TOUGHNESS OF ORIENTED POLYMERS

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

This review article supported by some original photographs and model diagrams summarizes the mechanisms of toughness in oriented semicrystalline polymeric materials. In particular, crack propagation mechanisms in rubber-modified and oriented polymeric systems are compared. The Cook–Gordon mechanism of crack blunting in anisotropic materials can explain the low-temperature impact resistance of oriented semicrystalline polymers, fracture behaviour of biological composite structures and also the effects of photo-oxidative degradation on mechanical behaviour of oriented films.

MORPHOLOGICAL MODELS OF SEMICRYSTALLINE POLYMERS

It is generally accepted that single crystals prepared from dilute solutions of crystallizing flexible-chain polymers (polyethylenes, polypropylene, polyamides, etc.) contain molecules more or less regularly folded and aligned perpendicularly to the largest surface plane[1]. It is also well known that these polymers, when solidified from a melt, could be considered as composite materials consisting of a continuous amorphous matrix with embedded crystalline regions (crystallites). (The interphase between the crystalline and amorphous regions is sometimes considered as a third structural component.) The degree of crystallinity and the morphology of a semicrystalline polymer are important factors controlling mechanical properties. Surprisingly, no unique structural model has been generally accepted for the detailed structure of these materials[2,3].

The old *fringe-micelle model*[4] schematically depicted in Fig. 1 was abandoned, as X-ray results repeatedly confirm geometrical regularity of crystalline lamellae and perpendicularity of molecules to their base planes. The present models of semicrystalline polymers can be divided into several groups[2]. The classical (Peterlin) model is based on the notion of folded chain lamellae, similar to the monocrystals prepared from solution[5]. This model suggests adjacent re-entry of folded molecules into the same crystal-

line region. If individual chains form more loose loops and frequently enter more distant sites at the crystalline surface, we speak about *switch-board model*. Imperfect folded chain structure of single polymer crystals was also included in the *paracrystalline model* by Hoseman[6].

The above models did not conclude the development of morphological concepts. Neutron scattering studies on the crystallization of polymers[7] have shown that the radius of gyration in the crystalline state often does not differ markedly from that in the melt. It could be concluded from this experiment that individual molecules when solidified from a melt cannot crystallize by chain folding and repeated entry into the same lamella. This would inevitably group the molecule tighter together. The simplest explanation of the experimental observation is based on the so-called *solidification model* ("*Erstarrungsmodell*"). According to this model, the crystallization of a molecule occurs only by straightening suitably oriented sequences which are incorporated into different crystalline lamellae. It is possible that real lamellar structure represents a transition between the above mentioned extreme cases (Fig. 2).

In a semicrystalline polymer which solidifies from a melt quite slowly and without mechanical stress, the crystalline lamellae are organized into more complex centrally symmetrical configurations known as spherulites and observable under optical microscope. Clearly, spherulites of different polymers occurring under different conditions may differ substantially. However, it is always their size, perfection and number on which optical and in particular mechanical properties of the polymer depend.
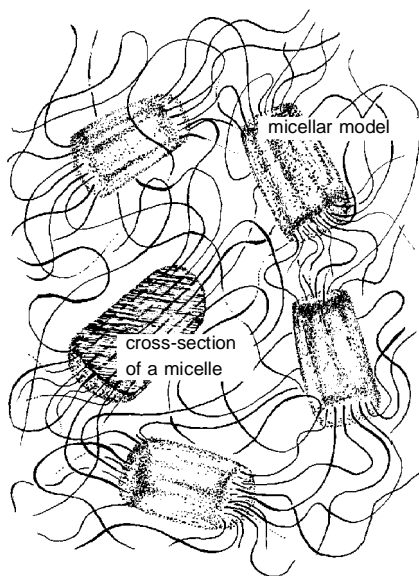

F<small>IG</small>. 1
Schematic illustration of fringed micelles (one of them in section) in an outdated model of crystalline areas in polymers

For the sake of completeness, it should be noted that polyethylene, and evidently other crystallizing polymers as well, may also crystallize with extended chains. Extremely thick extended-chain crystallites occur during crystallization at high pressure of the order of 500 MPa (ref.[1]). A certain proportion of small crystallites with extended chains is also formed at normal pressure and the probability of their occurrence is greater when the melt crystallization temperature is either immediately below the melting point or closely above the glass transition temperature[8].

A special case also arises if, during crystallization, the polymer molecules are subject to shear stresses. This may occur in solution, in gel, in melt or in the solid state during mixing, extrusion or solid-state drawing. For example, if a dilute solution of polyethylene crystallizes in a shear field, fibrous configurations occur which are known as *shish-kebabs* (Fig. 3). On the fibrous nucleus formed by extended chains, disc lamellae made from folded chains occurring through epitaxial crystallization are threaded at regular intervals. The axes of the molecules in both components are therefore oriented accordingly. Similar morphological configurations were also found in extruded profiles, pipes and fibres which solidified from a melt in a shear field. According to some authors, shish-kebabs may also be formed in a neck during solid-state drawing[9].

THE RIDDLE OF NECK PROPAGATION

Typically, semicrystalline polymers during solid-state deformation develop a "telescopical" neck which propagates along the specimen (Fig. 4). The material which has
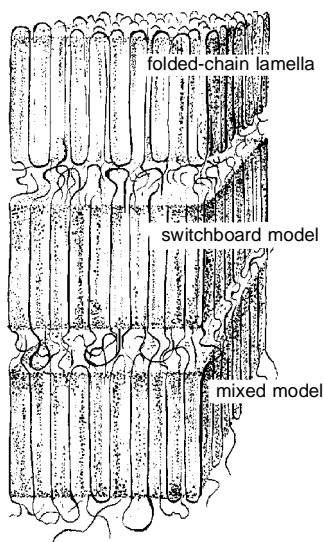

FIG. 2

Three possible models of lamellar semi-crystalline structure

passed through the neck carries the same load as the non-oriented portion of the sample, in spite of the markedly reduced cross-section. This is possible because the drawn polymer shows higher rigidity and strength than the isotropic material[10]. Originally, this was ascribed to molecular orientation. More recently attention has been paid to polymer chain extension which is also induced by deformation and which, for some mechanical properties, becomes even more important. Two molecules, shown in Fig. 5,
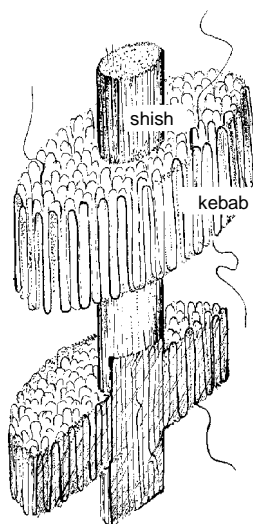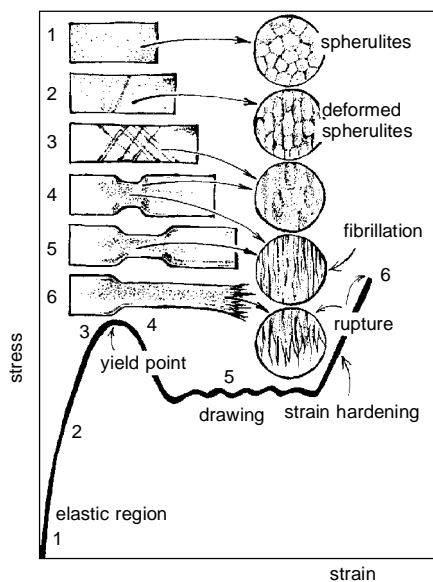

FIG. 3
A shish-kebab

FIG. 4
Typical stress-strain curve of a semicrystal-line polymer together with the corresponding neck development and structural transformations

have the same orientation factor but differ substantially in their conformation. In particular, chain extension plays a key role in determining the macroscopic tensile strength[11].

When passing through the neck, the morphology of semicrystalline polymers undergoes a marked transition. The original lamellar morphology is transformed into fibrillar structure with molecules oriented preferentially along the direction of draw. Again, the mechanism of this transformation and even the resulting structure is still an object of controversy.
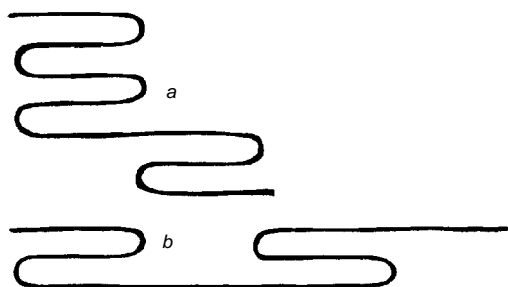

FIG. 5
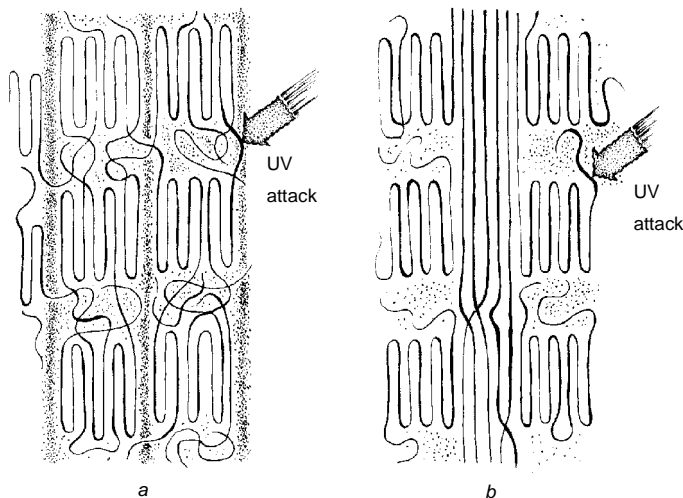Two chain molecules (*a*, *b*) showing the same orientation factor but one of them (*b*) having higher chain extension[11]

FIG. 6
Two models of an oriented semicrystalline polymer: according to (*a*) Peterlin[5], (*b*) Juska and Harrison[9]; environmental attack is represented by arrows

The classical model supposes[5] that the transformation from lamellae to microfibrils merely demands a chain tilt and slip in a limited region of "micronecks". This model explains the increase of strength and modulus upon orientation by the so-called *taut-tie molecules* connecting individual crystallite blocks. It is suggested that these load-bearing molecules are included in the amorphous regions of the material.

More recently, an alternative concept has been proposed in which the transformation from lamella to fibril depends solely on phase transition[9]. The stored mechanical energy is supposed to cause local "melting" of the semicrystalline polymer at the drawing temperature. In the second step, the action of the mechanical stress field causes an extension and strain-induced recrystallization of the polymer molecules. It is supposed that the resulting morphology consists of shish-kebabs similar to those produced by crystallization from polymer solution in a flow field. In contrast to the preceding (Peterlin) model, the high strength and rigidity of the oriented polymer is ascribed to covalent bonds in the crystalline extended chain core. The proportion of the load-bearing molecules can vary dramatically according to the drawing conditions. (The two models of oriented semicrystalline polymers are shown diagrammatically in Fig. 6.)

The Role and Transformations of Heterogeneities During Neck Propagation

During neck propagation, not only individual molecules but also larger structural units, heterogeneities, inclusions or even macroscopic fibres can be oriented along the drawing direction. Thus an interesting class of unidirectionally oriented composites can arise[12]. Isotactic polypropylene containing short glass fibres easily develops a typical neck during drawing if no surface treatment has been applied to the glass fibres. The resulting composite shows high toughness across the orientation direction. (However, the neck propagation is hindered, if an adhesion promoter has been applied on the fibre surfaces.)

It is interesting to note that during drawing the glass fibres turn to the orientation direction rather suddenly in a narrow portion of the shoulder of the propagating neck. Moreover, the fiber orientation occurs simultaneously with the transformation from spherulitic to fibrillar morphology. The free motion of macroscopic fibres indicates high compliance of the matrix thus supporting indirectly the hypothesis of strain-induced melting in the neck shoulder (Fig. 7).

Loose fibres, small defects and inclusions can pass through the neck and become oriented along the draw direction. However, starting from a certain critical size, defects and inclusions cannot be "processed" by the propagating neck any more. They represent obstacles to plasticity and further neck propagation. If a propagating neck approaches a heterogeneity larger than the critical size, it stops and breaks in its shoulder. The origin of the failure is then located at a distance from the fracture zone[13] unlike in

brittle fracture when the fracture origin can always be found on the fracture surface. The dual role of defects in a semicrystalline polymer under stress is illustrated in Fig. 8.

Finally, it must be noted that the critical effect of an inclusion on the plasticity in a neck depends not only on its size and shape, but also on the interfacial adhesion, temperature and speed of the neck propagation. At higher temperatures and lower strain rates the neck is more likely to proceed and "process" larger defects[12].

STRUCTURAL MECHANISMS OF TOUGHNESS

Toughness of any material as a property opposite to brittleness is the expression of material ability to withstand the energy of an impact or to hinder crack propagation. Correspondingly, there are two approaches to the study and interpretation of toughness:
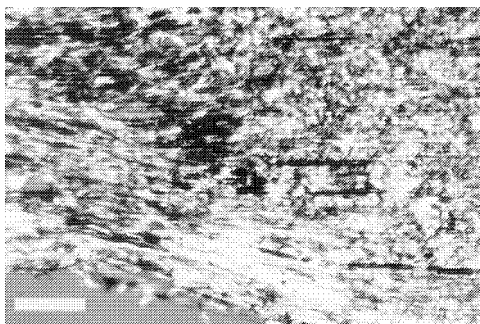

FIG. 7
Optical micrograph of a neck shoulder of a polypropylene sample with short glass fibres. Structural transformation and fibre orientation occur in the same region. (Bar = 200 μm)
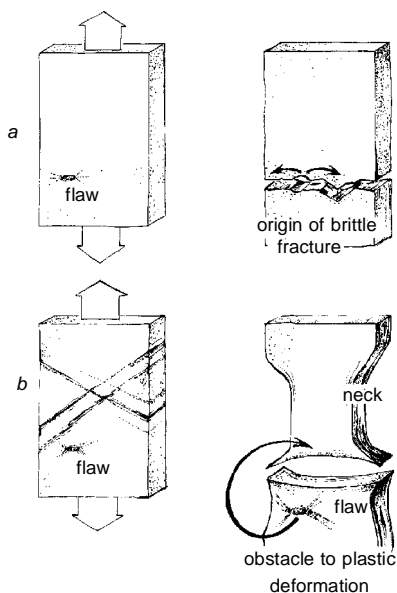

FIG. 8
A flaw in a semicrystalline polymeric material can act either as a locus of brittle fracture (*a*) or as a hindrance to plastic deformation in the neck shoulder (*b*)

G-concept (see for example ref.[14]) and K-concept (see for example ref.[15]). In the first case, toughness is expressed as critical value of specific fracture energy (crack resistance force, stress release rate) G_c, in the second it is the critical value of stress intensity factor (fracture toughness) K_c, which characterizes toughness[16]. In plane stress and linear elastic condition, characterized by Young's modulus E, the values G and K are interrelated by a simple expression

$$G_c = (K_c)^2/E \quad . \tag{1}$$

From a structural point of view, the G-approach is focused on the explanation of toughness by various mechanisms of energy dissipation. As energy is the product of force and displacement, high fracture energy implies sufficient ductility of the material. Ductility is a term that can be used to describe either the overall plastic deformation of a material under stress or the way in which the material fractures (local plasticity blunting the crack tip). In polymers, the incorporation of soft rubber particles into a hard matrix stimulates local plasticity (crazing and shear banding), which is macroscopically manifested by isotropical increase of toughness[17]. This toughening mechanism ceases at temperatures below the glass transition temperature of the rubber employed.

The second approach tries to identify mechanisms that prevent crack propagation, such as crack blunting, crack branching, and the effect of barriers (crack stoppers)[18–21]. In particular, toughness of fibrous polymer composites has been ascribed to several
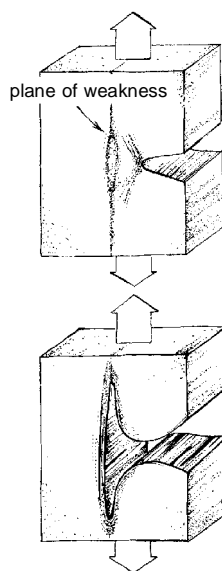

FIG. 9
The Cook–Gordon mechanism of crack blunting. At a plane of weakness a secondary crack develops thus deflecting and branching the main crack[23]

micromechanisms[18]. It has been suggested that the external impact energy in fibrous composites is dissipated as interfacial surface energy, post-debond friction energy, the work of fibre pull-out, and the release of elastic strain energy from the fibres.

There is a specific mechanism of crack blunting that often dominates in highly anisotropic materials, referred to as the Cook–Gordon (CG) mechanism[22–25]. In a uniaxially loaded plate containing a crack, there are two systems of stresses that act around the crack tip. Stress parallel to the external force shows a maximum at the crack tip, but stress acting in the perpendicular direction has a maximum located somewhat ahead of the crack tip. In the elastic case this cross-stress maximum is close to one-fifth of the maximum longitudinal stress. Therefore, if there is an interface perpendicular to the crack directiom five or more times weaker than the longitudinal strength, it can open before the approaching crack thus blunting and deflecting it (Fig. 9). Macroscopically, this is manifested in anisotropical increase in material toughness[22–25]. The CG mechanism comprises some of the energy dissipation modes mentioned above, by increasing the toughness anisotropically. Also, it is basically temperature independent and can therefore increase the toughness down to very low temperatures.

Indeed, notched impact strength of oriented polypropylene with short glass fibres measured at liquid nitrogen temperature reaches 65 kJ/m^2. This value surpasses both that of the original composite (14 kJ/m^2) and of the neat oriented polypropylene (59 kJ/m^2). Inspection of the crack surfaces after impact testing reveals that macroscopic failure is accompanied by multiple fractures at individual fiber-matrix interfaces[12] (Fig. 10).

TOUGHNESS OF BIOLOGICAL MATERIALS

Mother Nature when "designing" strong and tough structural materials depends more on the K-concept rather than on the G-concept of impact resistance. Many biological materials are anisotropic composites containing aligned strong fibres in a soft ductile matrix. Their toughness is caused predominantly by the CG mechanism. Therefore, it is interesting to find out which relation between longitudinal and transversal strength has resulted from long-term natural selection.
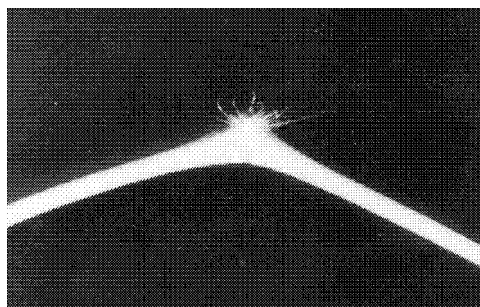

Fig. 10
Oriented polypropylene with short glass fibres after impact test at liquid nitrogen temperature. Note multiple fractures at individual fibre interfaces

   All biological structural materials such as bones, teeth, shells, nuts, woods, and particularly bamboo stalks show distinct anisotropy. Wood may serve here as a typical example[23] (Fig. 11). Average values of tensile strength for two wood types are given in Table I. It can be seen that hard and soft wood specimens differ substantially in their transverse strength values. Nevertheless, in both cases the ratio characterizing the strength anisotropy exceeds markedly the critical value of 5 calculated by Cook and Gordon as necessary for the CG mechanism to be effective. Therefore wood posseses a great deal of safety reserve so that the CG mechanism of crack blocking remains active even if the longitudinal strength decreased during ageing or decay.

   In fibrous composites there exists another possibility of absorbing mechanical energy and paralyzing crack propagation, namely the use of reinforcing fibres with high extensibility. A typical example is again a natural composite material, a leaf of broad-leaved plantain (*Plantago major*)[26]. The stress-strain behaviour of a plantain leaf along the fibres is illustrated in Fig. 12. The fibres show not only higher strength but also higher

TABLE I
Anisotropy of tensile strength in two wood types[23]

Wood type	s_a, MPa	s_b, MPa	s_a/s_b
Beech	90.7 ± 6.3	5.4 ± 0.8	17
Spruce	83.3 ± 4.0	1.9 ± 0.7	44

s_a Tensile strength in the fibre direction. s_b Tensile strength transverse to the fibre.
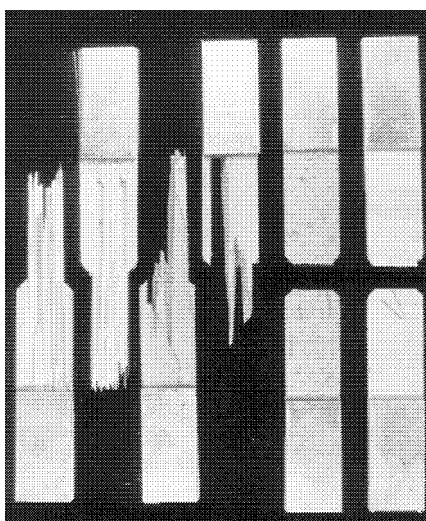

FIG. 11
Tensile fracture surfaces of two wood types. Extreme left and right, soft wood (spruce), centre, hard wood (beech). Left, fractured along grain direction, right, across the grain direction

extensibility than the remaining leaf material and the moderate fiber-matrix adhesion allows mutual slippage of the components before final fracture.

The advantage of extensible reinforcing fibres in biological systems is obviously also worth application in man-made composites. Indeed, a one-polymer two-phase polyethylene film shows similar behaviour[26]. It has been prepared by embedding high-modulus polyethylene fibres between two layers of common-grade linear polyethylene film in a heated press. Crack propagation in the resulting composite film was then studied. At low strains the material shows nearly isostrain behaviour, i.e. strains in the matrix and fibre are approximately equal. This also means that even one single fibre exhibits a reinforcing effect. However, after the yield point of the matrix film is reached and the crack starts to grow, large fibre pull-out in the crack zone occurs. This furnishes an additional mechanism of energy dissipation. By analogy to plantain leaves, the behaviour of a composite with extensible fibres, low fibre-to-matrix adhesion and zero critical fibre concentration is described as *the plantain effect*[26].

ORIENTATION AND DEGRADATION

Degradation of semicrystalline polymers, caused either by ultraviolet (UV) radiation or a chemical attack, is a markedly heterogeneous process. In particular, chain scission by UV light occurs exclusively in amorphous regions, while molecular chains packed within crystallites are protected. This does not mean, however, that the UV light cannot penetrate into the crystalline regions. The UV light energy quantum which happens to
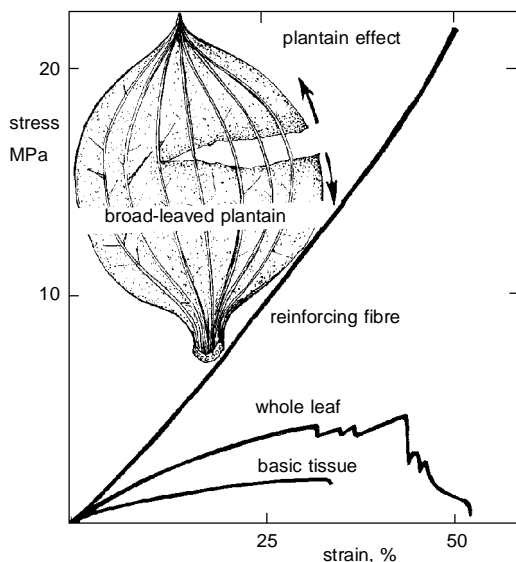
FIG. 12

The stress-strain behaviour of a plaintain leaf and its constituents. The reinforcing fibres show both higher strength and extensibility than the matrix[26]

hit the crystallite is more likely to migrate to the interphase region and evoke a molecular "explosion" within the amorphous portion of a molecule. A chain scission and radical formation in the crystallite interior would namely cause a large-scale distortion of the whole crystallite thus demanding much more energy.

Macroscopically, degradation causes embrittlement which can be followed by strain-at-break measurement[27,28]. In oriented semicrystalline polymers, this embrittlement is markedly anisotropic[13,28]. This is demonstrated in Fig. 13. As one would expect with non-degraded film, the extensibility is lower in the machine direction and larger in the cross direction, where some reserve in plastic deformation is still preserved. With degradation, however, the situation can be different. After certain exposure time the strain-at-break values along and across the orientation can even change their order. In other words, the oriented film is less vulnerable to degradation (as monitored by the strain at break) in the orientation direction. Several models of this behaviour have been offered[13], but none of them has been generally accepted.

It is possible that various mechanisms act simultaneously. Thus, the Juska and Harrison model[9,29] can explain the anisotropy in degradation at a molecular level (see Fig. 6). Indeed, the load-bearing extended molecules in this model are included in the crystalline regions (shish) and therefore not affected by the photo-oxidative degradation, at least at its first stage. They impart mechanical continuity to the material in this direction so that not only strength but also strain-at-break values are less affected. Moreover, oxidation rate as a function of the drawing ratio shows a maximum corresponding to the onset of yielding[30] as shown in Fig. 14. The Juska and Harrison model suggests
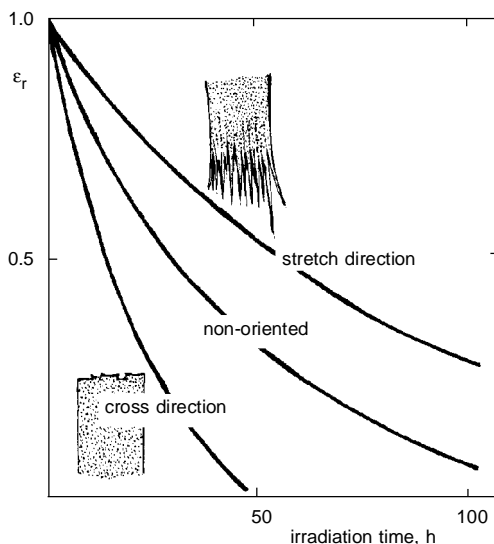

Fig. 13
The anisotropy of photo-oxidative degradation in oriented polyethylene film. The strain at break related to the non-degraded material is less sensitive to the irradiation in the orientation direction than in the cross direction. These two directions also differ in the fracture morphology[13]
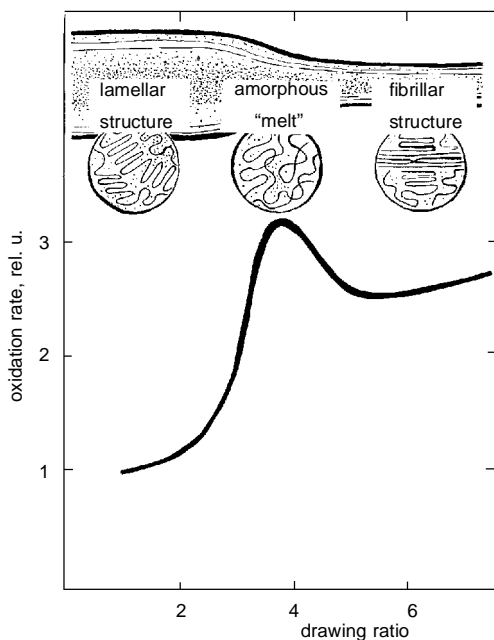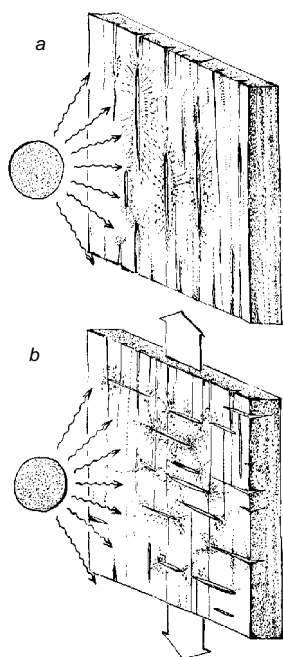
more or less amorphous structure under such conditions. The observed behaviour, in turn, supplies another indirect support to the Juska and Harrison concept[29].

On the other hand, the CG model of crack blunting[23] can offer a plausible explanation of macroscopically observed effects. Indeed, a tendency to fibrillation has been observed with oriented films of polypropylene and polyethylene after prolonged exposure to UV radiation. If cohesion in the cross direction is lowered upon degradation, the CG mechanism becomes more pronounced and the toughness and extensibility of the material are less affected in the orientation direction than in the cross direction. When, however, the longitudinal strength drops below a certain critical value, the crack-blunting CG mechanism is no longer effective and a dramatic embrittlement occurs even along the orientation. Such embrittlement is markedly enhanced if an external stress is applied during the environmental exposure[31] (Fig. 15). Then a system of cracks develop perpendicularly to the stress direction thus affecting the strength and toughness dramatically.

CONCLUSIONS

Orientation of semicrystalline polymers is an effective way that leads from common-grade materials to extremely stiff, strong and tough products. The CG mechanism of crack blunting dominates among the various processes of enhancing toughness upon orientation. An interesting class of composite materials can be prepared by solid-state drawing of polypropylenes modified by short glass fibres or rubber particles. These materials possess high toughness down to liquid nitrogen temperature if the main crack propagates across the the drawing direction. Their properties can be further optimized by varying interfacial adhesion, drawing conditions and subsequent treatment[32].

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