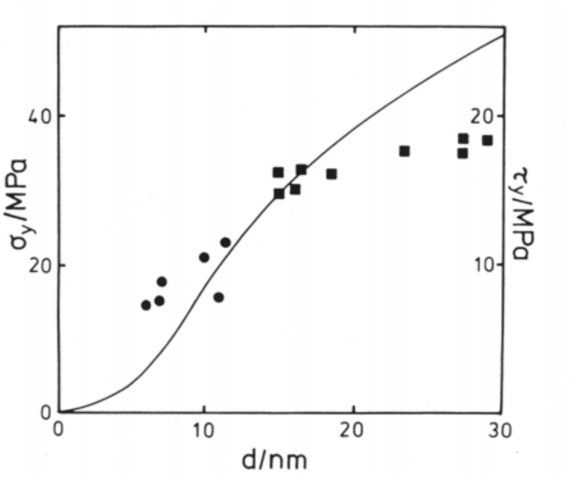


Fig. 7. Experimental and predicted yield stress for PE as a function of crystal thickness, at room temperature: (■, ●) experimental data from various sources; (—) prediction from Young's dislocation model (reproduced from ref. 50 with permission of The Institute of Physics Australia, Copyright 1988).

Modelling of semi- crystalline polymer plasticity

Theoretical approaches of semi-crystalline polymer plastic behaviour have been tempted in order to help understanding the mechanisms of the phenomenon. The Eyring formalization of thermally activated processes has been applied to account for the temperature and strain rate dependency of the flow stress for a number of semi-crystalline polymers [43-46]. In the case of PE and PP, Truss et al. [44, 45] showed a good correlation with the activation of the relaxation processes that govern the viscoelastic behaviour. The authors emphasized the role of the molecular mobility in the crystal for temperatures above the glass transition. This point of view has been later reinforced by the observation of double yield phenomenon in ethylene copolymers [46] that could be ascribed to the activation of two relaxation processes in the crystalline phase of PE already demonstrated by several authors [47-49]. Nylon 6 has also been shown to obey a similar plastic behaviour, with an interpretation based on the motion of dislocations in the crystalline phase [32].

A different approach has been proposed by Young [8] by introducing concepts of solid state physics. The quite low thickness of the crystal lamella enables the thermal nucleation, from the lateral surface of polymer lamellar crystals, of screw dislocations parallel to the chain axis. The model predicts a monotonous decrease of yield stress with decreasing crystal thickness which fairly follows experimental data from various sources [50], as reported in Fig. 7.

Lee *et al.* [51, 52] reported a very sophisticated micromechanical simulation involving both physical ingredients to account for the crystallographic processes and semi-empirical equations to account for the kinetic aspects of the plastic deformation. The representative element of this self-consistent model is composed of crystal lamellae adjacent to an amorphous layer. The activation of several crystallographic slip processes is taken into consideration, assuming an empirical visco-plastic law for every slip system. Some uncertainty exists on the values of the critical shear stress of a great number of slip planes that cannot be obtained experimentally. The model also assumes an empirical kinetic law for the amorphous layer that makes the stress transfer between neighbouring lamellae. The straining of the chain segments of the amorphous layer is assumed to follow hyper-elastic non-gaussian behaviour. In the case of PE, the model fairly well predicts both the stress-strain relationship and the orientational behaviour of the crystalline phase, over a very large strain domain, for various deformation modes.

In the meantime, G'Sell and coworkers [53-57] have experimentally studied the true stress-strain behaviour and strain-induced crystallographic texturing of several isotropic semi-crystalline polymers, namely polyethylene, poly(aryl-ether-ether-ketone), poly(methylene-oxide) and polypropylene. Very nice simulations of both the mechanical behaviour and the crystallographic texture, under various deformation modes, have been computed using Molinari *et al.*'s self-consistent model [58] that only considers crystallographic slip processes for a set of randomly oriented crystallites in a purely crystalline material. The authors found it necessary to modify the model with an additive non-gaussian network contribution to account for a part of the strain-hardening due to chain unfolding. This procedure is somewhat different from that of Lee et al., although the purpose was the same.

The major benefit from the above mentioned self-consistent approaches is that they provide satisfying predictions of crystalline texture evolutions, as illustrated in Fig. 8 in the case of the (100) planes of PEEK under both uniaxial tensile testing and simple shear using a 8 slip system. Besides, based on equivalent stress-strain curves, the models enable accounting for the much stronger strain-hardening that is experimentally observed in tensile mode as compared with simple shear, for various polymers [55-57]. This is demonstrated in Fig. 9 in the case of PEEK [56].

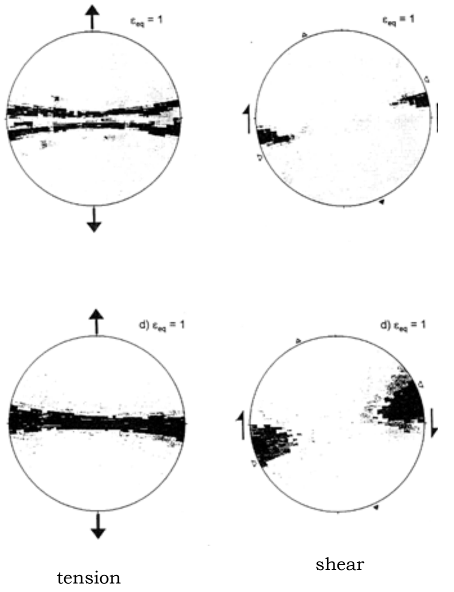


Fig. 8. Experimental (upper) and simulated (lower) pole figures for the texturing of PEEK under uniaxial tension and shear, at an equivalent strain ε_{eq}=1 (reproduced from ref. 56 with permission of John Wiley & Sons, Copyright 1995).

This kind of modelling has aroused interest from other groups [59, 60] in spite of the following shortcomings : (1) no indication was given about the strain contributions of the various slip systems to the overall plastic deformation of the materials, (2) the models did not account for the strong influence of crystal thickness on the flow stress that has been reported by several authors [50, 61-66], (3) they do not account for the fibrillar transition resulting from the fragmentation of the crystalline lamellae and the chain-unfolding from the fracture surfaces of the crystal blocks and (4) they do not contain ingredients that could account for the deformation heterogeneity in the case of well-formed spherulitic morphology. This last point has recently received attention from several groups but very few reports are available at present [67].

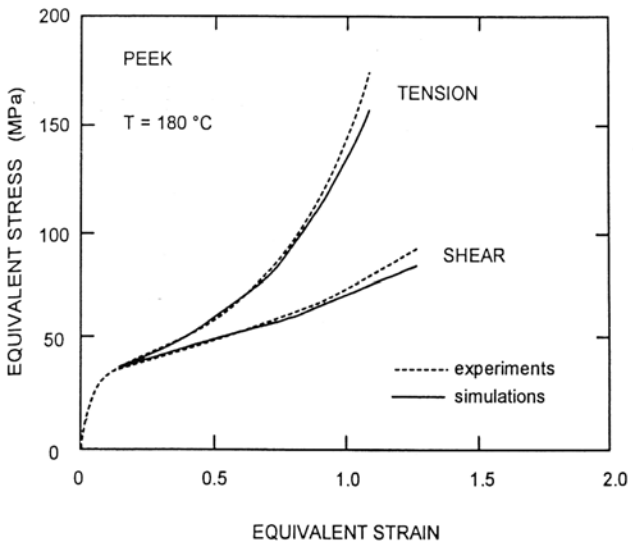


Fig. 9. Experimental and simulated stress-strain curves for PEEK under tensile and shear deformation modes (reproduced from ref. 56 with permission of John Wiley & Sons, Copyright 1995).

The melting-recrystallization approach

Considering that the plastic deformation of semi-crystalline polymer beyond the yield point involves a tremendous molecular rearrangement from the chain-folded lamellar microstructure to the more or less chain-extended fibrillar microstructure, Flory and Yoon [16] formerly suggested that a melting-recrystallization process is likely to occur during drawing. Indeed, it is easy to figure out that the above mentioned metamorphosis proceeds via an intermediate state of high molecular disorder that can be compared with the molten state. This strain-induced melting should occur gradually at a local scale and for short duration, in such a way that the overall material remains solid at any moment of the drawing. In spite of the fact that many authors often referred to Flory-Yoon's paper, the authors did not provide any proof for the melting-recrystallization process, and they just suggested its occurrence.

Abnormal behaviour of the fibrillar morphology

The main experimental fact in support to the melting-recrystallization phenomenon is that the stacking long period of the fibrillar structure of drawn semi-crystalline polymers only depends on the temperature of the drawing experiment, irrespective of the initial long period of the material [13-15, 68-70]. Fig. 10 shows that the long period of drawn HDPE as a function of the draw temperature, T_d, follows the same trend as the long period of isotropic HDPE as a function of isothermal crystallization temperature, T_c [69].

Such a long period dependency on draw temperature is a strong hint of drastic structural rearrangements in the crystalline phase that cannot be ascribed just to an annealing effect considering, on one hand, of the relative short time of the drawing experiment and, on the other hand, that the long period may be reduced with respect to the initial one at low draw temperature. Besides, high strain rates have been reported to increase the long period in drawn PP with respect to low strain rates due to self-heating [68]. It is therefore much likely that the final long period of the microfibrils has something to do with the recrystallization of chains unfolded from the crystalline lamellae, at the actual temperature of the material during the experiment.

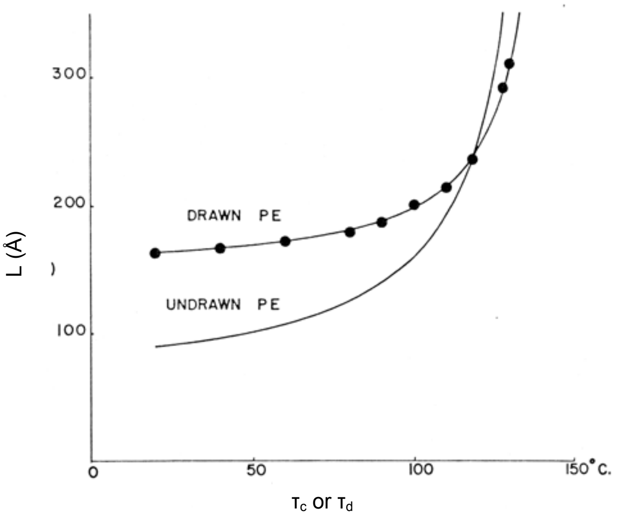


Fig. 10. HDPE long period as a function of temperature for isothermal crystallization (——) and for drawing (•) (reproduced from ref. 69 with permission of John Wiley & Sons, Copyright 1969).

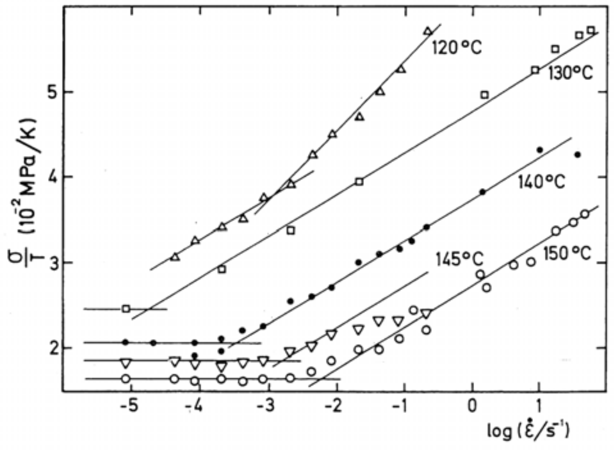


Fig. 11. Yield stress to temperature ratio as a function of strain rate for PVDF (reproduced from ref. 75 with permission of Springer Verlag, copyright 1995).

It is however to be noticed that, in the case of experiments involving a confining hydrostatic stress component, such as uniaxial compression, simple shear or die drawing, no or very little change of long period has been reported [71]. This finding suggests that melting-recrystallization is not necessary for plastic drawing, and may be only a consequence of the sudden unfolding of the chains.

Energetic considerations

Some attempts have been made to support the strain-induced melting-recrystallization model on energetic grounds. Harrison *et al.* [72, 73] have proposed a mechanical model involving the melting enthalpy in the process of craze formation in

PP. Data for metals have also been reported, which support the correlation between the melting enthalpy, ΔH_m, and the plastic work density, W_p. Gent and Madan [74] reported good correlations of the draw stress or the yield stress as a function of the thermodynamic work of melting for several semi-crystalline polymers, for various draw temperatures. Studying the plastic yielding of poly(vinylidene fluoride) (PVDF) in the framework of Eyring formalization, Hellinckx and Bauwens [75] also proposed the occurrence of melting-recrystallization to account for the insensitivity of the yield stress to strain rate when the latter is low, as shown in Fig. 11. Besides, the thermal activation energy of yielding was found close to the melting enthalpy.

From a physical standpoint, this experimental analogy between melting and plastic deformation can be understood by the fact that, in both cases, the same type and amount of intermolecular interactions sustaining the crystalline structure have to be cooperatively broken during the process.

Strain-induced phase transition

Several authors have tried modelling the strain-induced phase transition as an activated process involving an energy barrier that is directly connected with the melting enthalpy. Nylon 6 [76], polycaprolactone [77] and poly(buthylene-terephthalate) [78] have been the subject of such an approach without regard to the structural aspects of the transition mechanisms. However, in spite of the analogy between crystal phase transition and melting on energetic grounds, the authors did not conclude that the phase transition resulted from a strain-induced melting.

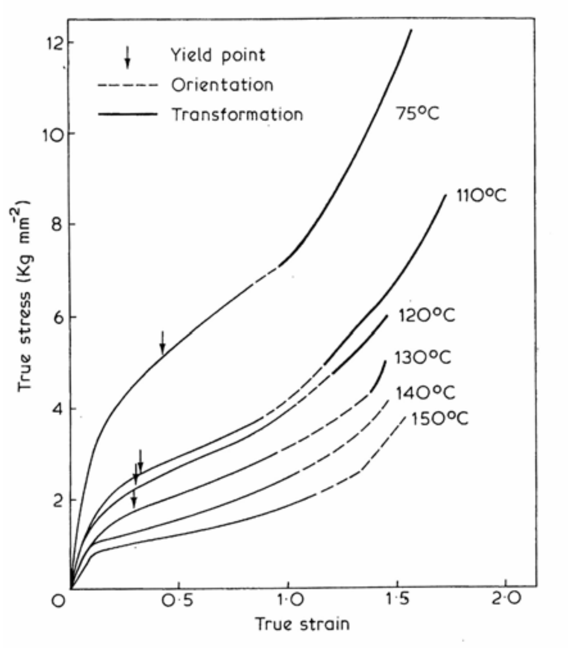


Fig. 12. Engineering stress-strain curves for the uniaxial tensile drawing of PVDF films as a function of draw temperature (reproduced from ref. 80 with permission of Elsevier, Copyright 1980).

As a general trend, it is worth noticing that strain-induced phase transitions occur in the post-yield strain range [79], except the case of the martensitic-like transition in PE. This suggests that the phenomenon requires a cooperative rearrangement of several adjacent chain stems that can be afforded at the stage of chain unfolding owing to transient chain disordering at a local scale. The case of PVDF is particularly relevant to this behaviour [80] as judged from Fig. 12 showing that the phase transition from the twisted-chain α form to the planar-chain β form occurs far beyond the yield point. Regarding the case of polypropylene, it has been claimed that the β–α strain-induced phase change should necessarily proceed via a melting-recrystallization process [81] because the β phase displays domains where the 3/1 helix chains have the same handedness whereas the α phase has alternating right-handed and left-hand helices. Indeed, one may hardly believe that a pure shear-driven crystallographic mechanism such as the one involved in the martensitic transition of PE (Fig. 6) could account for the reversing of the PP helix handedness during drawing. Notwithstanding, in a very recent work [82], Xu et al. proposed a β–α solid state transition operating via crystal slip on the (110) and (120) planes of β crystal lattice. The disordered smectic phase of PP has also been shown to contribute to the strain-induced phase transition process [83, 84].

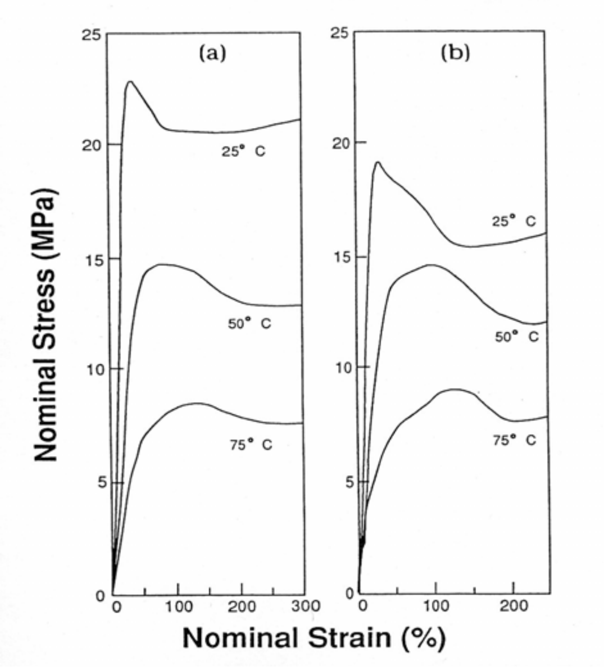


Fig. 13. Engineering tensile stress-strain curves about the yield point of (a) high density PE and (b) medium density PE versus draw temperature (reproduced from ref. 85 with permission of John Wiley & Sons, Copyright 1995).

Double yield phenomenon

Mandelkern *et al.* [85, 86] have discussed the occurrence of double yield points in PE and ethylene copolymers in relation to two populations of crystalline lamellae having different size distributions. The smaller and less perfect crystals undergo strain-induced melting, and then the fraction of recrystallized material can undergo yielding again at higher strain level. The incidence of crystal content, molar weight, temperature and strain has been shown to support this interpretation of the phenomenon. Fig. 13 shows the changes in the engineering strain-stress curves about the yield point for high and medium density PE materials for various draw temperatures : the higher the temperature, the more important the strain-induced melting, and therefore the more pronounced the second yield point.

Molecular topology from SANS

Several authors have tried to benefit from Small-Angle Neutron Scattering (SANS) for probing, at the scale of chain coil conformation, the structural changes in plastically deformed semi-crystalline polymers. Mandelkern and coworkers [87, 88] reported a drastic decrease of scattering intensity at zero angle as a function of plastic deformation of HDPE that was similar to melting. Borrowing from this analogy, the authors ascribed the observed changes to a partial strain-induced melting followed by recrystallization. However, not any detail was given about the occurrence of the double yielding already studied by the same authors.

A few years before, Sadler and Barham [89] reported more contrasted findings depending on sample preparation and drawing conditions : at a draw temperature above 90 °C, the appearance on an isotropic segregation signal in the SANS patterns of melt-crystallized HDPE was attributed to a local melting during necking. But no evidence of local melting was observed at lower temperature, the deformation being nearly affine at a molecular scale. According to the same authors [90], the plastic drawing of single crystal mats did not result in an affine deformation and the crystalline lamellae broke into blocks whose lateral extent was greater than the size of the individual chains. In that case, signs of isotopic segregation suggested local melting due to self-heating during necking, notably for drawing above 95 °C. Drawing beyond the neck for both melt- and solution-crystallized HDPE appeared roughly affine at a molecular scale, provided that temperature was kept below 80 °C [91]. Mechanical properties were then ascribed to the molecular draw ratio rather than to the macroscopic draw ratio. In the case of low molar weight materials [92], major departure from affinity was observed.

Electron microscopy

Thomas and coworkers [93, 94] reported a very meticulous study of the plastic drawing of oriented PE thin films at room temperature by means of Transmission Electron Microscopy (TEM). Besides giving clear evidence of homogeneous and localized crystal slip, the micrographs revealed strain-induced decrystallization via chain unfolding and recrystallization of the oriented chains, as shown in Fig. 14. The mechanical decrystallization was ascribed to the loss of thermodynamic stability of the crystal block when the block size reduces to a critical value, resulting in a very large drop of melting point. To our knowledge, this is the only direct piece of evidence of strain-induced melting-recrystallization that has been ever reported. Further TEM studies from various authors [95-98] on semi-crystalline polymer thin films have mainly reported on the mechanisms of crazing and lamella fragmentation, with little interest if any to the occurrence of strain-induced melting-recrystallization.

Self-heating and melting point depression

Another point of view for the strain-induced melting-recrystallization of semi-crystalline polymers has been argued in consideration that the actual temperature of the material during plastic deformation may be locally higher than the regulation temperature of the experiment due to self-heating, and eventually higher than the melting point. Calculations based on adiabatic conversion of plastic work into heat and heat transfer capabilities for several polymers suggested that temperature may locally increase up to several tens of degrees at strain rates of about 0.1 s^{-1}, or higher [71, 99-101]. Infrared emission has been used for capturing the self-heating effect in the case of localized plastic deformation due to necking [102], ductile propagation of cracks or tensile impact [103]. However, temperature increase above the melting point has rarely been recorded experimentally [104], and the general conclusion is that strain-induced self-heating can only trigger melting in the case of draw temperature close to the melting point [71].

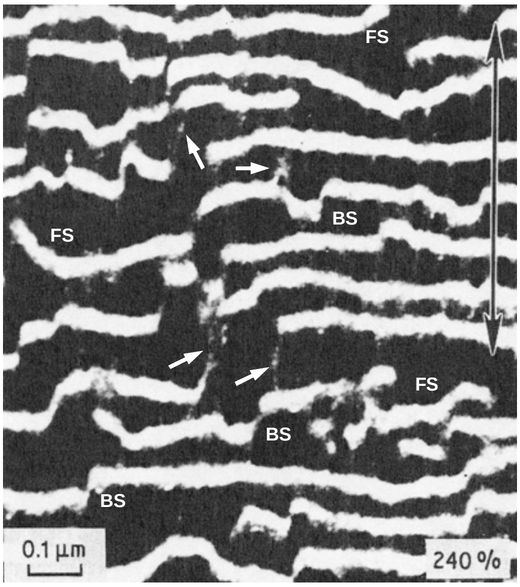


Fig. 14. Dark field TEM micrograph of a drawn HDPE thin film: (FS) fine crystal slip; (BS) bloc sliding; white arrows indicate the strain-induced crystals (reproduced from ref. 93 with permission of Kluwer Inc., Copyright 1986).

Fig. 15. Scanning electron micrograph of the etched surface of a high pressure crystallized HDPE after compressive deformation at a compressive strain CR≈3 (reproduced from ref. 66 with permission of Elsevier, Copyright 2005).

In another instance, the actual material temperature may be higher than its melting point as a result of the melting point depression due to the negative hydrostatic component of the stress tensor in the case of tensile drawing [71]. No experimental evidence or calculation has been yet reported for demonstrating the physical relevance of this hypothesis. A rough estimation can be made considering that the hydrostatic stress component is σ_h=1/3 σ, where σ is the applied tensile stress. In the case of HDPE, σ_h should be about 10MPa for the yielding at room temperature [see the data from Fig. 7]. Considering now a piezo-dependence factor of 0.3°C/MPa for PE melting point [105], the resulting depression could be of just a few degrees at yield. Therefore, strain-induced melting might only occur for draw temperatures very close to the melting point, as already suggested by Peterlin [71].

Discussion

Macroscopic shear banding obeys a plasticity Tresca-like criterion and can in no way be accounted for by melting-recrystallization. Besides, direct observation of crystallographic slip, crystal twinning and martensitic-like phase transition is a clear cut evidence of shear-driven phenomena. These processes have been reported to occur both at the early stages of plastic deformation and at large strain levels (see Fig. 14). Modelling the plastic behaviour of semi-crystalline polymers over a large range of strain up to rupture has been successfully achieved on the basis of such processes. However, the fibrillar transformation and the strain-induced change of long period under tensile drawing were not accounted for. It is however worth noting that Argon and coworkers have proposed a structural model that accounts for the draw temperature dependency of the long period on crystallographic grounds [29]: after fragmentation of the crystalline lamellae, the crystal blocks are rearranged into a new periodic structure whose long period adjusts to the actual temperature of the experiment by annealing.

Crystallographic processes are undoubtedly highly active over the whole strain range, whereas strain-induced melting or decrystallization are more likely to occur at large strains, as a result of chain unravelling. Notwithstanding, the fact that the long period is not affected in the case of plastic processes involving confining hydrostatic pressure, such as solid state co-extrusion, die-drawing or rolling, strongly suggests that melting-recrystallization is not a necessary path to the plastic drawing of semi-crystalline polymers, whereas crystallographic processes are. Scanning electron micrographs on high-pressure-crystallized HDPE deformed in compression [66] corroborate this argument: Fig. 15 shows highly kinked lamellae indicating that fine crystal slip has been activated as a dominant process up to a compression ratio CR≈3 with neither lamella fragmentation nor change of crystal thickness.

The occurrence of strain-induced crystalline phase changes is consistent with a melting-recrystallization phenomenon for two main reasons: (1) most of the findings have been reported for strain levels corresponding to the occurrence of chain unravelling and (2) some cases are concerned with crystal cell modifications needing large scale rearrangements of the chain stems that are *a priori* inconsistent with purely crystallographic processes. However, one cannot exclude the intervention of the latter processes, in the case where only conformational changes are required without change of relative position of neighbour stems in the crystal.

Regarding the occurrence of double yield points, one may have serious doubts about the assumption of the strain-induced melting of a double crystal population. Mandelkern *et al.* did not actually discuss the mechanism of yielding, they just argued about the occurrence of a second yield point: so, what about the absence of the second yield point (see Fig. 13a T_d=25 °C)? Besides, benefiting from highly intense synchrotron radiation, and combining in situ WAXS and SAXS measurements, Butler and Donald [39] have revealed the successive occurrence of fine and coarse crystal slip in HDPE under tensile testing, whereas no structural feature could account for a melting-recrystallization event. These data support the previous attribution of double yielding to a combination of two thermally activated processes [46], namely homogenous and localized crystal slip [106]. Finally, the eventual recrystallization of defective crystals formerly destroyed at the first yield point should generate fibrillar crystals [93] for which further stretching should result in uniform plastic drawing without yielding again. Indeed, yielding is typical to lamellar crystals in isotropic or not too much textured materials.

A particular aspect of the double yield phenomenon, and more generally the plastic deformation of semi-crystalline polymers, is the strong strain-rate and temperature dependency. Only the crystal slip approach is able to explicitly account for the thermal activation of plastic yielding via kinetic considerations [8, 32, 51]. Notwithstanding, no specific formalization has been proposed for predicting the occurrence of double yield points.

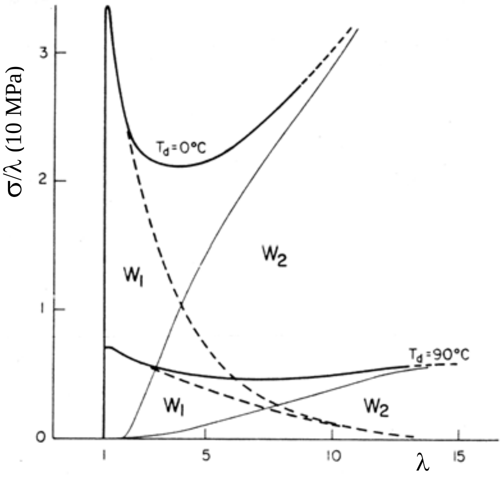


Fig. 16. Variations versus draw ratio, λ, of the plastic work density, σ/λ, for HDPE at T_d=0 °C and T_d=90 °C : destruction of the spherulitic structure, W_1, and drawing of the fibrillar structure, W_2 (reproduced from ref. 107 with permission of John Wiley and Sons, Copyright 1971).

The analogy between the plastic work density and the melting enthalpy is certainly one of the most serious arguments in favour of the strain-induced melting. However, the relevance of this comparison can be seriously disputed in consideration of the opposite temperature dependency of W_p and ΔH_m. The former one monotonically decreases with increasing temperature, as experimentally shown by Meinel and Peterlin in the case of PE [107]. Fig. 16 shows a drastic drop of the plastic work density for destruction of the spherulitic structure between 0 °C and 90 °C, in the whole strain range before the yield point. Hartmann *et al.* [108-110] reported a general trend of linear plastic work decrease as a function of increasing deformation temperature for various polyolefins and nylon66. This phenomenon can be ascribed to the gradual decrease of the plastic flow stress, due to increasing thermal vibrations and parallel weakening of the intermolecular interaction field [111]. Several authors have reported a monotonic drop of yield stress with increasing deformation temperature for PVDF [75] and nylon 6 [112] that compares with the above observations. In contrast, ΔH_m surprisingly increases with increasing temperature, as illustrated on Fig. 17 with data regarding PE [103]. More recently, PET and PEEK were shown to display the same thermal behaviour [113]. The reason for this ΔH_m evolution is the faster variation with temperature of the liquid heat capacity as compared with that of the solid [114]. This holds true for all semi-crystalline polymers. The irrelevance of the energetic aspect of the melting-recrystallization hypothesis is particularly obvious for temperatures close to the melting point for which W_p drops to about nil whereas ΔH_m is maximum.

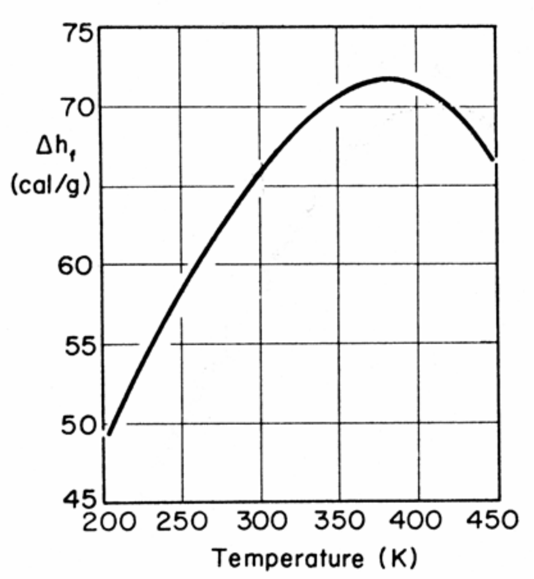


Fig. 17. Temperature-dependence of the melting enthalpy of PE (reproduced from ref. 105 with permission of B. Wunderlich, copyright owner).

In their study of the plastic behaviour of a series of semi-crystalline polymers, Gent and Madan [74] compared the plastic work with the thermodynamic work of melting instead of the melting enthalpy, and found a very good correlation for polymers having a low natural draw ratio. However a departure by a factor 3 or 4 was observed for polymers having a high natural draw ratio. This discrepancy was ascribed to neglecting the elastic work released upon retraction of the chains that undergo stress-induced melting. This argument is not convincing if considering (1) that the elastic work is generally much lower than the plastic work and (2) that polymers drawn below the melting point are highly orientated, which is evidence that chain retraction is a minor effect during solid state drawing.

The above critical discussion does not mean that the occurrence of some very high degree of molecular disorder similar to that of the molten state may not occur, at a local scale, when chains unfold beyond the yield point. The striking plastic instability that is observed in the case of polymers such as high density PE, accompanied with a very high natural draw ratio, is relevant to the suddenness of the chain unfolding phenomenon. It is highly probable that a large portion of chains should be concerned with both high molecular disorder and very local self-heating that would turn them into unstable state equivalent to melt below the melting point. But this phenomenon is mainly the consequence of the chain continuity between crystals via tie molecules and entanglements, and has little to do with thermo-mechanical equivalence. As a matter of fact, metallurgists never suggested that the plastic deformation of metals takes place via melting-recrystallization, although similar discussion could be made on the energetic standpoint [73]. In fact, plastic deformation in metals, minerals and even ceramics is mainly governed by the motion of dislocations which are very narrow linear defects. One may therefore suggest that the molecular and structural reorganization accompanying the plastic drawing of semi-crystalline polymers is a consequence of the plastic processes rather than a leading contribution to it.

Regarding SANS, the observed affine deformation at the scale of chain coils does not necessarily witness the absence of melting-recrystallization. One may assume that strain-induced melting and subsequent recrystallization might occur at the scale of crystal blocks, *i.e.* only crystal fragments could be involved step by step in the melting process concomitantly to chain unfolding, so that the overall chain coil conformation should not be affected by the phenomenon. All chain coils should thus be able to obey a roughly affine deformation law thanks to stress transfer between them via the entanglements, in spite of the occurrence of transient local melting.

Combining SANS with Raman spectroscopy, Okoroafor and Spells [115, 116] concluded that no melting-recrystallization occurs upon rolling of HDPE, as judged from the invariance of zero-angle SANS [116] and preservation of crystal thickness [115]. Fourier Transform Infrared spectroscopy of co-crystallized protonated and deuterated species suggested lamella fragmentation with preservation of the chain stems arrangement from the original lamellae [115]. This is consistent with the previous discussion regarding plastic deformation under confining pressure.

Lastly, it is to be noticed that a frequent factor contributing to the controversy of the present topic lies in the missing of discussion about the way melting-recrystallization may occur. Self-heating at high strain rates, decrystallization due to sudden and collective chain unfolding at large strains, as well as melting point depression under tensile drawing are quite different ways for promoting the phenomenon. This often missing information reveals the difficulty of controlling all the relevant factors involved in the plastic yielding of semi-crystalline polymers.

Conclusions

Plastic deformation in semi-crystalline polymers does obey conventional plastic process based on crystal slip for which plentiful direct experimental evidence have been provided. However, if such processes are able to account for the occurrence of plastic instability, they are unable to account for the large scale phenomena such as chain unfolding. The high degree of molecular disorder that should transiently occur during the collective unfolding of chains is likely to be accompanied with local melting, except if an external hydrostatic pressure is applied for preventing plastic instability and compelling gradual chain unfolding. Therefore, melting-recrystallization can be viewed as a corollary of plastic drawing whereas crystallographic slip and lamella fragmentation are its driving force.

The confusion on that topic is partly due to the fact that a good number of papers refer to melting-recrystallization without discussing explicitly the origin of the phenomenon. Besides, this aspect of the plastic deformation of polymers is a very brief phenomenon for which only indirect evidences have been provided as compared with the direct footprints reported for the crystallographic process.

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