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Deformation of semicrystalline polymers – the contribution of crystalline and amorphous phases*)

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Abstract: The plastic deformation process of semicrystalline polymers and the micromechanisms involved are discussed. The particular attention is paid to the dependence of deformation on structure and mutual influence of deformation of crystalline and amorphous components. Deformation of a semicrystalline polymer appears a complex series of continuous processes, involving mostly crystallographic deformation mechanisms operating in the crystalline phase. However, a very important role in that sequence is played by the deformation of amorphous interlamellar layers, partially reversible on unloading, which produces not only the high orientation of amorphous component but also influences deeply and supports the deformation of crystalline phase since crystalline lamellae and amorphous interlamellar layers, intimately connected through covalent bonds of chains crossing the interface, can deform only simultaneously and consistently. In particular, an influence of the topology of the amorphous phase, including the density of the molecular network of entangled chains and number of chains connecting adjacent crystalline and amorphous layers, on deformation instabilities of crystalline component in polyethylene are discussed. The induced instabilities of crystallographic slip lead to formation of lamellar kinks and frequently to an extensive fragmentation of lamellae. These transformations of crystalline structure together with restructurization of amorphous phase at high strains influence deeply the formation of the final highly oriented structure of the deformed semicrystalline polymer.

Keywords: deformation, semicrystalline polymer, polyethylene, deformation mechanism.

Deformacja polimerów semikrystalicznych – wkład fazy krystalicznej i amorficznej

Streszczenie: Rozważano przebieg procesu odkształcenia plastycznego polimerów semikrystalicznych i zaangażowane w nim mikromechanizmy, zwracając szczególną uwagę na zależność deformacji od struktury materiału oraz na wzajemny wpływ odkształcenia fazy amorficznej i krystalicznej. Deformacja polimeru semikrystalicznego obejmuje szereg ciągłych procesów, w których zaangażowane są głównie krystalograficzne mechanizmy deformacji, aktywne w fazie krystalicznej. Bardzo ważną rolę w procesie odgrywa też częściowo odwracalne odkształcenie amorficznych warstw międzylamelarnych, które nie tylko prowadzi do wysokiego stopnia orientacji molekularnej w fazie amorficznej, ale

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wpływa również na deformację fazy krystalicznej. Lamele krystaliczne i amorficzne warstwy międzylamelarne, ściśle połączone wzajemnie wiązaniami kowalencyjnymi w łańcuchach przekraczających granice międzyfazowe, mogą deformować się tylko jednocześnie i spójnie. Omówiono także wpływ topologii fazy amorficznej, w tym gęstości sieci molekularnej splątanych łańcuchów i liczby łańcuchów łączących sąsiednie warstwy krystaliczne i amorficzne, na niestabilności deformacji fazy krystalicznej w polietylenie. Pojawiające się niestabilności poślizgów krystalograficznych prowadzą do powstawania załamań lamel, a często nawet do ich rozległej i silnej fragmentacji. Takie transformacje struktury fazy krystalicznej wraz z restrukturyzacją fazy amorficznej przy dużych odkształceniach wpływają istotnie na końcową, silnie zorientowaną, strukturę zdeformowanego polimeru semikrystalicznego.

Słowa kluczowe: deformacja, polimer semikrystaliczny, polietylen, mechanizm deformacji.

The ability of polymeric materials to undergo extensive plastic deformation plays a very important role in technology, especially in the selection and use as engineering materials, as well as in production of the end-products by the cold-forming methods. Plasticity of polymers, including semicrystalline ones, although studied extensively over several past decades, is still one of the most important scientific and technical problems because of the very wide range of applications and continuously growing interest on polymeric materials by the modern technology [1].

The structure of the material under deformation plays the crucial role in its plasticity. In contrast to conventional low molecular materials, like metals or ceramics, semicrystalline polymers demonstrate quite complicated, hierarchical morphology. It is well recognized that at the basic microscopic level they consist of ribbon-like lamellar crystals which are separated each from the other by amorphous layers and all they are held together by chains crossing the crystal-amorphous interfaces, like *e.g.*, tie-molecules that connect two neighboring lamellae and amorphous layer between them [2, 3]. It has been found that chain folding is not perfectly regular and molecular packing in lamellae is characterized by a considerable and irregularly distributed disorder depending on undercooling that controls crystallization regimes [4]. Consequently, a quite significant number of chains leaves crystal and enters adjacent amorphous layer, in the form of tie-molecules, loose loops or loose chain ends that can entangle with other chains within amorphous phase and often enter the crystalline phase again (the same lamella in the case of loose loops or the next one in the case of tie-molecules). All these chains crossing the crystal-amorphous interface provide an intimate and very strong covalent bonding of the crystalline lamella with adjacent amorphous material. It is largely agreed that the mechanical properties of semicrystalline polymers are governed to a large extent by the presence of such molecular connections. If they did not exist, the crystallites would be held together only by weak van der Waals or hydrogen interactions, and would slip easily past one another or split away from one another under stress, which would result in macroscopic brittleness of the material, as in the case of mats of monocrystals, where regular chain folding does not allow for a significant connectivity of neighboring crystals.

Crystalline lamellae, separated by amorphous layers, commonly arranged in stacks, are usually organized in higher-level structures. Melt crystallized polymers exhibit commonly a spherulitic morphology – bundles of ribbon-like lamellae are arranged radially in polycrystalline aggregates, called spherulites. The amorphous material is incorporated evenly in layers between lamellae in the amount corresponding to the overall crystallinity. Amorphous phase fills also some occasional misfits between lamellae stacks of different shape and orientation.

Due to the multi-level, hierarchical structure of semicrystalline polymers, as *e.g.*, this outlined above (crystal-amorphous assembly → stack of lamellae → spherulite), their deformation appears generally also a complex and multistage process, in which both the ordered (crystalline) phase and the associated disordered (amorphous) phase are involved. Therefore, the course of the deformation process depends strongly on the structure and morphology of the polymer. The deformation mechanisms are quite complicated and can differ at the local scale depending on the local morphology. Therefore, the detailed knowledge of the structural parameters is essential for the understanding of the deformation mechanisms at the molecular level. These mechanisms can be additionally modified substantially with increasing strain by proceeding deformation as the structure and orientation change. A complete quantitative description of plastic behavior frequently requires different approaches at different scale levels of their structure [1]. At the microscopic level the basic micromechanisms of deformation of crystals and amorphous phase are considered. The mesoscopic level can include bending, rotations, translations, and fragmentation or other structural rearrangements of lamellar stacks, formation of shear bands, deformation of entire spherulites, *etc.* [1]. At macroscopic level formation of big deformation bands or a macroscopic neck are frequently observed and must be also taken into consideration. The plasticity mechanisms are different in different elements of the polymer structure and moreover depend not only on their size and orientation with respect to the direction of the acting force but also on mutual connections with adjacent elements of the other phase. Various deformation micromechanisms in such elements can operate together or compete with each other, affecting each other's response. Understanding the plasticity of such complex systems is possible only within the physics and mechanics of structurally non-uniform media, like composites [1].

Due to deformation-induced evolution of structure and morphology the deformation sequence consists of several stages, involving various micromechanisms, many of which being identified to be similar to those already known in non-polymer materials, as *e.g.*, generation of dislocation and their glide along the planes of crystals *i.e.*, crystallographic slip. However, these processes are not identical to the respective processes in non-polymer structures. Many specific features of plasticity in polymers strongly depend on their macromolecular nature. One of the most important consequences of this nature is that both crystalline and amorphous layers coexisting in a semicrystalline polymer are intimately connected by strong covalent bonds along numerous chains crossing the interfaces. Because of that it is virtually impossible to separate lamella from the adjacent amorphous layer. In fact, cavities being usually precursors of the fracture develop preferentially in the volume of amorphous layer rather than at interfaces [5]. As a result of such strong phase connectivity, lamellae and adjacent amorphous layers can deform only simultaneously and consistently to maintain continuity of the material. Any disobedience from this results in initiation of fracturing phenomena that lead soon to material failure. This condition induces, in turn, some additional strong deformation constraints in each phase. Therefore, the mutual influence of both component's deformation each on the other cannot be neglected [6, 7]. At the basic structural level of crystalline lamellae the identified crystallographic mechanism, like crystallographic slip, mechanical twinning, or the stress-induced phase transformations (martensitic transformations), active in the crystalline phase, are supported by interlamellar shear, lamella separation and stack rotations, all operating in the amorphous phase. All these mechanisms can be engaged in a complex deformation sequence in which particular mechanisms are activated and terminated at various strains.

Over the past several decades a vast number of research papers has been devoted to the plastic deformation of semicrystalline polymers and a significant progress has been achieved in understanding the process [1, 8–13]. Several models were formulated to describe the full deformation path, as *e.g.*, the Peterlin's 'micronecking' model, [14, 15], the melting-recrystallization model [16, 17], and the crystallographic model [8–10, 18–21]. However, a clear and consistent description is still far away, and clearly there is a need for further intensive research on the phenomena of plastic deformation in the semicrystalline polymers. The recent studies recalled the very important role of the amorphous phase in the deformation process and pointed out a deep interrelationship of deformation occurring in the crystalline and amorphous phase [6, 13, 22]. The role of the amorphous component appears far more important in the deformation process, than assumed in existing models of plastic deformation, especially at large strains. The hierarchical structure leads to numerous constraints and mutual interaction of deformation of crystalline and amorphous elements that must be additionally taken into consideration. All of these interactions are primarily a consequence of the strong connectivity of adjacent crystalline and amorphous layers forcing their cooperative deformation. It became clear that amorphous phase is not only a compliant medium that merely transmits stresses to crystals, as frequently assumed, but it is an active element of the structure that tunes deformation behavior of crystals and actually even is able to take control of the polymer response at large strains [23].

Most of the research, especially in the initial period, focused on uniaxial stretching. These studies resulted in the 70's in the formulation by A. Peterlin the so-called 'micronecking' deformation model [14, 15], which assumed that the main mechanism of the polymer deformation is the destruction of crystalline lamellae through their unfolding and transformation into a densely packed microfibrils in a virtually single "catastrophic" transformation, which inevitably leads locally to the loss of material continuity and consequently to the (micro) cavitation. It became clear in the 90's that the tensile deformation most frequently leads to structural transformations characteristic only for this particular deformation mode, including the cavitation occurring prior to the yield point, which do not have general meaning in the interpretation of the phenomenon of plastic deformation and micromechanisms involved and can be considered as a side-effect [1, 10]. Numerous studies (see *e.g.*, reviews [1, 10–12, 21]) led to a substantial revision of the notion on the deformation mechanisms of semicrystalline polymers: it was established that the deformation of the crystalline phase generally proceeds through a sequence of structural micro-transformations, based mainly on crystallographic mechanisms, analogous to those operating in the deformation of low-molecular crystals. Any catastrophic transformation of the initial, lamellar structure into microfibrillar, akin to this suggested by the Peterlin's 'micronecking' model, appeared specific only for those deformation modes, which develop a significant tensile stress that leads to the cavitation of the material, *e.g.*, for uniaxial tension [24, 25]. Because of that the particular attention will be paid in this report to the results obtained in compression, either uniaxial or plane-strain, since these deformation modes have several advantages over tension. Deformation by compression is usually macroscopically homogeneous in the entire strain range, with no instabilities like *e.g.*, necking observed in tension. It is also cavity-free as compressive stress prevents formation of cavities. Therefore, in contrast to tension, the experiments performed in compression mode can provide a 'clean' information about the deformation process, not obscured by any unwanted side-effects.

DEFORMATION OF POLYMER CRYSTALS

The plastic deformation of polymer crystals, like the deformation of crystals of other materials, is generally crystallographic in nature and usually proceeds without destroying the crystalline order. The only exception to this is a large tensile deformation, when cavitation and voiding can lead to a complete molecular rearrangement of the chain-folded lamellar morphology into a more or less chain-unfolded microfibrillar microstructure. This transformation is likely to occur through an intermediate state of some molecular disorder at a local scale. In contrast, several structural features occurring at moderate plastic strains are relevant to strictly crystallographic processes. Similar structural transformations observed also in cavity-free deformation modes at high strains appeared process instabilities resulting from well advanced action of crystallographic mechanisms.

Bowden and Young [8] considered in detail the classical crystallographic mechanisms of plasticity applied to polymer crystals, and demonstrated that the approach based on classical concepts of nucleation of dislocations and their glide along the crystal lattice describes well the deformation behavior observed in semicrystalline polymers. A vast experimental data evidenced the deformation of polymer crystals proceeding according to the crystallographic mechanisms, see *e.g.*, the reviews [1, 10–12]. Polymer crystals can deform by crystallographic slip, twinning or stress-induced (martensitic) transformation. Among these, the slip is the most important mechanism since it can accommodate much larger plastic strain than the other two mechanisms. Crystallographic slip in polymer crystals demonstrates several features unique to polymers and reflecting their macromolecular structure. The most important is the restriction imposed by the chain structure for the choice of the slip plane. As crystallographic process cannot lead to chain ruptures and lattice symmetry remains intact, the dislocation glide is possible only along the planes that are parallel to the chain axis. Furthermore, as polymer crystals exhibit usually the folded structure these folds impose another limitation; consequently the slip is preferred in planes containing chain folds. Moreover, the general rule is that a non-deficient plastic deformation of a crystal of any orientation requires operation of five independent slip systems [26]. However, the limitations mentioned above and generally low symmetry of polymer crystals usually allow only for at most three independent slip systems [1, 27]. This implies that the strain cannot be fully accommodated by polymer crystals. This shortfall of accessible slip systems can result in violation of crystal integrity and nucleation of microcracks. Consequently, polymer single crystals appear brittle. Fortunately, two additional glide systems that are necessary for the complete strain accommodation can be provided by amorphous layers, separating lamellar crystals in semicrystalline polymers. Interlamellar shear in the plane roughly perpendicular to the chain axis effectively substitutes the lacking slip systems in polymer crystals. Therefore, the full strain accommodation in plastic deformation is possible only in semicrystalline polymers, which in fact appear highly ductile.

More on plasticity of polymer crystals can be read in numerous reviews, see *e.g.* [1, 10–12].

DEFORMATION OF AMORPHOUS PHASE AND ITS ROLE IN THE PROCESS

The key structural parameter of the amorphous phase is chain topology resulting from mutual entanglements of macromolecules and their permanent chemical or physical crosslinks. Some chains are engaged only partially in crystalline phase and pass through the interface entering into amorphous layer. Entanglement knots have usually a certain, though often limited mobility, while segments immobilized at interfaces act as stable crosslinks. Chain entanglements and crosslinks produce in amorphous layers macroscopically continuous, quasi-isotropic network that tends to respond to strain similarly to a bulk amorphous material, and exhibits the rubber-like properties with finite extensibility, limited by the length of the segments trapped between the network nodes, mainly the length of the relatively short tie-molecules linking adjacent crystals through the amorphous crystal layer in between. Advancing strain results in stretching and orientation of the network segments, which significantly increases the local stress, particularly when approaching the deformation limit [6, 23].

Due to large length and width of lamellae as well as very strong phase connectivity the deformation of amorphous layer is significantly constrained by adjacent crystalline lamellae-interphase integrity condition enforces their only cooperative deformation. Therefore, the topology of the molecular network in amorphous layers influences deeply the deformation process of not only amorphous phase but also the crystalline phase, as well as the post-deformation behavior (strain recovery).

Three main mechanisms of deformation of the amorphous material in semicrystalline polymers were recognized: interlamellar slip (shear), interlamellar separation, and lamellae stack rotation [8]. Interlamellar slip involves glide of the lamellae parallel to each other with the amorphous layer undergoing simple shear. It is a relatively easy mechanism for the material above glass transition temperature (T_g) and was widely reported [1, 10–12]. The interlamellar shear appears highly reversible due to rubber-like behavior of the amorphous phase – it was established that the recoverable part of the deformation can be almost entirely attributed to the reversibility of the interlamellar slip [28–33].

Interlamellar separation is induced by tensile stress component perpendicular to the lamellae face. It leads to thickening of intercrystalline layers and increase of the long period along the tensile direction. This mechanism of deformation is rather difficult since a change in the lamellae distance has to be accompanied by a transverse contraction of the amorphous interlamellar layer, which is, however, hindered by strong lateral constraints imposed on this layer by adjacent crystalline lamellae, so that the deformation must involve a change in volume. However, it can be expected that amorphous phase, similarly to other rubbers demonstrating high bulk moduli and relative low shear moduli, is quite resistant to volume changes. This is frequently a source of the cavitation within amorphous layer between lamellar crystals in response to tensile stress [1, 25]. The most likely mechanism, which facilitates cavitation-free processes and reduction of the deformation resistance of the amorphous layer, is the cooperative bending of lamellae (kinking) between local bridges of tie-molecules [32, 34] – similar to shown in Fig. 1. Such kinking, achieved through localized crystallographic slip [35], releases some constraints that leads to reduction of material resistance and by reorientation of lamellae enables their further deformation along a relatively easy path.

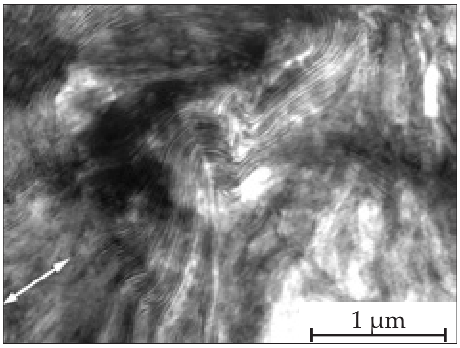

Fig. 1. TEM micrograph of ultra-thin section of polyethylene deformed in plane-strain compression to the true strain of ε_T = 0.8; arrow indicates the direction of compression loading (LD) and direction of flow is perpendicular to LD in the plane of section (reproduced from the reference [32] with permission of Elsevier© 2005)

In some places of the structure stacks of lamellae are embedded in the amorphous matrix. Such stacks can be easily rotated as a rigid body under the action of the stress. The stack rotation is a secondary process as rotations alone does not lead to any increase of the strain, although it can help the strain accommodation when acting simultaneously with other mechanisms.

Upon sample loading, right after completion of elastic deformation, some plastic rearrangements of amorphous phase on the microlevel become involved in the process of further deformation. When deformation proceeds above T_g the rubbery amorphous interlamellar layers are the most compliant parts of the material and are ready to deform by shear at quite low external stresses, earlier than any crystallite. However, that easy path of the unconstrained deformation exhausts quickly, as numerous chain segments passing through the interface and connecting both phases become stretched. This enforces further the only cooperative response of both phases – the crystalline lamellae must start to deform along, according to the their specific mechanisms. This constraints an independent deformation of an amorphous material already at low overall strains. The stresses transferred into the crystalline phase increase with local strain and very soon reach the level high enough to trigger the crystallographic slip. From this point on the plastic deformation of crystallites takes the control over the deformation kinetics of the sample, while the amorphous layers merely follow and adjust themselves to the deformation of crystalline component. The entire deformation process is reduced then to simultaneous, combined deformation of both components. Although the primary role of the amorphous layers at this stage is to transfer stress to and between the crystallites, their shear (interlamellar slip) supports significantly the deformation of crystalline lamellae by substituting the lacking crystallographic slip systems in planes intersecting the direction of the chain in the crystals, and hence allows the sample to accommodate the strain fully (adjust to the new shape forced by deformation). The cooperative action of crystallographic slips in crystals and interlamellar slip in amorphous layers leads to the gradual development of the lamellar orientation (crystalline texture) and molecular orientation in amorphous component.

Administering the deformation by crystalline phase lasts as long as the continuously increasing stress in sheared amorphous phase remains below the stress related to the deformation of crystallites. When, due to network stretching, amorphous stress component exceeds the level of the crystalline component the deformation process comes under the control of the deforming amorphous phase. This transition coincides frequently with breakdown of crystallites – at certain point the deformation of the amorphous phase accompanying deformation of crystallites must exhaust and 'lock' due to a very high stretch of the network, accompanied by an ultimate stretch of tie--molecules, which results in a very high deformation resistance and substantial stress built-up (beginning at the true strain above ε_T = 1–1.2 [19, 36]). These chains of the network, which are immobilized at the interface when entering the crystal, generate local stress concentrations at lamella surface. While the lamellae are already significantly thinned due to advanced crystallographic slip [8] such stress concentrations on lamellae surfaces together with possible slip instabilities due to uneven thickness of lamella lead to localization of the slip, inducing abrupt local thinning and consequently a heavy fragmentation of lamellae into smaller blocks.

While, except for a small elastic component, the deformation of the crystalline phase is primarily the stable and irreversible plastic deformation, the deformation of the amorphous phase appears reversible to a large extent, despite constraints imposed on its recovery by surrounding irreversibly deformed crystallites. It was found that the non-linear (time-dependent) strain recovery observed after unloading of deformed polyethylene (PE) is associated entirely with an earlier deformation of the amorphous phase [32], and depends on the amount of the amorphous phase as well as properties of the molecular network (entanglement density) within that phase. Both the deformation of the amorphous phase and its recovery are modified by the presence of tie-molecules and other chains immobilized at interface that influence greatly the deformation of the molecular network of the amorphous phase. Recovery of amorphous layers leads to back-rotation of adjacent crystals, therefore the preferred crystalline orientation produced upon loading is partially lost after strain recovery.

DEPENDENCE OF MECHANICAL RESPONSE ON THE STRUCTURE

The model calculations utilizing micromechanically based self-consistent composite model were performed by Lee *et al.* [6]. In this calculations a simulated sample consisting of randomly oriented crystal lamella-amorphous layer assemblies was subjected to uniaxial compression. Deformation of lamellar crystals by crystallographic slip while of amorphous layers as a shear of the molecular network of the rubber were assumed. The contribution of the crystalline phase to the stress was found nearly constant in a broad range of strain, while the stress component of the amorphous phase increased substantially with strain and became larger than crystalline component for ε_T well above 1. This is illustrated in Fig. 2. Such a behavior is explained in the following way: the slip processes in polymer lamellae are controlled by the nucleation of dislocations and these gliding dislocations are necessarily pushed out of the thin crystal core into the interface, *i.e.*, are not trapped in the crystal [1]. Consequently the strain hardening is not observed in polymer crystals [6, 7]. On the other hand, the molecular network in the amorphous layers is stretched during their deformation and chain segments become progressively oriented in the direction of maximum extension. As a result the stress needed for further deformation of the network continuously increases and consequently the strain hardening is observed. In the range of higher strains this network stress increases substantially over the stress related to the deformation of crystalline phase.

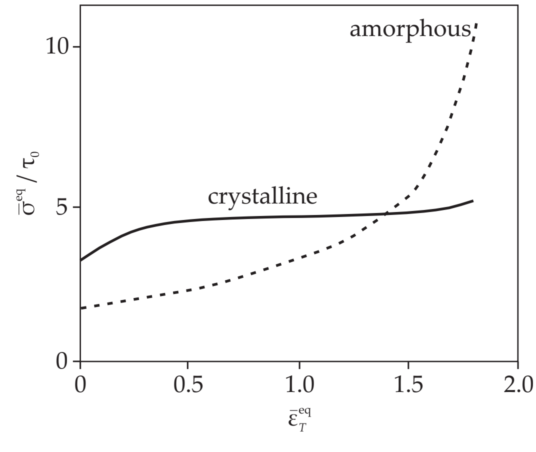

Fig. 2. Normalized equivalent phase-volume-averaged stress as a function of equivalent true strain, both calculated with self-consistent composite model for PE in uniaxial compression (according to [6])

The obtained result demonstrated clearly that the mechanical response of the material is controlled by crystalline phase at low strains, where the compliant amorphous layers are constrained by stiffer lamellae and comes under the control of deforming amorphous phase at high strains, where the stress generated within the molecular network due to strong molecular orientation becomes significantly higher than the stress related to crystallographic slips proceeding in crystalline layers. Experimental studies of deformation behavior of a series of PE of various chain architecture (linear, branched, random copolymers) and molecular mass fully confirmed these predictions [23]. An exemplary set of the true stress-true strain curves obtained in the plane-strain compression for the series of linear PE with very different molecular mass is present in Fig. 3. It was found that the initial part of the curves, at low strain depends on crystallinity and crystal thickness-modulus increases with overall crystallinity while the yield stress is controlled by the thickness of lamellae [23, 37]. On the other hand, in the strain hardening range the clear dependence on molecular mass can be observed. The molecular mass determines the state of the molecular network and the effective network density in the amorphous phase [23, 38]. Rubber-like elasticity of the molecular network, manifesting by a strong increase in stress upon the strain-hardening stage, is determined by the density of network created by entangling chains (showing a limited mobility at temperature above T_g) and chain fragments immobilized at interphase boundaries [solid network nodes, permanent below melting temperature (T_m)]. The model calculations [23] demonstrated that this density depends on the molecular weight of the polymer, chain architecture (including number of branches), the kinetics of crystallization, and the resulting crystallinity of the material: the higher the molecular weight and/or crystallization rate, the denser the molecular network in amorphous layers. These features differ substantially amorphous phase in a semicrystalline polymer from fully amorphous polymers, wherein the density of the network, created only by entanglements, is determined by flexibility of chains, while practically does not depend on the molecular mass or thermal history of the material. In addition, a part of the amorphous phase in the layer, adjacent the surface of the folded lamellar crystals, especially in polymers with semi-flexible or defected chains, have a lower mobility and a higher rigidity than the amorphous phase in the volume of the layer – this is so-called rigid amorphous phase (RAP) – presence of which results in

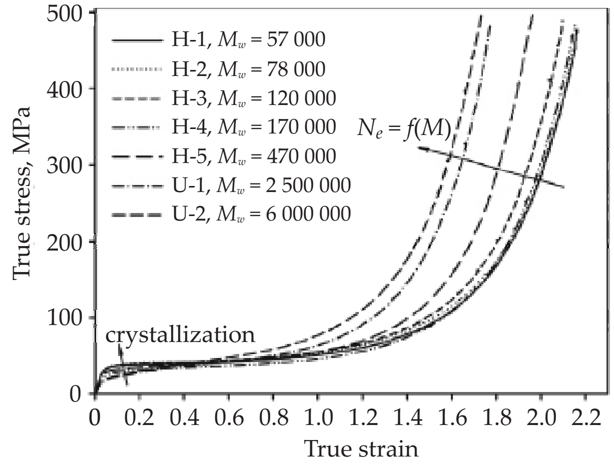

Fig. 3. Experimental true stress-true strain curves of a series of linear PE of various molecular mass deformed by plane-strain compression (according to [23])

different mechanical characteristics of such a 'sandwich' layer than a layer containing only mobile amorphous phase or an amorphous polymer in bulk.

THE STROBL'S DEFORMATION SCHEME

Strobl and coworkers [29–31, 39–45] focused on the aspects of the deformation of semicrystalline polymers related to the macromolecular network in the amorphous phase. They studied in detail the tensile deformation and recovery behavior of several semicrystalline polymers and found a rather simple deformation scheme, followed by all polymers studied. As it is shown in Fig. 4, along the true stress-true strain curves the differential compliance, recovery behavior as well as the crystalline texture change simultaneously at well-defined points. Four characteristic transition points were identified and ascribed to activation of various deformation mechanisms [29]. The critical strains at which these transitions take place were found nearly invariant over various strain rates and drawing temperatures [30, 39] as well as chain architecture or crystallinity of a polymer [29, 39, 41]. Bartczak and coworkers confirmed validity of this scheme also for compression [23, 32, 33, 36, 38, 46–49].

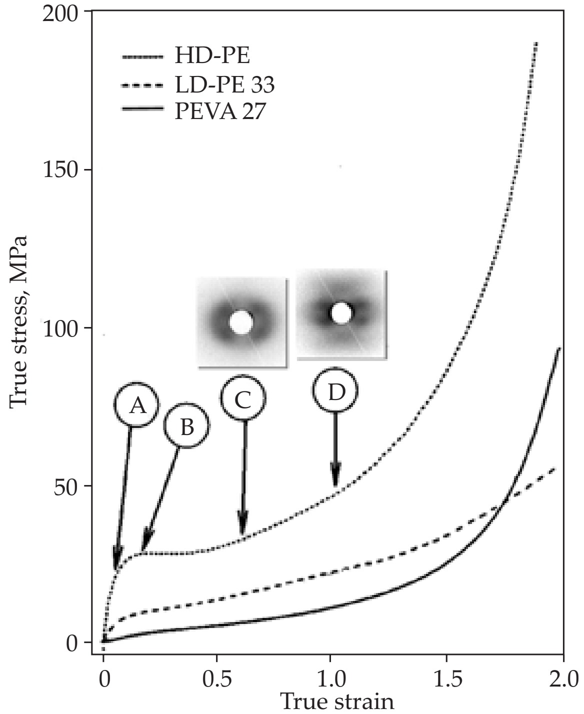

Fig. 4. The true stress-true strain curves tensile of high-density polyethylene (HD-PE), low-density polyethylene (LD-PE) and ethylene-vinylacetate copolymer (PEVA) with four critical points marked (description in the text); insets show 2D-SAXS patterns obtained for HD-PE near point C (lamella kinking) and D (fragmentation and restructurization) (the stress-strain curves taken from [29])

The four points of main transitions of the Strobl's scheme can be summarized as follows [11] (see Fig. 4):

– A corresponds to the end of the elastic proportionality range; the onset of isolated inter- and intralamellar slip processes ($\varepsilon_T \approx 0.02$);

– B shows a merge of local slip events into a widespread, collective activity of crystallographic slips and interlamellar shear, macroscopic yield point is reached ($\varepsilon_T \approx 0.1$);

– C presents exhaustion and a temporary lock of the shear of amorphous layers due to a stretch of tie-molecules, which causes generation of some stress concentration in lamellae, resulting in the slip localization and lamellae cooperative bending and kinking (cf. Fig. 1), often associated with limited lamella fragmentation; this releases partially the constraints imposed on amorphous phase and reduces its deformation resistance allowing deformation to continue along an easy deformation path at relatively low stress ($\varepsilon_T \approx 0.6$);

– D illustrates the second lock of the shear of amorphous layers due to nearly full stretch of the molecular network; corresponding stress increase leads to massive fragmentation of lamellar crystals into small blocks due to severe slip localization (slip instability) in lamellae already thinned substantially by advanced fine slip; this fragmentation again releases constraints, which in turn allows rotations and restructurization of highly sheared crystal blocks, resulting in appearance of a new long period in the direction of extension (formation of the final fibrillar structure). Strong orientation hardening of the amorphous phase brings also an onset of chain disentanglements, leading to partial destruction of the molecular network ($\varepsilon_T \approx 0.9–1.2$).

That universal deformation scheme, outlined above, relies on deformation micromechanisms which are predominantly of crystallographic nature. Plastic deformation starts at the yield point with widespread crystal slip processes, supported by interlamellar slip in the amorphous component. Occasionally, twinning modes and martensitic transformations are engaged, [19, 27, 50]. Also other phenomena, occurring at larger strains are closely related to the crystallographic mechanisms, *e.g.*, fragmentation of lamellae results from a heavy localization of the slip process, *i.e.*, its change from fine (homogeneous) to coar-

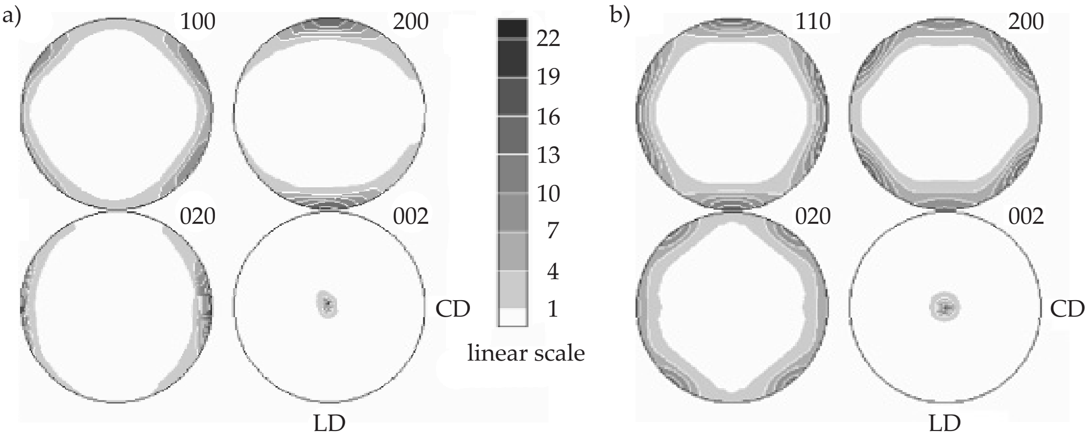

Fig. 5. The X-ray pole figures of the crystallographic planes indicated determined for HD-PE ($\overline{M}_w$ = 170 000) deformed by the plane-strain compression to $\varepsilon_T \approx 1.8$ at: a) 80 °C, b) room temperature

se mode, although these processes are influenced by the topology of the amorphous component (effective network density, number of chains crossing crystal-amorphous interfaces and connecting neighboring crystals). The discussed scheme shows quite clearly the deep mutual influence and cooperative deformation of both crystalline and amorphous components at virtually every stage of deformation process. This cooperation is the primary source of exceptional ductility of semicrystalline polymers.

ORIENTATION OF CRYSTALLINE AND AMORPHOUS PHASE

Advancing deformation of crystalline phase primarily by crystallographic slip systems results in a progressive rotation of the direction of the chain axis in crystals [8]. This eventually brings the high orientation of the crystalline phase with the chain direction approaching the direction of the maximum extension (direction of tension in tensile mode or the flow direction that is perpendicular to the loading direction in compression modes). It results in formation of a fiber-like crystalline texture for uniaxial tension or compression. In the case of plane-strain compression that introduces more constrains than uniaxial deformation the primary texture produced is the single-component texture, sometimes called a ‘quasi-single crystal’ texture [8, 51]. Such a single-component texture is illustrated by pole figures of HD-PE compressed in the plane-strain conditions, presented in Fig. 5. Frequently, especially at lower deformation temperatures and/or high deformation rates, this single-component texture transforms partially by twinning upon sample unloading into two-component texture, shown in Fig. 5. Twinning is activated by the tensile back-stress acting along the loading direction, generated by the amorphous phase recovering on unloading. Such a transformation is another example of the transition of crystalline component that is induced and entirely controlled by amorphous phase.

Along with formation of the crystalline texture the final lamellar structure is formed in the highly deformed samples. The 2D-SAXS patterns taken along the constrain direction and loading direction, respectively, for a series of highly deformed linear PE of various molecular weight are shown in Fig. 6. The presented patterns illustrate the lamellar structure and its orientation in these samples, which generally consists of short lamellae fragments oriented in a chevron-like pattern [36], as shown schematically in the cartoon on the right-hand side of the Fig. 6. However, one can observe here some differences between the respective patterns of various samples, which reflect variations in the extent of lamellae fragmentation and their final orientation with increasing molecular weight. This indicates that the details of the final lamellar structure depend on the properties of the amorphous component that influences both the fragmentation (through the number of tie-molecules, which produce stress concentrations leading to slip localization and finally fragmentation of lamellae) and the strain recovery behavior – the presented patterns were recorded after sample unloading, so that they reflect the orientation of lamellae initially gained upon deformation, yet that orientation was modified by lamellae back-rotations due to reversing interlamellar shear that occurred during the post-deformation recovery stage. The amount of that recovery is controlled by the effective density of the molecular network in the sample, which depends on molecular mass and crystallization conditions (identical for all samples) [32].

Figure 7 compares the evolution of the 2D-SAXS patterns with strain for two samples of the same linear PE ($\overline{M}_w$ = 170 000), one of which was crosslinked by irradiation in the solid state prior to deformation. That crosslinking increased the effective network density in amorphous component from about $3.7 \cdot 10^{-26}$ m^{-3} to $5.7 \cdot 10^{-26}$ m^{-3} [38], while left the crystalline phase not affected, so that the crystalline structure, including the overall crystallinity, was practically identical in both materials. Comparison of the patterns presented in Fig. 7 demonstrates that the deformation habits of crystalline lamellae were nearly the same in both samples – for a given strain the respective pattern of both samples demonstrate very similar features and differ each from the

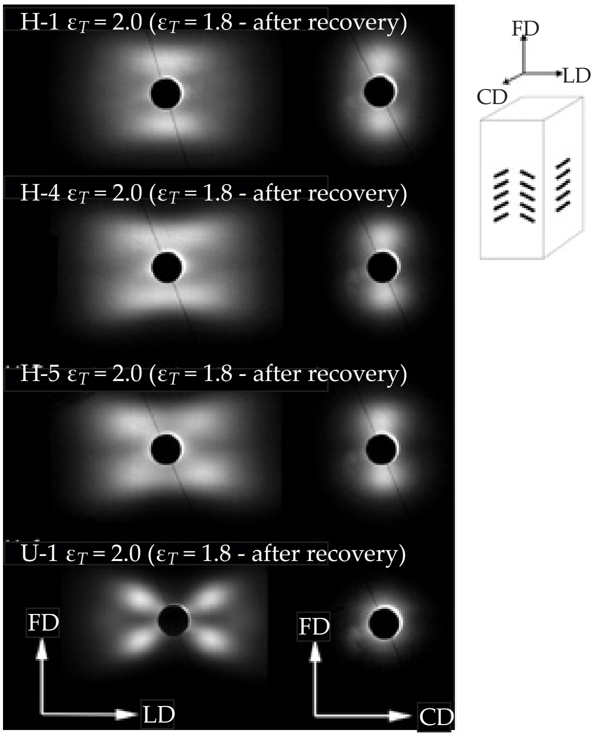

Fig. 6. 2D-SAXS pattern determined for linear PE homopolymers of various molecular mass (H-1: $\overline{M}_w$ = 56 000; H-4: $\overline{M}_w$ = 170 000; H-5: $\overline{M}_w$ = 480 000; U-1: $\overline{M}_w$ = 6 000 000), deformed to $\varepsilon_T \approx 2$, at *T* = 80 °C; left-hand side column presents CD view and right-hand side column LD view (according to [36]; the cartoon on the right side illustrates schematically the lamellar structure)

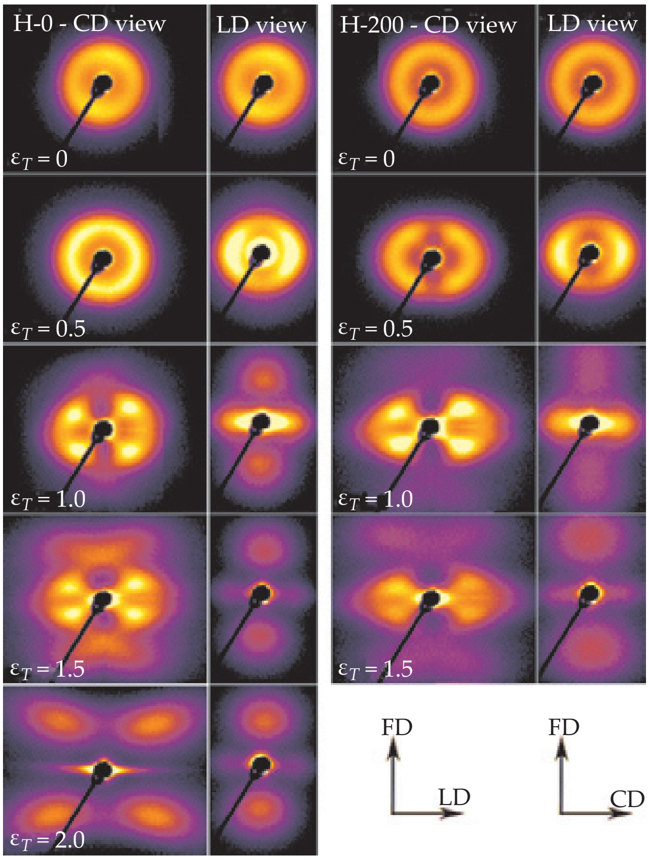

Fig. 7. 2D-SAXS patterns obtained for HD-PE ($\overline{M}_w$ = 170 000): the virgin sample H-0 (not crosslinked, left panel) and crosslinked H-200 (200 kGy dose, right panel), compressed to indicated ε_T value; for every sample two patterns are presented: sample illuminated along the CD or LD directions; the flow direction (FD) is vertical in all patterns (reproduced from reference [49] with permission of Elsevier© 2016)

other only in fine details. This means that the same structural transformations (as *e.g.*, kinking and lamellae fragmentation) occurred at nearly the same level of strain in both samples, irrespective of the topology of the amorphous phase and the network density. This indicates that they were controlled primarily by the deformation of crystalline phase and the dependence on topology of the amorphous phase is minor compared to the properties of crystals.

At high strains, well above $\varepsilon_T = 1$, the large deformation of the amorphous phase by interlamellar shear accompanying deformation of crystalline phase leads to very high molecular orientation. Segments of macromolecules between the nodes of the molecular network become almost completely stretched and significantly ordered lognitudinally. At this point a widespread joint structural rearrangements begin, especially in polymers of relatively low and moderate molecular mass, in which lamellae are less constrained [11]. The taut tie-molecules generate stress concentrations on lamellae surfaces, which together with slip instabilities lead to strong slip localization. As a consequence, lamellae undergo splitting and heavy fragmentation into smaller blocks, while the interface undergoes intense movements between crystalline and amorphous component. This includes incorporation of some tie-molecules into crystallites and transfer of some fraction of the crystalline material into the ordered fraction of the amorphous phase. During such rearrangements the interfaces become diffuse, while the amorphous phase becomes extremely oriented and ordered [1, 52, 53]. Detailed structural studies using X-ray methods demonstrated that in highly deformed linear PE ($\varepsilon_T \approx 1.8$) the amorphous phase in interlamellar layers reaches a clear ordering of the close-packing quasi-hexagonal type [53]. The distance between the oriented chain segments is similar to those typical in orthorhombic crystal structure of PE, characteristic of the surrounding crystallites. Oriented and well-ordered amorphous phase differs from the oriented crystalline phase practically only in the lack of a full in-register ordering of chains along the direction of orientation. Such very high order allows amorphous domains to become capable of transmitting the chain slip from one crystallite to another – dislocations can probably move from one crystallite to another through the "structured" amorphous phase [1, 54].

EROSION OF THE MOLECULAR NETWORK

Large deformation of the amorphous layers and domains leads also to a partial destruction (erosion) of the molecular network [23, 32, 36, 49], primarily by the dissociation of links created by the entangled chains (disentangling). Scission of chains is a marginal process – detailed gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FT-IR) studies of linear PE deformed in compression demonstrated that less than 1 chain scission per 1000 average chains occurred when ε_T reached the high value of 2 [49]. The network erosion phenomena occur at relatively high and quickly increasing stress in the range of strain hardening of a polymer, above ε_T of 1 [49]. As a result of the gradual destruction of the network a growing part of the deformation becomes irreversible, so that a 'memory' of the polymer of the initial state is erased: the deformed sample is no longer able to return close to its original shape even after heating above the melting point of the crystalline phase. This behavior is illustrated in Fig. 8 that presents the residual strain left in the HD-PE samples, raw and crosslinked, after their compression to various ε_T, up to 2, followed by recovery at temperature of 145 °C, *i.e.*, above T_m of PE crystals. It can be seen that all samples, deformed initially to the applied ε_T below 1, recovered completely, irrespective of the crosslinking degree. On the other hand, for samples deformed to $\varepsilon_T > 1$ the permanent, non-recoverable residual strain was observed, but only in pristine samples that have not been crosslinked, thus consisting of only entangled chains in amorphous phase, whereas all crosslinked samples, containing significant fraction of permanent chemical crosslinks were still able to recover fully to the initial state. The finite residual strain left in the raw, not-crosslinked sample after melting the crystalline skeleton indicates that the molecular network in the amorphous component had to be partially destroyed, which allowed an irreversible plastic flow irreversibly upon deformation. On contrary, the chemical network in all crosslinked samples appeared robust enough to prevent any irreversible flow. As already said the primary mechanism of the network erosion is chain disentanglement, not their scission.

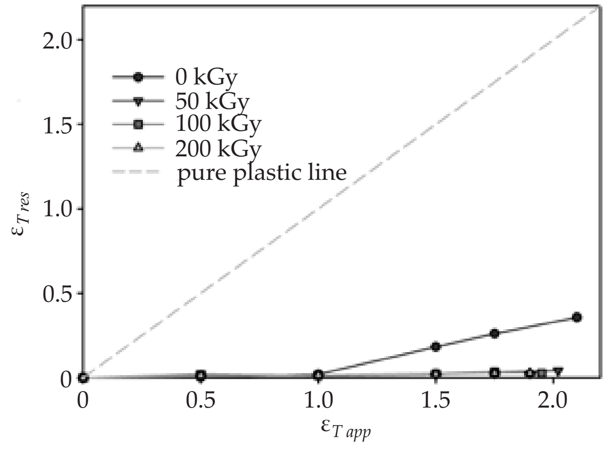

Fig. 8. The dependence of the residual true strain ($\varepsilon_{T\,res}$) on applied true strain ($\varepsilon_{T\,app}$) for PE samples of different crosslinking degree deformed by plane-strain compression at room temperature and then recovered at 145 °C by 30 min (according to [49])

INFLUENCE OF NETWORK PROPERTIES ON LAMELLAE FRAGMENTATION PHENOMENA

To learn more how the properties of amorphous phase can influence deformation of crystalline phase, especially the two structural transitions related to lamellae fragmentation: lamellae kinking and a widespread fragmentation, it is worth to compare deformation behavior of samples that differ each from the other only in properties of the amorphous phase, while crystalline phase being essentially the same. Such samples can be prepared for example by radiation crosslinking in the solid state. That treatment increases the network density in the amorphous phase by introduction of chemical crosslinks, while the crystalline phase remains intact [38] and is practically identical in the modified and reference material. Samples of linear PE ($\overline{M}_w = 170\,000$) modified in this way were studied. It was estimated that crosslinking increased the effective network density in amorphous component from about $3.7 \cdot 10^{-26}$ m^{-3} up to $5.7 \cdot 10^{-26}$ m^{-3} with radiation dose increasing from 0 to 200 kGy [38].

An evolution of the 2D-SAXS patterns with strain, reflecting formation of the oriented lamellar structure in such samples was presented in Fig. 7 of the previous section. It can be observed that the same structural transformations – lamellae kinking above $\varepsilon_T = 0.5$ giving rise to the 4-point pattern in the CD-view pattern and gradual fragmentation of lamellae producing a new long period along the flow direction, seen in both CD- and LD-view patterns, at $\varepsilon_T > 1$ – occurred practically at the same level of strain, irrespective of the topology of the amorphous phase and the effective network density. For a given strain the respective patterns of the raw and crosslinked samples show basically the same features and differ only in fine details. This suggests that the orientation habits of lamellae are controlled generally by the deformation of crystalline phase, and depend probably much less on topology of the amorphous phase. The similar orientation behavior of the crystalline phase can additionally support the view that the clear differences in mechanical response, which were observed in the strain hardening range of samples of various level of crosslinking, are related to deformation of the amorphous phase rather than crystalline component.

Closer examination of the SAXS patterns reveals fine differences appearing with increasing network density as it is presented in Fig. 9. Figure presents the patterns obtained for samples of different network density (crosslinked with the dose of 0, 50, 100 or 200 kGy) deformed to two particular strains: $\varepsilon_T = 0.5$, which is close to the kinking/fragmentation transformation (point C of the Strobl's deformation scheme at $\varepsilon_T = 0.6$) and $\varepsilon_T = 1.5$ (well within the range of heavy fragmentation of lamellae, starting around $\varepsilon_T = 1$ – point D of the Strobl's scheme). Comparison of the SAXS patterns of samples of various crosslinking obtained at $\varepsilon_T = 0.5$ suggests that the effect of increasing network density is perhaps a little earlier kinking (in con-

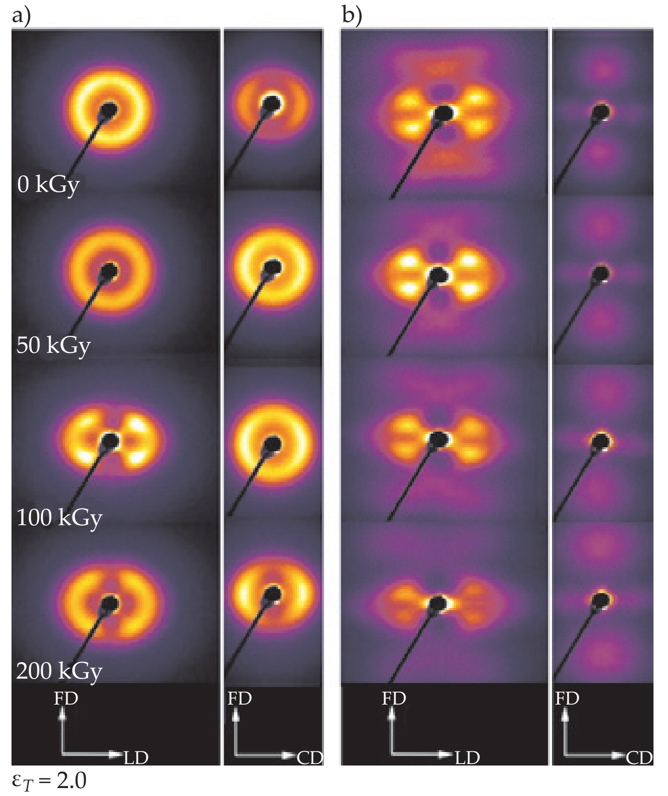

Fig. 9. 2D-SAXS patterns obtained for samples of HD-PE ($\overline{M}_w = 170\,000$) crosslinked with electron beam at different doses (for every sample two patterns are presented: sample illuminated along the CD or LD directions, FD is vertical in all patterns), as indicated and deformed in the plane strain compression to ε_T value: a) 0.5, b) 1.5

trast to raw and slightly crosslinked samples, the SAXS patterns of highly crosslinked samples, radiated with the dose of 100 and 200 kGy, show an emerging 4-point signature, characteristic for kinking). Comparison of SAXS patterns of samples deformed to $\varepsilon_T = 1.5$ revealed in turn a stronger fragmentation of the lamella structure in crosslinked samples (increasing signal of new long period emerging along LD in expense of 4-point signature tending to fade away). The notion of stronger lamellae fragmentation in crosslinked material is supported by DSC results that demonstrate significantly stronger reduction of crystallinity in highly deformed crosslinked samples than in the pristine material deformed to the same strain [49]. The heavier lamellae fragmentation in the crosslinked material can be understood easily if one recall that increased network density results in higher stress generated by the network, which facilitates earlier slip localization and easier fragmentation of lamellae. The molecular network containing numerous solid chemical crosslinks cannot relax this high stress through disentanglement, as does the network of entangled chains (see previous section) and the very high stress is transmitted to neighboring crystals making their fragmentation easier.

Another possibility of easy modification of the molecular network in amorphous layers is by adding to the polymer a diluent of lower molecular weight. That diluent molecules have not evaporate out of the sample within experimental timescale and must remain solely in the amorphous phase (*i.e.*, do not co-crystallize, and be rejected by growing crystallites to the amorphous surrounding upon material solidification). Then, the presence of such diluent results in some reduction of the number of mutual entanglements of polymer chains in amorphous phase, while it nearly does not affect the crystalline phase. One can expect also in such a system a lower connectivity between phases, *i.e.*, fewer tie-molecules. One of possible systems demonstrating such properties is, *e.g.*, linear PE mixed with small amount of paraffin oil or wax (below the level of any phase separation phenomena). Preliminary deformation experiments of the blend of HD-PE ($\overline{M}_w = 70\,000$) with 6 wt % of paraffin wax demonstrated that PE crystals grow a little thinner in the blend than in plain HD-PE (reduction of T_m by about 1 °C) and the crystallinity of PE component is slightly reduced (68 *vs.* 70 wt %), while wax does not contribute to crystalline phase and remains molecularly dispersed in amorphous phase. As a result the blend shows slightly lower stiffness and yield strength than the plain material. The presence of wax molecules in amorphous phase leads to reduced entanglement density and lower phase connectivity, which results in a weaker strain hardening of the blend and less recovery of the strain after deformation than of plain HD-PE. As demonstrated by 2D-SAXS studies a lower entanglement density and connectivity between phases in blends than in plain HD-PE results also in some changes in kinking and lamellae fragmentation upon deformation. The 2D-SAXS patterns of plain HD-PE and the blend with paraffin wax are shown in Fig. 10 for ε_T increasing from 0.4 to 1.75. Comparing the respective patterns of plain HD-PE and the blend one can find out that lamellar kinks in the blend seem to form easier than

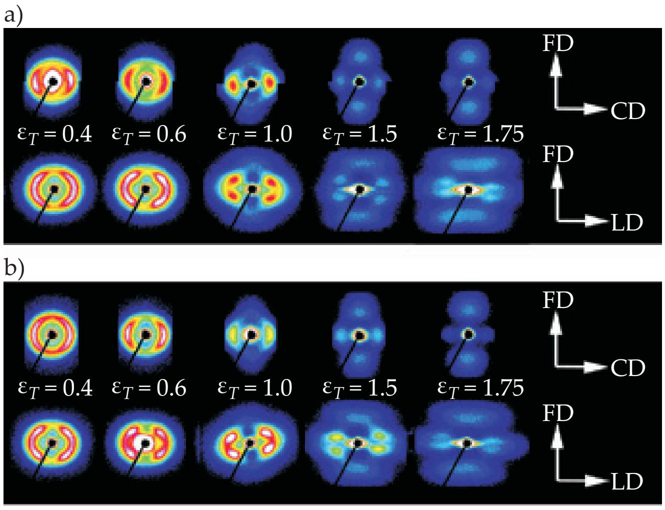

Fig. 10. 2D-SAXS patterns obtained for samples (for every sample two patterns are presented: sample illuminated along the CD or LD directions, FD is vertical in all patterns) deformed in the plane-strain compression to indicated ε_T value for: a) plain HD-PE of $\overline{M}_w = 70\,000$, b) the blend of HD-PE with 6 wt % of paraffin wax

in plain HD-PE; their 4-point signature can be detected in the blend at slightly lower strains than in plain PE. This result was not expected for blend samples that were anticipated to have lower phase connectivity than plain HD-PE. However, it can be explained that when the phase connectivity is reduced only moderately (not lost completely), roughly the same stress generated within amorphous phase must be transmitted across the interface by fewer chains, which apparently leads to stronger stress concentrations at the surface of the lamellae, which in turn results in more slip instabilities and consequently easier kinking in the blend than in the plain HD-PE.

A second observation is that the new long period along FD related to heavy fragmentation of lamellae emerges later while the scattering related to it is less intense in the blend than in plain PE. This indicates a less intense fragmentation of lamellae in the blend than in plain HD-PE at high strains above $\varepsilon_T = 1$. That less advanced fragmentation in the blend is probably related to the lower network stress generated within amorphous phase of lower entanglement density. The lower network stress results in the less intense fragmentation than in plain HD-PE.

CONCLUSIONS

The results discussed in this report demonstrate that the plastic deformation of a semicrystalline polymer is a complex series of continuous processes, involving mostly crystallographic deformation mechanisms. However, a very important role in the sequence is played by the deformation of amorphous interlamellar layers, partially reversible on unloading, which produces not only high orientation of amorphous component but also influences deeply the deformation of crystalline phase since crystalline lamellae and amorphous interlamellar layers, intimately connected through covalent bonds of chains crossing the interface, must deform simultaneously and consistently.

At low strains the deformation process is governed by the crystalline phase, while amorphous layers merely adjust themselves to the deforming crystals and substitute slip systems lacking in crystals, which helps in full strain accommodation. In the more advanced deformation stages, including the strain hardening, the control comes however, to the amorphous phase due to strongly increasing molecular network stress. This stress depends on the network density that in turn is controlled by topology of amorphous phase, including chain entanglements and chain immobilized at interfaces, providing physical crosslinks.

As the stress is transmitted between amorphous phase and crystallites primarily through chains that cross the interface and physically connect both phases, the stress concentrations are generated around the points of crossing the interface. When the segments of such chains belonging to amorphous phase become stretched due to advancing deformation the stress concentrations grow, which eventually leads to local instabilities of deformation of crystals that result in lamellar kinks and later in fragmentation of lamellae into smaller blocks. These transformations allow further deformation to proceed along easier deformation path and lead to formation of the final highly oriented structure.

Hyperelasticity of the molecular network in the amorphous layers causes partial strain recovery upon unloading by reversed interlamellar shear. This results in partial loss of high orientation, also of crystalline phase. The molecular network remains unaltered up to the true strain of approximately $\varepsilon_T = 1$. Above it, in the strain hardening range, the quickly increasing network stress and partial release of constraints due to heavy fragmentation of lamellae lead to a gradual erosion of the network through chain disentanglements. This results in permanent plastic flow within amorphous layers. Consequently, a part of the strain becomes truly irreversible, even after melting of the crystalline phase.

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