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# Yield and plastic resistance of $\alpha$ -crystals of isotactic polypropylene

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#### Abstract

Yield behaviour and plastic resistance of the (100)[001] chain slip system in  $\alpha$ -crystals of isotactic polypropylene (iPP) were studied in samples of biaxially oriented films of plain iPP and blends of iPP with hydrogenated oligo(cyclopentadiene) (HOCP). Due to the orientation process the films investigated exhibit sharp and nearly one-component texture with the (010) plane parallel to the film surface and the chain direction parallel to the direction of final drawing (transverse direction, TD). The films were studied in tension at various angles with respect to the orientation direction. It was found that the yield stress obeys the Coulomb yield criterion, provided that the angle between the chain orientation axis and tensile axis is within the range of 30–50°. The results suggest that the (100)[001] chain slip is active as a single deformation mechanism in this range of sample orientation. The critical resolved shear stress necessary to activate this slip,  $\tau_c$ , was determined for iPP and iPP/HOCP blend samples. It was also found that the slip process is sensitive to the stress normal to the slip plane, similarly to the slip processes observed in linear polyethylene crystals. The value of  $\tau_c$  determined for plain iPP was 22.6 MPa, while for the 8:2 blend its value increased to 35.5 MPa. The increase is caused most probably by the presence of a small amount of HOCP molecules incorporated within iPP crystals, as well as by the layers of higher concentration of HOCP located at crystal–amorphous interfaces, which both cause immobilization of a part of dislocations and consequently an increase of the yield stress observed in the blend samples. The third probable cause of the increase of yield stress in blends may be an increase of the glass transition temperature of the amorphous phase of iPP in the blend, as compared with plain iPP samples. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Yield; Plastic resistance;  $\alpha$ -crystals

## 1. Introduction

Considerable attention has been paid in the past to the theoretical and experimental aspects of deformation mechanisms in semi-crystalline polymers [1–4]. The plastic deformation of such polymers is a complex process; many competing phenomena are likely to occur simultaneously when a polymer is plastically deformed. Crystalline lamellae, separated by amorphous layers and connected by tie molecules, are arranged spatially to form higher level morphological forms, e.g. spherulites. Thus, the mechanisms of plastic deformation of semi-crystalline polymers have to be considered at different levels: individual lamellar crystals, stacks of lamellae, spherulites, etc. It is particularly interesting to study the deformation behaviour of the crystalline component. This can be done either on a microscopic level in polymer single crystals or in macroscopic samples of oriented polymer with well-defined single-component texture. In such a material, the common spherulitic superstructure is replaced by well aligned molecular structure obtained through an orientation process in which crystallites

Most of the investigations of the mechanisms of deformation in oriented semi-crystalline polymers have concerned polyethylene (PE). Numerous studies have revealed the principal deformation mechanisms of semi-crystalline PE (see the reviews [2–4]). In the recent work the plastic resistances of several known deformation mechanisms were determined for this polymer [5]. These quantities were used as input parameters in mathematical modeling of the deformation process [6].

Relatively little attention was paid to the plastic deformation of other semicrystalline polymers, including isotactic polypropylene, iPP [1,2]. In particular, there are only few papers [7,8] describing the investigations of the yield behaviour and plastic resistance of oriented iPP. However, quantitative information on the mechanisms involved in the plastic deformation of this polymer is needed for mathematical modeling or application studies.

Easy processing, extensive applicability and the relative low cost of iPP have resulted in very high annual world

have been rearranged parallel to each other with the chain axes aligned along the orientation direction throughout the sample. Macromolecules within amorphous layers separating crystals are also oriented in the same direction.

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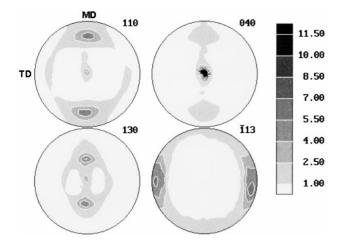


Fig. 1. The pole figures of (110), (040), (130) and ( $\bar{1}13$ ) planes of the monoclinic  $\alpha$ -form iPP crystals measured in the sample of oriented plain iPP, plotted in stereographic projection. The machine and transverse direction denoted as MD and TD, respectively.

production and wide use of this polymer for engineering, packaging and other purposes. The application of iPP in a plain form, as well as in various blends and composites, including oriented materials, is very wide and still expanding. Therefore, studies of deformation behaviour as well as main mechanisms active during plastic deformation of this polymer seem to be of special importance.

In the preceding paper we have studied the deformation behaviour and found active mechanisms in plain iPP and in the blend of iPP with hydrogenated oligo(cyclopentadiene) (HOCP) [9]. This pair of polymers is miscible in any proportion and exhibits both upper and lower critical solution temperature behaviour [10]. It is easy to obtain by an appropriate thermal treatment, a solid blend in which the amorphous phase constitutes the homogeneous mixture of both components dispersed at the molecular level. Moreover, the molecules of HOCP being relatively short and stiff can act in this system as molecular reinforcements of the amorphous component, which leads to a considerable change of the properties of this component itself, as well as the properties of the entire semicrystalline material. In order to study the influence of the properties of the amorphous component, to which the crystalline component is intimately connected, on the plastic deformation of this crystalline component it was decided to include this blend in the intended investigations of deformation mechanisms of iPP. The direct aim of the present work was to determine the plastic resistances for one of the most important deformation mechanisms acting in the iPP crystalline component, i.e., the (100)[001] chain slip [9,11]. In order to test the applicability of yield criterion and to obtain accurate information on the slip, the deformation behaviour of textured iPP using specimens covering a wide range of angles between the initial orientation direction and the load direction was investigated. It was decided to study also the samples of iPP/HOCP blend with similar orientation, yet different properties of amorphous components in order to determine if there is any influence of that amorphous component, connected to the crystals, on their deformation behaviour.

# 2. Experimental

## 2.1. Oriented films

The materials used were a commercial iPP, Moplen T305 supplied by Montedison, with  $M_{\rm w}=3.0\times10^5~{\rm gmol}^{-1}$ , and a hydrogenated oligo(cyclopentadiene) (HOCP), Escorez 5120 from Esso Chemicals Co., with  $M_{\rm w}=630~{\rm gmol}^{-1}$  and  $T_{\rm g}=85^{\circ}{\rm C}$  and density  $\rho=1.07~{\rm g/cm}^3$ . The films were prepared by extrusion followed by sequential stretching: in the direction of extrusion with the extension ratio of 1:5 and in the transverse direction with the extension ratio of 1:8. The details of blending, extrusion and orientation processes are described elsewhere [9].

## 2.2. Measurements

The orientation of the isotactic polypropylene crystalline component in the deformed blend samples was studied by means of X-ray diffraction measurements including the pole figure technique and small-angle X-ray scattering (SAXS). Details of the experimental procedure are described elsewhere [9].

The mechanical tests of oriented samples were carried out in a tensile mode at room temperature using an Instron tensile testing machine. Oar-shaped tensile specimens with a gauge length of 20 mm and a width of 4 mm (according to DIN 53504) were cut out from the oriented films at various angles to the transverse direction, TD (direction of the final drawing). The initial deformation rate was  $4.2 \times 10^{-4} \,\mathrm{s}^{-1}$ for all tests (crosshead speed of 0.5 mm/min). From experimentally determined load-displacement curves the yield stress was calculated. Usually the yield point is defined as the stress at the maximum of the load-displacement curve. However, such a maximum was not always observed in our load-displacement curves and the load frequently increased continuously with increasing elongation. Therefore, an alternative definition of yield stress was used in the reported study: for these specimens which have not exhibited a load drop on the load-displacement curve the yield stress was determined as the stress calculated at the intersection of the measured load-displacement curve and a straight line parallel to the initial slope of the curve at an offset equivalent to 4% nominal strain [1]. It appeared that when the loaddisplacement curve of a particular specimen exhibited a clear load maximum, the determined offset yield stress was usually very close to the stress observed at the maximum of the curve.

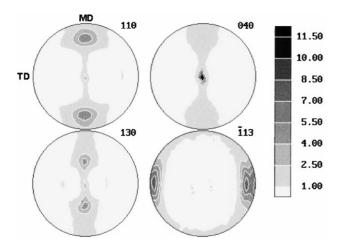


Fig. 2. The pole figures of (110), (040), (130) and ( $\bar{1}13$ ) planes of the monoclinic  $\alpha$ -form iPP crystals measured in the sample of oriented 8:2 iPP/HOCP blend, plotted in stereographic projection. The machine and transverse direction denoted as MD and TD, respectively.

#### 3. Results and discussion

Wide-angle X-ray scattering studies have demonstrated that both plain iPP and iPP/HOCP blend oriented samples contain exclusively the crystals of monoclinic  $\alpha$ -modification [9]. Fig. 1 shows the pole figures of normals to (110), (040), (130) and  $(\bar{1}13)$  planes of monoclinic  $\alpha$  form of iPP in the oriented sample of plain iPP, plotted in stereographic projection. A similar set of pole figures determined for the 8:2 iPP/HOCP oriented blend is presented in Fig. 2. The pole figures for 9:1 iPP/HOCP oriented blend, not presented here, are almost identical to those obtained for the 8:2 blend. For each pole figure the raw experimental data were corrected for background scattering, sample absorption, defocusing and other instrumental effects and then normalized to the random distribution density and plotted in stereographic projection (details are described in ref. [9]). These figures demonstrate that the oriented films show sharp and well developed texture of the (010)[001] type, i.e. the texture in which nearly all crystals are oriented with their (010) planes parallel to the film surface and c axis equivalent to the chain axis oriented along the direction of final elongation, i.e. transverse direction, TD. There is an

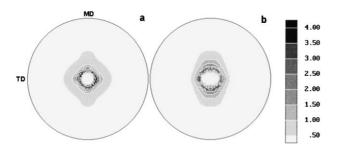


Fig. 3. Two-dimensional SAXS patterns of oriented plain iPP (a) and 8:2 iPP/HOCP blend (b). The machine and transverse direction denoted as MD and TD, respectively.

additional weak (110)[001] component present in the texture. This component is characterized by the clustering of orientation of normals in the pole figures one order of magnitude lower than those for the (010)[001] component. There is no evidence of (100)[001] and {110} twinning components. Therefore, the texture of iPP as well as blend samples may be considered practically as a single-component texture (called also *a quasi-monocrystal* texture).

Fig. 3 presents the two-dimensional small-angle X-ray scattering (SAXS) patterns of oriented iPP and 8:2 blend samples. The patterns do not show the scattering characteristic for a lamellar structure, except for the faint scattering along the direction of the first drawing (machine direction, MD). There is also no scattering characteristic for voids or cracks. Such scattering patterns indicate that the lamellar structure of the iPP and iPP/HOCP films was destroyed almost completely during the second drawing, along TD (although after the first drawing along MD all samples did show a lamellar structure oriented along MD [9]). The lamellae were fragmented into smaller crystalline blocks due to advanced crystal slip without formation of microvoids. Those very small crystals in the deformed films are arranged with no spatial correlation in the directions perpendicular to the chain axis but they are all oriented in the same way, as revealed by pole figures.

From the DSC measurements of the oriented samples their crystallinities were determined [9]. The overall crystallinities are: 51% for plain iPP, 45% for 9:1 blend and 40.5% for 8:2 blend. The decrease of the overall crystallinity reflects only the decrease of the amount of iPP in the blend—the crystallinity calculated for the iPP component is nearly constant for all compositions studied [9]. The amorphous phase present in the samples in quite large quantities is also well oriented due to high strain, with the direction of molecular orientation along TD, similar to the crystalline component [2–4].

The oriented films with a structure described above are well suited for studies of one particular mechanism of plastic deformation of iPP crystals, namely the crystallographic slip in the (100) planes along the chain direction, i.e. (100)[001] chain slip [5,6]. This slip system is one of the most important deformation mechanisms of iPP crystals of the most common monoclinic  $\alpha$ -modification. According to theoretical predictions [11] and experimental studies [9] the easiest slip system in iPP crystals is (010)[001] slip, while (100)[001] and (110)[001] systems should have higher critical resolved shear stress (CRSS). The study of the abovementioned slip system can be made by investigation of the yield behaviour of the specimens deformed in tension with the tensile axis oriented in those specimens at various angles,  $\Theta$ , to the orientation direction (which is equivalent to TD). One can expect that for the certain range of this angle only the (100)[001] slip system will be activated due to proper orientation of crystallites providing high shear stress on the (100) plane in the [001] direction, while other deformation mechanisms will remain inactive

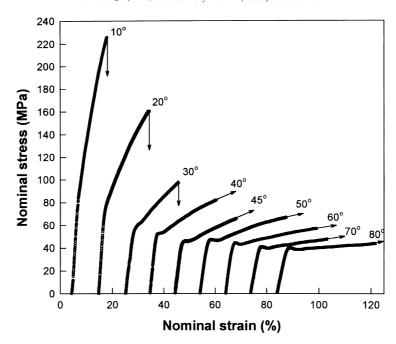


Fig. 4. Nominal stress-strain curves for oriented iPP/HOCP films elongated at various angles (marked on the curves) with respect to the molecular direction. For clarity of presentation the curves are shifted along the strain axis.

due to much smaller resolved shear stresses in appropriate directions [5,6]. Analysis of the yield stress of such samples would give the value of the CRSS of the (100)[001] slip, i.e. the shear stress necessary to activate this slip [2–5]. Similar studies for oriented iPP in tension and compression were performed by Shinozaki and Groves [7], but the samples they used were of uniaxially oriented iPP with a fibre symmetry, so that the critical shear stress they determined,  $\tau_c = 25$  MPa, was an average over several chain slip mechanisms, including the easiest one, (010)[001] chain slip. In the case of our samples with much better defined single component texture one can expect more precise data concerning the single mechanism. The only problem with

the blend samples investigated here could be a relatively high amount of the amorphous component located between crystallites and connected intimately to them by covalent bonds. In an oriented semicrystalline polymer of high crystallinity subjected to the deformation described above the amorphous layers transmit only the stress between crystallites and accommodate their strain. However, when crystallinity is low there are possible deformation paths running entirely through the amorphous phase and bypassing crystallites. The amorphous phase, when in a rubbery state, has lower resistance than the crystalline component, so that the yield stress observed in such samples might be lowered by that

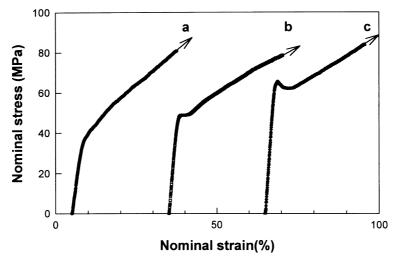


Fig. 5. Nominal stress—strain curves obtained for oriented films of iPP (a), 9:1 iPP/HOCP (b) and 8:2 iPP/HOCP blend (c) tested in tension. The angle between the orientation direction and the tensile axis was 45° for each sample. The curves are shifted along the strain axis for clarity of presentation.

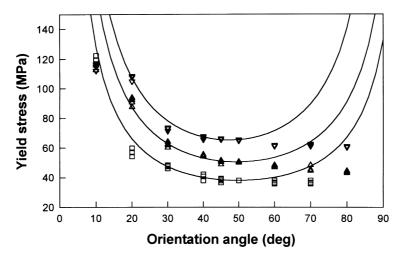


Fig. 6. Dependence of the yield stress on the initial orientation angle  $\Theta_0$  in specimens of iPP ( $\square$ ), 9:1 iPP/HOCP ( $\triangle$ ) and 8:2 iPP/HOCP blend ( $\nabla$ ) deformed in tension. The curves were calculated using Eq. (1), Eq. (3), Eq. (4) and the 'best fit' values of  $\tau_c$  and k.

deformation mode. The situation is complicated when the amorphous component becomes glassy.

A typical set of stress-strain curves (nominal values) obtained in tensile experiments of samples of 9:1 iPP/HOCP blends cut along directions at various angles to the molecular orientation direction, c is shown in Fig. 4. The curves obtained for the 8:2 blend look similar, except for a slightly larger load drop at yield points. In contrast, the stress-strain curves of plain iPP do not show such a load drop at yield for any orientation of tensile axis against molecular orientation direction. In every curve obtained for iPP samples the stress increases continuously with strain, showing only a change of slope near the yield point. The variation of shape of the stress-strain curves with sample composition can be illustrated by the set of representative curves presented in Fig. 5.

Fig. 6 shows the yield stresses of the oriented iPP, 9:1 and

8:2 iPP/HOCP blend specimens calculated from the stress–strain curves. plotted against the initial orientation angle  $\Theta$ , i.e. angle between  $\mathbf{c}$  (equivalent to TD) and tensile axis. These yield data were used to examine the applicability of the Coulomb yield criterion for describing plastic deformation of polypropylene crystals by (100)[001] chain slip. The Coulomb yield criterion has the following form [1]:

$$\tau = \tau_{\rm c} - k\sigma_{\rm n} \tag{1}$$

where  $\tau$  is the shear stress resolved in the shear plane,  $\sigma_n$  is the resolved stress normal to the shear plane,  $\tau_c$  is critical resolved shear stress required to activate the slip system in question in simple shear and k is a constant demonstrating the sensitivity of the shear to the normal stress. If a material obeys the Coulomb yield criterion, the yield condition reduces to a straight line with the slope -k in  $\tau$  vs  $\sigma_n$  coordinates. For uniaxial tension under the applied stress

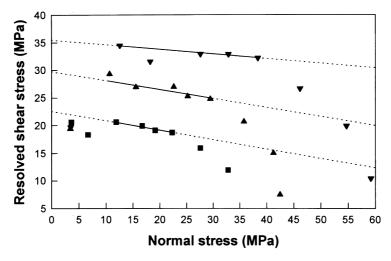


Fig. 7. Normal stress dependence of the resolved shear stress on the (100) plane in the [001] direction for specimens of iPP ( $\blacksquare$ ), 9:1 iPP/HOCP ( $\blacktriangle$ ) and 8:2 iPP/HOCP blend ( $\blacktriangledown$ ). For clarity only the average values of stresses for each sample orientation are plotted. The solid lines indicate the range of data taken for fitting to the Coulomb criterion.

 $\sigma$ , the resolved shear stress is given by:

$$\tau = \sigma \cos \xi \cos \varphi \tag{2}$$

where  $\xi$  is the angle between the normal to slip plane and the loading direction and  $\phi$  is the angle between the slip direction and loading direction.

For the geometry employed here,  $\xi = 90^{\circ} - \Theta$  and  $\varphi = \Theta$ , where  $\Theta$  is the angle between the loading direction and the direction of the chain axis c, hence:

$$\tau = \sigma \sin\theta \cos\theta \tag{3}$$

The normal stress can be expressed similarly as:

$$\sigma_{\rm n} = \sigma \cos \xi \sin = \sigma \sin^2 \theta \tag{4}$$

Using Eq. (3) and Eq. (4) the shear stress and normal stress were calculated from the yield data shown in Fig. 6. The results are presented in Fig. 7; for clarity only the average values of stresses at yield for each sample orientation were plotted.

Fig. 7 shows that it is possible to fit a straight line to the stress data provided that the fit is limited to the range of the orientation angle  $\Theta$  of approximately  $20-50^\circ$  ( $30-60^\circ$  for plain iPP), i.e. the range in which the (100)[001] chain slip is anticipated to be active as a single deformation mechanism. This is highly probable because within this range of  $\Theta$  the shear stress resolved in the [001] direction in (100) planes is relatively high (with a maximum at  $\Theta=45^\circ$ ) while it remains low for any other slip system (see Appendix in ref. [5]).

The best fit values give  $\tau_c = 22.6$  MPa and a normal stress coefficient k = 0.17 for the yield data obtained for samples of plain iPP, whereas for 9:1 and 8:2 blend samples the values of  $\tau_c = 29.7$  MPa, k = 0.16 and  $\tau_c = 35.5$  MPa, k = 0.09, respectively were calculated as the best fit values. The errors involved may be estimated as 0.5 MPa and 0.01 for  $\tau_c$  and k, respectively. It is seen that while the value of normal stress sensitivity coefficient, k does not vary too much with the composition, the value of critical resolved shear stress,  $\tau_c$  increases substantially with increasing content of HOCP in the blend. Such large differences in  $\tau_c$ were not expected, because for all compositions the same (100)[001] slip system was anticipated to be a primary deformation mechanism, so that the values of  $\tau_c$  determined for plain iPP and blend samples should be rather similar. The differences in that parameter found in our studies indicate that HOCP molecularly dispersed in the blend markedly influences the deformation process.

The critical resolved shear stress for a particular slip system is not an absolute material parameter. In terms of the dislocation theory crystallographic slips occur via travel of the system of crystallographic dislocations along the slip plane. The critical resolved shear stress for a crystal depends then on the number of mobile dislocations, their mobility and ease of generation of new mobile dislocations upon deformation. In plasticity of metals several sources of the increase of the yield stress are distinguished [12]: (i) misor-

ientation of crystallites; (ii) lower purity of the crystalline phase; (iii) change of crystal surface conditions; and (iv) change in the number of movable dislocations.

# 3.1. Misorientation of crystallistes

If the crystallites in the material are not oriented perfectly (i.e. there is some distribution of orientation) the deformation can proceed on other than the intended primary slip system in those crystals which are misoriented. This, in turn, can increase stress at the yield point. Fig. 1 and Fig. 2 show that there is some distribution of orientation in the samples studied. The textures of all these samples are, however, almost identical and are sharp and well developed. An increase of the yield stress due to crystal misorientation should, therefore, be relatively low and practically the same for both plain iPP and iPP/HOCP blend oriented samples.

# 3.2. Purity of crystalline phase

The purity of the crystalline phase is known to influence both yield stress and Stage I of strain hardening in metals [12]. For example, the shear stress-shear strain behaviour near yielding of niobium crystals of various purity [13] shows high yield stress and the drop of load after yielding for higher concentration of impurities while for highly pure nobium crystals the yield occurs at low shear stress and no load drop is observed after yielding. If the crystal contains molecular impurities or small inclusions they encourage localized slip on other than the primary slip plane, which usually causes an increase of yield stress and eliminates the first stage of strain hardening. These impurities can also immobilize a part of the dislocations capable of moving through a crystal. The slip process is realized by the movement of numerous dislocations on the slip plane, so their trapping by impurities would impede the slip process. In the case of the iPP/HOCP blend the components are mutually soluble in the molten state. It is highly probable that during fast crystallization at high cooling rates (iPP crystallizes then according to Regime III), as in the present study, a certain number of relative small HOCP molecules can be entrapped within crystals instead of being rejected by growing the crystal front into the amorphous phase. Such molecules will act in the same way as do the impurities in metals, which in turn, should lead to an increase of stress at the yield point. Consequently, the critical resolved shear stress determined in the blends might be higher than that in plain iPP.

# 3.3. Crystal surface

The next source of an increase of  $\tau_c$  with composition could be the change in conditions at crystal surfaces. It was found for metals that when the crystal surfaces were covered with a thin oxide film the initial deformation stages were substantially modified, which manifested in a significant increase of the yield stress and also in the reduction of Stage I hardening [12,14]. This is due to the obstruction for

dislocation movement caused by the layer deposited on the crystal surface. In an extreme case the surface layer can prevent the dislocations from moving completely out of the crystal and their piling-up near the crystal surface. Such locked dislocations constitute a serious obstacle for movement of other dislocations and therefore make the slip process more difficult. As a consequence, an increase of the yield stress was frequently observed. In the case of the iPP crystallites in the iPP/HOCP blend their interfaces with amorphous layers are substantially modified as compared with plain iPP. The HOCP molecules, which were rejected by growing crystallite, tend to concentrate in the amorphous phase near the interfaces. Such layers of higher concentration of HOCP (there are additionally numerous chain loops, cilia, tie molecules and other defects usually present in those layers) can act in a similar way to the oxide film deposited on the surface of metal crystals and cause locking of a large number of dislocations which, of course, would lead to an increase of the yield stress in the blend compared with plain iPP.

## 3.4. Number of movable dislocations

Another possible reason for an increase of the yield stress in the blend is the decrease of the number of movable dislocations in the iPP crystals in the blend samples and is related to the two previously mentioned causes. It was found for metals that when the number of dislocations present in the crystal and able to move across it decreases the yield stress of such crystal increases. Moreover, this modifies also the shape of the stress-strain curve near the yield point. If the number of movable dislocations is high the curve does not exhibit load drop at the yield point. When this number decreases the load drop appears on the curve at the yield point and moreover, becomes more pronounced with a further decrease in the number of free dislocations. The upper yield stress continuously increases at the same time. The load drop results from either unlocking of the existing dislocation or generation of new mobile dislocations, both due to stress build-up. The yield point develops and stress decreases as the mobile dislocations multiply. The polymer crystals are highly imperfect and the number of dislocations is high. Those dislocations present in the crystal prior to deformation are immobilized mostly due to impurities and in some cases due to crystal interfaces. According to the above discussion this can be the case of the studied iPP/ HOCP blend in which iPP crystals are contaminated with HOCP molecules and have interfaces modified by the presence of HOCP chains which most probably cause locking of dislocations. Such a hypothesis may be confirmed by the shapes of the stress-strain curves in plain iPP and in the blend, presented in Fig. 5. Yielding in oriented plain iPP samples is not accompanied by a load drop, but this drop appears in the 9:1 blend and is even more pronounced in 8:2 blend samples. Such evolution of the shape of the stressstrain curves near the yield point strongly suggests that the

number of mobile dislocations present in iPP crystals in the plain iPP sample prior to its deformation is reasonably higher than in the respective crystals in the blend samples. As a result an increase of the yield stress and hence critical resolved shear stress on the slip plane is observed in the samples of the blend.

There is another possible reason for the increase of the yield stress and therefore the critical resolved shear stress in blend samples. In the blend the crystallinity is lower than in plain iPP i.e. the amount of amorphous phase is larger than in plain iPP. The amorphous phase participates in the deformation process together with crystallites. In a semicrystalline polymer of high crystallinity subjected to tensile deformation at angles near 45° to the orientation direction the amorphous layers transmit only the stress between crystallites and accommodate their strain. The lamellar structure in the studied samples was destroyed by the orientation process and the crystallites are arranged in space with no correlation in directions perpendicular to the chain axis. This makes the shear in the amorphous phase similar to interlamellar sliding rather difficult because crystallites constitute serious obstacles for such shear. When the crystallinity of the sample is low, however, there are possible shear deformation paths entirely through the amorphous phase and bypassing crystallites. If the deformation experiment is performed above the glass transition the amorphous component has a lower plastic resistance than the crystalline component, and consequently the yield stress observed in such samples should be depressed by that secondary deformation mode. On the other hand, when glass transition is above the temperature of deformation the amorphous phase become glassy, which makes both the accommodation of the crystalline strain and the shear through the amorphous component more difficult and consequently the yield stress can increase. The glass transition of plain iPP (measured by DMTA at 1 Hz) is  $-3^{\circ}$ C, while in the 9:1 iPP/HOCP blend it is 18°C and in the 8:2 blend 24°C[15]. The deformation experiments were all performed at room temperature (22°C), thus the amorphous phase of deformed blends was in a glass transition region. According to the above discussion this could increase the yield stress in the blend samples as compared with plain iPP in which the amorphous phase was in a rubbery state during the deformation process.

Summarizing, the observed increase of the critical resolved shear stress of the (100)[001] slip system results probably from several phenomena: HOCP molecules entrapped in iPP crystals and other molecules concentrated at the crystal–amorphous interface, which both cause a decrease in the number of mobile dislocations in polypropylene crystallites in the blend and possibly from the increase of the glass transition temperature of the amorphous phase with the increase of HOCP concentration. On the basis of the accessible experimental data it is difficult to evaluate to what proportion they influence the yield behaviour of the blend or whether there are any other phenomena which might influence the yield observed in blend samples.

In any case, the values of  $\tau_c = 22.6 \pm 0.5$  MPa and  $k = 0.17 \pm 0.01$ , obtained for a sample of plain iPP should be considered as close to that characteristic for (100)[001] chain slip in polypropylene crystals, while those determined for the blend samples are influenced by the presence of the second component in the blend.

The value of  $\tau_c = 22.6$  MPa obtained in this study is slightly lower than  $\tau_c = 25$  MPa reported by Shinozaki and Groves [7], but it must be recalled that the sample of oriented iPP they used had a fibre symmetry, so that critical stress they determined cannot be considered as characteristic of a single mechanism. It was rather a weighted average of plastic resistances of several deformation mechanisms, including the easiest (010)[001] slip system, as well as other more difficult mechanisms, characterized by higher plastic resistances.

There are no other data on the plastic resistance of iPP crystallites available in the literature. Theoretical considerations [11] verified by experimental studies [9] indicate that the chain slip of the (010)[001] system should have significantly lower plastic resistance than (100)[001] or any other slip system. Sadowski et al. [16] measured the shear strength of heavily rolled iPP sheets along the plane parallel to the sheet surface, which in highly textured rolled iPP coincide with the (010) crystal plane. The primary deformation mechanism active during the deformation experiments was most probably the (010)[001] chain slip. They obtained values of a shear strength near 10 MPa, thus the yield stress (not reported) had to be lower. In the shear geometry they used the yield stress is simply equal to the plastic resistance,  $\tau_c$  of the (010)[001] slip. Thus,  $\tau_c$  of this slip system may be expected to be slightly lower than 10 MPa.

# 4. Conclusions

The results presented in this paper demonstrate that in the tensile deformation experiments of highly textured iPP films with a sharp nearly single-component texture it is possible to activate a single deformation mechanism, provided the angle between orientation direction and the tensile axis is not far from 45°. In this range of orientation angles the dependence of shear stress resolved in the expected shear plane and direction on the resolved normal stress is a straight line, which indicates that a single deformation mechanism operated at such conditions. This expected mechanism was (100)[001] crystallographic slip, operating along chain direction. The plastic resistance determined from the yield data,  $\tau_c = 22.6$  MPa. This slip appears to be sensitive to the stress normal to the slip plane with a coefficient k = 0.17, which is similar to the behaviour

found in the studies of slip systems in linear PE [5]. Measurements of the plastic resistance of the same slip system in samples of the iPP/HOCP give higher values of  $\tau_c$ , dependent on blend composition. The increase of plastic resistance in blend is probably the result of a decrease of the number of mobile dislocations in the crystallites due to the presence of HOCP molecules at the interfaces between crystalline and amorphous phases and due to those HOCP molecules entrapped within crystallites and constituting crystal impurities, which can lock dislocations. The second possible explanation of the observed increase of plastic resistance could be an increase of the glass transition temperature in the blend, so that during deformation at room temperature the amorphous phase in plain iPP remains rubbery, while it becomes glassy in the blend samples. This change of the properties of the amorphous phase can substantially influence the yield stress observed in the iPP/HOCP oriented blend.

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## References

- Ward IM, Hadley DW. An introduction to the mechanical properties of solid polymers. New York: Wiley, 1993.
- [2] Bowden PB, Young RJ. J Mater Sci 1974;9:2034.
- [3] Haudin JM. In: Escaig B, G'Sell C. Plastic deformation of amorphous and semi-crystalline materials. Paris: Les Editions de Physique, 1982, p. 291.
- [4] Lin L, Argon AS. J Mater Sci 1994;29:294.
- [5] Bartczak Z, Argon AS, Cohen RE. Macromolecules 1992;25:5036.
- [6] Lee BJ, Argon AS, Parks DM, Ahzi S, Bartczak Z. Polymer 1993;34:3555.
- [7] Shinozaki D, Groves GW. J Mater Sci 1973;8:71.
- [8] Cadell RM, Raghava RS, Atkins AG. J Mater Sci 1973;8:1641.
- [9] Bartczak Z, Martuscelli E. Polymer 1997;38:4139.
- [10] Cimmino S, Di Pace E, Karasz FE, Martuscelli E, Silvestre C. Polymer 1993;34:72.
- [11] Aboulfaraj M, G'Sell C, Ulrich B, Dahoun A. Polymer 1995;36:731.
- [12] Honeycombe RWK. The plastic deformation of metals. London: Edward Arnold, 1968
- [13] Mitchell TE, Foxall RA, Hirsch PB. Phil Mag 1963;8:1895.
- [14] Andrade EN da C, Henderson C. Phil Trans R Soc 1951;A244:177.
- [15] Cecere A, Greco R, Taglialatela A. Polymer 1992;33:1411.
- [16] Sadowski MM, North TH, Weatherly GC. J Mater Sci Lett 1991;10:1007.