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Rolling of polymeric materials with side constraints

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Abstract

It is often observed that the plastic deformation of crystalline polymers, especially on drawing, causes significant amount of cavitation. Cavitation can be suppressed in the process of rolling due to compressive component. An innovative method of obtaining highly oriented polymeric materials is by unidirectional rolling in a channel formed on the circumference of one roll with another roll, having the thickness matching the width of the channel. The side-walls of the channel on one roll constitute the side constraints while the other roll works like a plunger in channel-die. Rolling with side constraints is cavity-free and is advantageous over conventional rolling, channel-die compression or solid state extrusion since it gives the possibility of obtaining relatively thick and infinitely long highly-oriented shapes or profiles in a fast continuous manner. The resulting profiles can have considerably high cross-section area. The design of the rolling machine is described. Few examples of rolling with the rate 4.23 m min^{-1} of isotactic polypropylene (iPP) and high density polyethylene (HDPE) shapes are presented. Tensile strength of the rods rolled to the compression ratio 5.4–6.6 with final cross-section of 10–12 mm approached 200 MPa for both polymers. The oriented rods of iPP and HDPE demonstrated high and sharp texture produced in HDPE by the activity of (100) [001], (010) [001] and (100) [010] crystallographic slips while in iPP (010) [001], (110) [001] and (100) [001] slip systems were active. In addition to those slips twinning modes were active on unloading. Appropriate combination of rolling rate, temperature, initial thickness of rolled bar, as well as molecular weight of the polymer will apparently lead to rods with higher strength. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Plastic deformation; Crystalline polymers; Cavitation

1. Introduction

Molecular orientation is one of the advantageous results of plastic deformation of polymeric materials. In most cases, it leads to an increase in material's toughness and strength. Permanent deformation of polymeric materials is usually obtained by simple elongation.

It is often observed that the plastic deformation of crystalline polymers causes significant amount of cavitation. One of the sign of cavitation is a sudden polymer whitening near the yield point. Galeski, Argon and Cohen [1] showed by transmission electron microscopy investigation of polyamide-6 that cavities were formed in polyamide bulk during plastic deformation, preferentially in places with mechanical mismatch of adjacent stacks of lamellae. The size of OsO_4-stained cavities reflects the lateral sizes of polyamide lamellae. Cavitation associated with chain scission was found to be a massive phenomenon in several bulk polyamides.

Duffo et al. [2] observed by light microscope the formation of pores during drawing of polypropylene film. The pores were of sizes ranging up to few microns and most of them were generated in the yield zone on both sides of the neck region.

The internal cavitation of the type observed in tension experiments has been referred to as '*micronecking*' by Peterlin (see e.g. [3]). Such *micronecking* had been considered for a long time to be essential mechanism for obtaining large-strain deformation of aggregates of chain folded crystals. It was regarded that it removes kinematical constraints between lamellae and allows them to untangle. While this picture looks reasonable in tensile deformation, it flaws for modes of deformation not producing cavitation, e.g. compression, in which positive normal stress component prevents for any cavitation. It has been shown that *micronecking* is inessential for the development of nearly perfect single crystal textures for several semicrystalline polymers that result from high plane-strain compression in a channel-die [4]. Although plane strain compression is kinematically

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very similar to drawing of wide strips, cavitation is not occurring here due to positive normal stress component. The numerous observations confirmed that the crystalline and associated amorphous regions of the material undergo a continuous series of shear induced morphological transformations without any cavitational process.

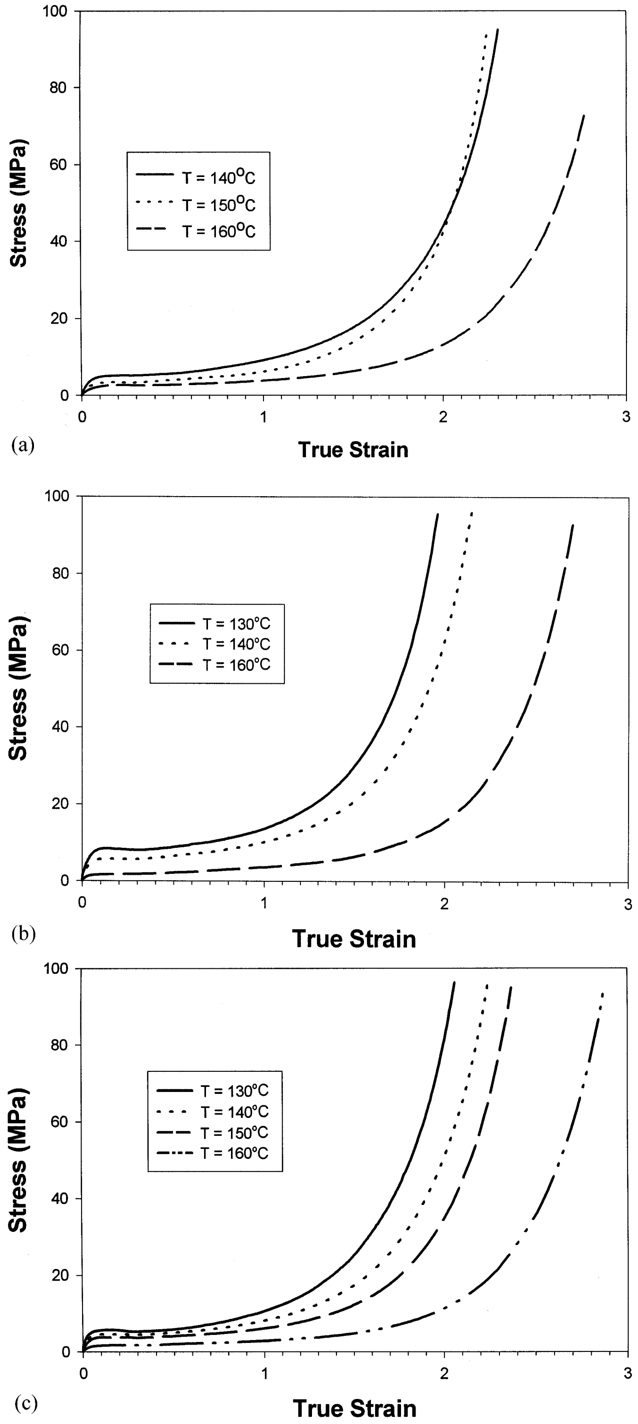

Fig. 1. The stress–true strain curves of plane-strain compression in a channel-die with the deformation rate: (a) 1 mm min^{-1}; (b) 5 mm min^{-1}; (c) 10 mm min^{-1}. Temperature of deformation indicated on each plot.

Among other known methods of plastic deformation the rolling is one of the best ways of producing high preferred orientation. Similarly to compression cavitation is usually not observed due to a high pressure component. Rolling is an attractive process of plastic deformation since it could be designed as a continuos process. However, the force required to roll significantly a wide strip of the polymeric material increases sometimes unacceptably high while for narrow strips, there is an unwanted component of a transverse deformation deteriorating the final texture. The side effect of a transverse deformation can be also the formation of fissures, cracks and cavitation at edges of a rolled material.

A novel method of obtaining of highly oriented polymeric materials, developed in our laboratory, being a combination of channel-die compression and rolling, is by rolling with side constraints [5]. This process relies on rolling of a material inside a channel formed on the circumference of a roll with another roll having the thickness matching the width of the channel. The side walls of the channel on the roll constitute lateral constraints as in channel-die. The other roll plays a role similar to plunger. The system of rolls with a channel develops conditions close to plane-strain compression of the rolled material. That deformation mode is known to produce a *quasi* single crystal texture of compressed materials. The advantage of such constraint rolling is the possibility of compressing relatively thick and wide and infinitely long rods or profiles in a continuous manner. The resulting profiles may have considerably high cross-section area and superior mechanical properties comparable to fibres.

In this paper, the construction of the rolling machine and the preliminary results obtained for constraint rolling of isotactic polypropylene are reported.

2. Design of the rolling machine

Conventional channel-die [6] was used to assess the forces and rates required for constraint rolling. The results of the channel-die compression were used for the design of the rolling machine. Polypropylene slabs 13 × 51 × 100 mm cut from extruded shapes were used for compression experiments. The temperature of the channel-die was maintained at 120, 130, 140, 150 or 160°C. The rate of compression, set in the Instron loading frame, varied from 1 to 50 mm min^{-1} The exemplary stress-compression ratio curves for different temperatures and different compression rates are presented in Fig. 1a and c. No fracture of samples was observed on compression up to the 50 kN limit of load of the machine. It is seen that the temperature has stronger effect on the attainable strain than the compression rate

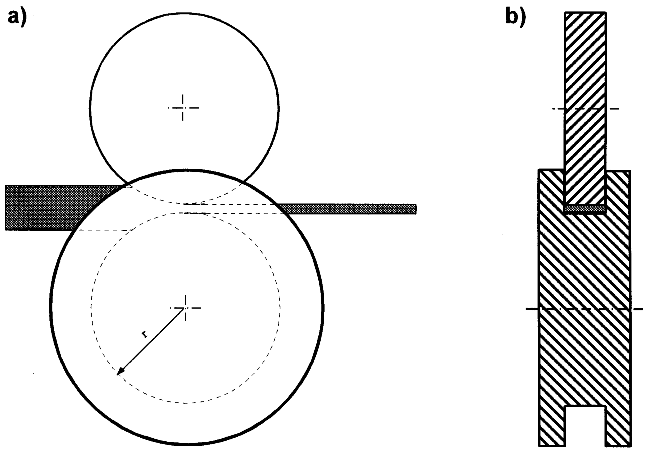

Fig. 2. The scheme of the apparatus for rolling with side constraints (a) side view; (b) front view.

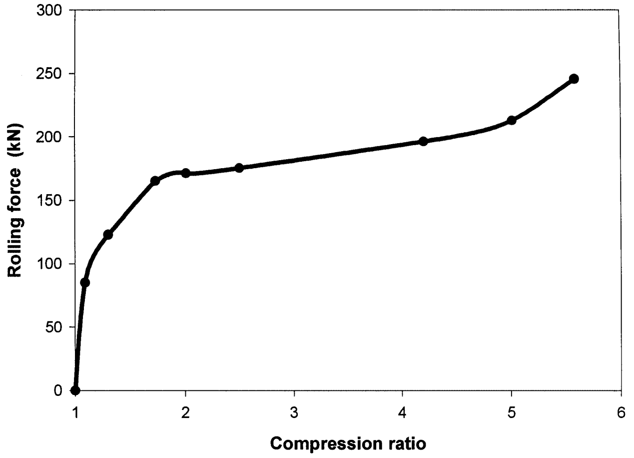

Fig. 3. The dependence of load on the compression ratio measured during rolling test of iPP with the linear rate of 170 mm min^{-1} at room temperature.

from the ranges explored. At 160°C, the compression ratio above 15 could be easily reached at the stress of 100 MPa while only 6 at 120°C. At lower deformation rate, the samples are more compliant.

The scheme of the constrained rolling is depicted in Fig. 2. The prototype apparatus consists of rolls 300 mm in diameter, the depth and width of the channel on one roll is 80 and 13 mm, respectively. The spindles and the base of the machine were designed sturdy enough to resist expected high loads. One of the spindles was mounted on a movable arm equipped with the load cell for measurements of the force exerted on the rolled material. Both rolls were driven by an electric motor through a 2-speed gear box, resulting in two rolling rates: 170 or 4230 mm min^{-1}.

The rolling machine was tested by performing deformation of a $13 \times 51 \times 400$ mm polypropylene bar at room temperature. An exemplary load-compression curve is presented in Fig. 3. It is seen that the load first increases rapidly reaching the yield at ca. 100 kN followed by strain hardening and exceeds 250 kN at the compression ratio of 6.

3. Experimental

Isotactic polypropylene Malen-P F401 (MFI = 3.2 g 10 min^{-1}, isotacticity index 95%, density 0.91 g cm^{-3}, by Petrochemia SA, Poland) was used in the form of a long, 13 mm thick and 51 mm wide slabs formed by extrusion.

The rolling of specimens was performed on the prototype apparatus described in previous section. The rolling speed was set to 170 and 4230 mm min^{-1} while the temperature of rolled material was 20, 90, 110, 120 and 150°C.

The texture of rolled samples was studied using the X-ray pole figure technique: A WAXS system consisted of a computer controlled pole figure attachment associated with a wide angle goniometer coupled to a sealed-tube source of CuK$_\alpha$ radiation. The technique of pole figure preparation was described elsewhere [7]. The following diffraction reflections from monoclinic crystal form of iPP were analyzed: (110), (040), (130), (060) and ($\bar{1}13$) at the 2θ diffraction angles: 14.1, 16.9, 18.5, 25.5 and 42.5°, respectively.

Tensile tests were performed using an Instron tensile testing machine with the rate 5 mm min^{-1} on oar-shaped specimens machined from the rolled samples.

Impact experiments were performed with the instrumented Izod impact tester (Resil 5.5 by CEAST, Italy) equipped with 4 J instrumented hammer. The specimens were machined out from rolled rods in FD–CD and FD–LD planes and notched with a standard notch of 0.25 mm tip radius.

4. Results

Permanent deformation of polymeric materials is usually obtained by simple drawing with no or little side constraints, which results in cavitation. In deformation by compression the cavitation is less probable due to positive normal stresses. However, the side constraints in compression prevent for any cavitation.

The presence of side constraints changes completely the process of plastic deformation in compression: no neck is formed and although the yield stress remains at a similar level, further deformation of the polymer leads to dramatically higher loads. This is illustrated in Fig. 4 where true stress–true strain curves for iPP deformed in a channel-die compression (with constraints) is plotted. The material responds with the stress of nearly 300 MPa. For comparison, when there is no constraints in tensile deformation mode an intense cavitation leads to the ultimate strength of merely 120 MPa (see Fig. 4), and fracture occurs by sequential break of single microfibrils. Moreover, the drawn cavitated material has little transverse strength due to loose connection between microfibrils formed during deformation.

The rolling of iPP bars was performed with the linear speed of 170 mm min^{-1} at room temperature and at 90°C. No fracture of the samples was observed even on heavy rolling. Samples with the compression ratio around 4 became translucent in contrary to opaque bars of virgin iPP. With higher compression ratio the samples became even more transparent-printed letters were clearly visible through the rolled iPP sample of the thickness of 9.5 mm (compression ratio 5.4). The force exerted on the rolls increased highly with the increase of compression ratio in spite of continuous reduction of the cross-section of the rolled material.

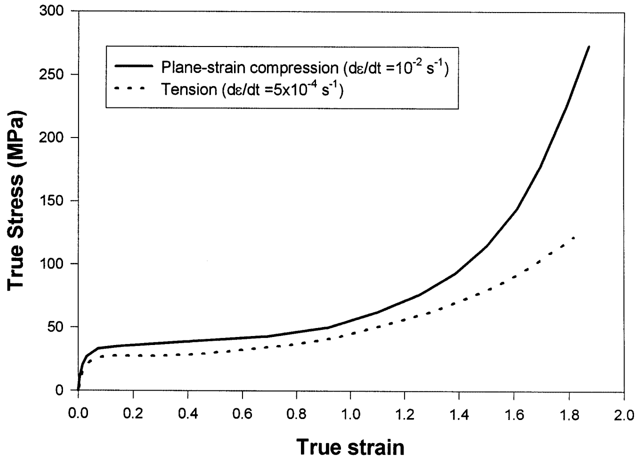

Fig. 4. The true stress–true strain curves for iPP deformed in tension (without constraints) and in a channel-die compression (with constraints). The data for tension taken from [9].

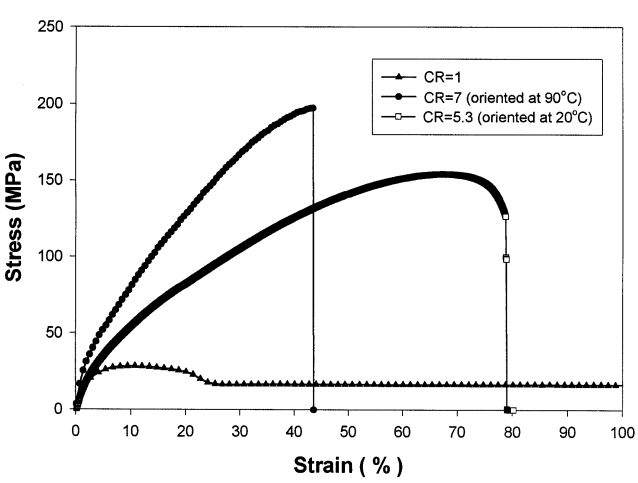

Fig. 5. The stress–strain curves obtained in tensile tests of samples of unoriented iPP and those cut from the bars of iPP rolled at 170 mm min^{-1}.

The stress–strain curves obtained for samples cut from iPP bar rolled at 170 mm min^{-1} are presented in Fig. 5. It can be noted that for low temperature of rolling the initial elastic response of the sample is relatively short and followed by a limited region of plastic deformation — the samples can accommodate up to 80% of elongation in addition to the strain imposed already by rolling. In samples cut from the bar rolled at 90°C, the initial elastic response is longer while the second segment, associated with plastic deformation is shorter than in samples rolled at room temperature (40%). The ultimate strength of the material reaches 200 MPa.

The rolling of iPP at the rate of 4230 mm min^{-1} was performed at the room temperature, at 110, 120 and 150°C, sequentially by several steps of lower compression up to the final compression ratio above 6. Rolling to higher compressions led to a fracture of the samples. The fracture started from the surfaces being in contact with rolling faces of the rolls. Tensile tests of the samples of iPP rolled at higher temperatures show longer elastic response than for lower temperature of rolling, up to 15% of elongation, followed by fracture. The ultimate strength of the samples varies from ca. 90 MPa for samples rolled to CR = 4 to ca. 200 MPa for samples rolled to CR = 5.4.

The fracture process in tensile tests of the rolled samples of high CR starts with numerous small cleavages in the rolling plane spreading soon over the whole gauge length of the sample. Microfibrils are formed on this stage of tensile deformation. With increasing elongation some microfibrils break at stress concentration points which quickly leads to an avalanche fracture of the remaining microfibrils at the smallest cross-section of the sample.

The textures of the iPP samples rolled to CR = 4.0, 6.25 and 7.46 are presented in Fig. 6 in the form of pole figures of normals to (040) and ($\bar{1}$13) planes. The pole figure of the ($\bar{1}$13) plane of the monoclinic α modification of iPP is the closest accessible measure of the chain orientation within crystalline component — the normals to this plane are oriented only 5.8° away from chain axis direction. One can note easily that the ($\bar{1}$13) pole figures indicate increasing chain orientation with increasing compression ratio. The pole figure obtained for sample of CR = 7.46 suggests nearly perfect alignment of macromolecular chain axes along the flow direction.

The pole figures of the (040) plane indicate that for the sample of CR = 4.0 the normals to (040) plane are clustered in LD–CD plane with the main maxima along the constraint direction, CD. For higher compression ratios new maxima in loading direction, LD, become develop and eventually dominate over those in CD.

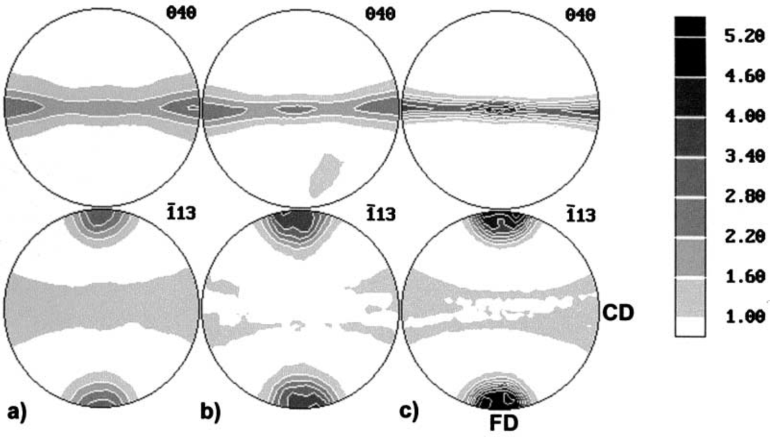

Fig. 6. The pole figures of textures of (040) and ($\bar{1}13$) planes determined for iPP samples rolled to compression ratio: (a) 4.0; (b) 6.25; and (c) 7.46.

At lower compression ratio, the texture of rolled samples is quite similar to the texture obtained in our laboratory in a channel die compressed iPP samples [8]. The conclusion that follows is that similar slip mechanisms are acting during rolling: (0k0) plane are parallel to the side walls of the channel as the result of the (100) [001] chain slip system accompanied at latter stages by the (010) [001] and (110) [001] chain slips. For higher compression the pole figures, especially of (110) plane may suggests some twinning mechanism active, possibly on unloading, although such texture can be obtained as well by joint activity of (010) [001], (110) [001] and (100) [001] crystallographic slips. Further studies are necessary to identify more precisely the mechanism(s) responsible for observed texture.

The DMTA spectra obtained at 1 Hz in bending mode for rolled iPP samples cut along or perpendicular to the loading (rolling) direction, LD (see Fig. 6) show that in the sample bent along loading direction (sample cut in the FD–CD plane), the well pronounced β relaxation (glass transition) is located at 13.6°C while for bending in CD (sample cut parallel to the FD–LD plane) much less pronounced transition at around 11°C, followed by another relaxation peak centered at 35°C are observed. That large shift of the glass transition temperature by more than 20°C as compared with initial unoriented material ($T_g \approx -10$°C), observed for both sample orientations, is the result of very strong alignment of polymer chains within amorphous component along the flow direction similar to orientation of chain axes within crystalline component. Such alignment reduces considerably mobility of the chain segments which manifests in observed increase of relaxation temperature. Since the β relaxation is attributed exclusively to an amorphous phase, the observed differences in tanδ data suggests also strong anisotropy of packing of fragments of polymer chains within amorphous component with respect to CD and LD directions, respectively.

Instrumented Izod impact tests were conducted on rolled samples with the notch placed on rolled surface and on surface parallel to side walls. The respective force-time curves are illustrated in Fig. 7, Fig. 8a and b together with the pictures of broken samples. It is seen that the sample with notch cut on FD–LD (i.e. loaded along CD direction) plane broke partially (fracture behind the notch), while the sample with the notch on FD–CD plane (loaded along LD) showed longitudinal cleavage and delamination along FD–CD plane rather than fracture behind the notch. The impact strength for those samples is equal 59 and 67 kJ m^{-2}, respectively.

5. Conclusions

Cavitation on plastic deformation reduces greatly the strength of oriented polymeric materials. The cav-

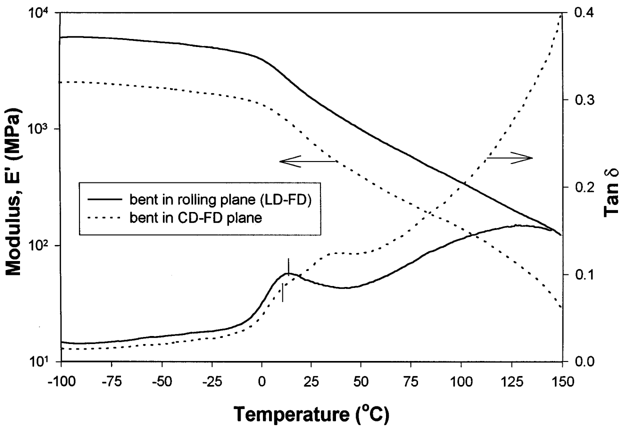

Fig. 7. The DMTA spectra obtained at 1 Hz in the bending mode for samples of rolled iPP cut along or perpendicular to the loading direction.

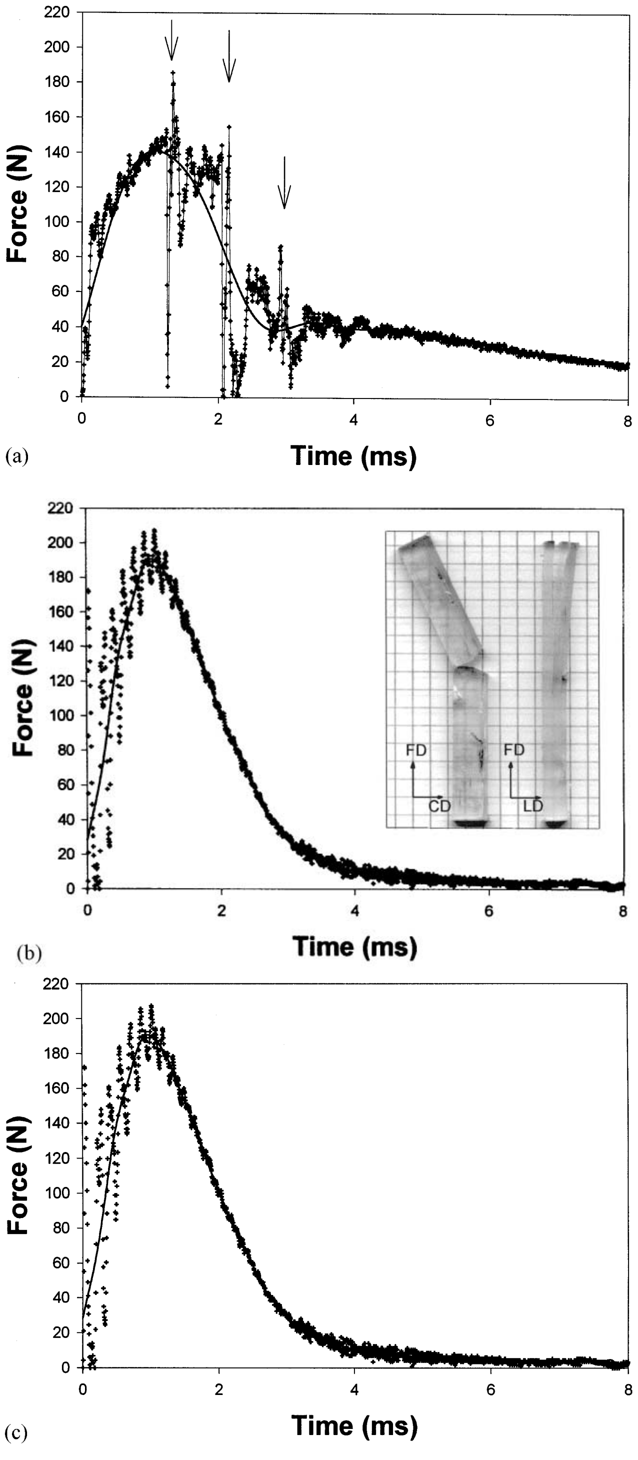

Fig. 8. The time dependence of the stress during the Izod impact test (a) sample cut out from the rolled bar in the FD–LD plane and impacted along LD; (b) sample cut out in the FD–CD plane and impacted along CD. The inset in (b) shows the samples after their impact fracture. The arrows in (a) indicate the partial fracture by delamination during the test.

ity-free deformation as the plane-strain compression leads to oriented polymeric materials with the strength much higher than the material oriented by deformation with no constraints imposed. In that deformation mode the side constraints imposed on the material during its compression help to prevent unwanted cavitation, as well as to produce material with well defined and sharp texture. The reported here new method of rolling inside a channel resembles the plane–strain compression in a channel-die. The properties of the oriented material obtained by such rolling are similar to that deformed by channel die compression. The proposed method has, however, a big advantage over the compression mode allowing continuous production of oriented material of unlimited length, similarly to conventional rolling. On the other hand, the constraint rolling method seems to be better than conventional rolling, in which the side constraints result merely from friction forces between the material and rolls, which limits the conventional rolling to production of oriented relatively thin sheets or foils only (in which additionally unwanted fissures or cracks are frequently produced on edges of rolled material). In contrary, the constraint rolling allows for production of the rod or profiles with relatively large cross-section — in the laboratory setup we could make easily the rods of the 13×10 mm^2 cross-section. Such material may become a very attractive engineering material of superior mechanical properties.

The experimental studies of the rolled iPP samples reported in this study were designed to find the structure and properties of the material rolled at various conditions. It was found that rolling leads to strong orientation (texture) of both crystalline and amorphous components comparable to that obtained by channel-die compression. It was demonstrated that iPP rolled in the channel show a significant increase in tensile strength which depends on the conditions of rolling (temperature, deformation rate and compression ratio). The stress–strain curves of samples of rolled material exhibit first elastic response and then depending on the temperature of rolling, followed by region of plastic deformation. This indicates that the material still has a potential to higher orientation and much better ultimate properties. A cleavage and delamination phenomena were found to occur right before fracture of highly oriented samples.

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