Plastic Behavior of Monoclinic Polypropylene under Hydrostatic Pressure in Compressive Testing

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ABSTRACT: The plastic deformation of monoclinic isotactic polypropylene is studied in compressive testing with particular attention to the effect of hydrostatic pressure up to 300 MPa, in the temperature range $20-60^{\circ}$ C. The coefficients of the Coulomb criterion are fairly consistent with those assessed from the comparison of the tensile and compressive yield stresses at atmospheric pressure, in the same temperature range. The high friction coefficient of polypropylene is ascribed to a strain-induced order-to-disorder transition from the monoclinic to the smectic form accompanied by an increase of specific volume. This local and transient phase change is assumed to result from the mobile conformational chain defects that govern the elementary mechanism of plasticity in the crystalline phase of polypropylene that displays a much lower friction coefficient. The dislocation-based approach that is proposed in relation to the viscoelastic relaxation processes provides a new insight into the molecular grounds of the elementary mechanism of plasticity of polypropylene. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1241–1247, 1999

Key words: polypropylene; plasticity criterion; pressure effect; dislocations; molecular mobility; monoclinic form; smectic form

INTRODUCTION

Most of the techniques for processing thermoplastic polymers in the solid state such as stamping, forging, rolling, die-drawing, etc., involve hydrostatic pressure effects. The determination of the constitutive equation of plastic flow that is a necessary stage toward the modeling of these solid state-forming processes needs an adequate pressure sensitivity evaluation. Besides, parts processed by solid state forming under pressure have

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Journal of Applied Polymer Science, Vol. 72, 1241–1247 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/101241-07 improved mechanical properties compared to parts processed without pressure. The understanding of the basic grounds of this phenomenon also deserves a good characterization of the pressure sensitivity to assess its effect on the deformation processes.

Several studies have been carried out to establish a constitutive equation for the plastic flow of polypropylene,¹⁻⁴ but they generally lack from an appropriate knowledge of the pressure effect. In another connection, quantitative data on the yield behavior of a wide variety of polymers have shown a very strong pressure sensitivity compared to metals, for glassy materials⁵⁻⁸ as well as for semicrystalline materials above the glass transition temperature.⁸⁻¹¹

Our goal is to investigate the incidence of hydrostatic pressure on the plastic deformation of

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isotactic polypropylene to gain additional informations on the elementary mechanisms of plasticity in comparison with the mechanical studies of uniaxial drawing, simple shear, and compression at normal pressure.

EXPERIMENTAL

The polypropylene (PP) supplied by ATOCHEM had a tacticity index of 98% and a weight-average molar weight $M_w = 260,000$. For the tensile experiments, sheets about 3 mm thick have been compression molded at 230°C and cooled down to room temperature at about 5°C/min. Dumbbellshaped specimens with 60 mm and 15 mm in gauge length and width, respectively, were cut from the sheets by means of a cutting die. Cylinders for compressive experiments have been molded under vacuum into quartz tubes of diameter 6 mm, following the same heating and cooling procedure as above. Samples 15 mm long were cut from the cylinders, particular attention being taken for making the basal surfaces well parallel. The weight fraction crystallinity of the molded pieces was $X_c = 0.60 \pm 0.02$ from the melting enthalpy measurements, taking 165 J/g for the enthalpy of melting of a perfect isotactic PP crystal.¹²

The deformation tests were conducted on an Instron testing machine provided with tensile and compressive load cells. The initial strain rate for the two kinds of experiments was $\dot{\varepsilon} = 10^{-3}$ s⁻¹. An air-pulsed oven was used for the temperature regulation of the tensile experiments. The compressive deformation vessel was provided with a heating collar connected to a temperatureregulating system. In both cases the maximum deviation of the measured temperature was $\pm 1^{\circ}$ C. The hydrostatic pressure of the oil-confining medium was directly measured from the pressure-delivering device. The compressive stress data were derived from the compressive load measurements after correction for the friction force between the compression piston and the tightening rings of the deformation vessel that was assessed from a blank experiment. The accuracy of the yield stress data is about 3 and 10% for measurements at atmospheric pressure or under confining pressure, respectively. The experiments were carried out at 20, 40, and 60°C, i.e., above the glass transition that takes place at about 10°C, as judged from the β relaxation peak of the loss factor curve at 1 Hz.¹³ Neither changes of

Table I Compressive Yield Stress, σ_{YC} , and Tensile Yield Stress, σ_{YT} , at Atmospheric Pressure^a

	20°C	40°C	60°C
$\sigma_{\rm YC}^{\circ}$ (MPa) $\sigma_{\rm YT}^{\circ}$ (MPa)	50 33	$\frac{34}{24}$	$\begin{array}{c} 22\\17\end{array}$

^a Every data is an average of three measurements.

crystallinity nor aging effects are expected to occur in the samples during the maintain at the test temperature due to the large gap to the α crystalline relaxation in the range 70–110°C.¹³

RESULTS

Compressive and Tensile Testing at Atmospheric Pressure

The yield stress data in compressive and tensile loading, $\sigma_{\rm YC}^{\circ}$ and $\sigma_{\rm YT}^{\circ}$, respectively, at atmospheric pressure and various temperatures are collected in Table I. The tensile data for the bulk PP material crystallized by slow cooling from the melt are somewhat greater than those reported elsewhere¹³ for thin PP films annealed at 140°C from the guenched state, at the same strain rate. This is probably due to an improved perfectness in the crystalline structure of the present material due to the crystallization procedure from the melt, as revealed, for instance, by the slightly higher crystal weight fraction. The yield stress data of Table I indicate quite a large difference between the two kinds of experiments, at any temperature. Similar findings have been reported by Duckett and Zihlif¹⁴ at room temperature, but with a lesser departure notably because of a lower value of the compressive yield stress compared to ours. In the framework of slip-governed plasticity of solids, the difference between $\sigma_{\rm YC}^{\circ}$ and $\sigma_{\rm YT}^{\circ}$ is relevant to a strong effect of the normal stress component. This effect is accounted for by the following Coulomb criterion of plasticity

$$au > au^\circ - \mu \sigma_n$$

where τ and σ_n are the resolved shear stress and the normal stress operating on the slip interface, respectively, τ° is the critical shear stress for the onset of the slip process and μ is the friction coefficient. The two parameters of the Coulomb

	20°C	40°C	60°C
$ au^{\circ}$ (MPa) μ	$\begin{array}{rrr} 20.3 \pm & 0.6 \\ 0.21 \pm 0.02 \end{array}$	$\begin{array}{rrr} 14.3 \pm & 0.4 \\ 0.17 \pm 0.01 \end{array}$	$\begin{array}{rrr} 9.7 \pm & 0.3 \\ 0.12 \pm 0.01 \end{array}$

Table II Critical Shear Stress, τ° , and Friction Coefficient, μ , Derived from eqs. (2) and (3)

criterion can be computed from the following relations derived by Escaig^{15}

$$\tau^{\circ} = 0.5 (\sigma_{YC}^{\circ} \sigma_{YT}^{\circ})^{1/2} \tag{2}$$

$$\mu = \frac{\sigma_{YC}^{\circ} - \sigma_{YT}^{\circ}}{2(\sigma_{YC}^{\circ}\sigma_{YT}^{\circ})^{1/2}}$$
(3)

The data reported in Table II display unusually high value of μ at 20°C and strong dependence of both μ and τ° on temperature.

Compressive Yield Behavior under Pressure

Figure 1 shows the compressive yield stress vs. pressure, for three temperatures. The strong dependence of $\sigma_{\rm YC}$ with pressure is consistent with the above conclusion of a strong normal stress effect on the slip process. From the Coulomb criterion, a linear pressure dependence of the effective axial stress at the point yield, $\sigma_{\rm YC} + P$, can be conviniently expressed into the form¹⁵

$$\sigma_{YC} + P = \sigma_{YC}^{\circ} + P \frac{\sigma_{YC}^{\circ}}{\sigma_{YT}^{\circ}}$$
(4)

where *P* is the applied hydrostatic pressure. Using the data of Table I, the theoretical variations of $\sigma_{\rm YC}$ + *P* vs. *P* computed from eq. (4) have been plotted in Figure 2, together with the experimental data, for the three temperatures. The predicted straight line is in excellent agreement with the experimental data, for every temperature, indicating that the Coulomb criterion accounts very well for the normal stress contribution to the slip process in the present case of PP. This agreement also means that atmospheric pressure measurements of tensile and compressive yield stresses provide an accurate prediction of the high-pressure plastic behavior of PP, as previously reported for thermosetting polyesters.¹⁵ It is worth mentioning that the modified Tresca and von Mises criteria involving a pressure dependence give overestimations of the $\sigma_{
m YC}$ compared to the

Coulomb criteria based on a normal stress dependence.¹⁶

DISCUSSION

Yield Criterion and Pressure Effect

It is well known that brittle polymers benefit from an improved plastic behavior under pressure, i.e., increase of yield stress, yield strain, and breaking strain.⁵ Ductile polymers also gain increased yield stress under pressure, but in contrast, they display reduced strain at break.^{6,9} Dealing with the first polymer species, the embrittlement phenomenon of crazing involves a positive volume strain that is gradually hindered by the increase of pressure, thus preventing void opening. A brittle-to-ductile transition occurs with increasing pressure, as for polystyrene, for instance.⁵ Re-



Figure 1 Compressive yield stress, $\sigma_{\rm YC}$, vs. hydrostatic pressure, P (every data is a single test measurement).



Figure 2 Plot of axial stress at yield, $\sigma_{\rm YC}$ + P, vs. hydrostatic pressure, P (the straight lines are predicted from eq. (4) using the data of Table I).

garding ductile polymers, which have high propensity for shear banding, the chains may suffer from a reduced mobility with increasing pressure, in both the crystalline and the amorphous phases. As a matter of fact, the melting point and the glass transition temperature increase with pressure is indicative of enhanced molecular interactions in the two phases.^{12,17}

Bowden¹⁸ has discussed the usefulness of plasticity criteria based on either pressure dependence or normal stress dependence, the former one being more appropriate to account for free volume modifications, in contrast to dilatation effects associated with molecular slip. In the instance of a pressure dependence of the plastic flow, the slip direction should follow the maximum resolved shear stress at $\beta = 45^{\circ}$ from the applied stress direction, irrespective of the pressure level. But in the case of the Coulomb criterion [eq. (1)], the friction coefficient obeys the following relation

$$\mu = -\cot 2\beta \tag{5}$$

which means that slip direction departs from the above ideal value. In this connection, worth noticing is Li and Wu's¹⁹ work on polystyrene showing coarse and fine slip bands under both compressive and tensile deformation modes. Coarse bands were inclined at more than 45° with the tension axis or less than 45° with the compression axis and invariably led to fracture. Fine bands appeared at 45° and contributed largely to the plastic strain. This is relevant to the occurrence of two slip processes with and without a normal stress dependence on the yield stress in the same material.

The image of a PP sheet sample drawn at 20°C that is reported in Figure 3 shows clear cut shear bands with $\beta \approx 50 \pm 2^{\circ}$. This finding perfectly supports the Coulomb criterion. Moreover, the β value is in good agreement with the friction coefficient data reported at room temperature (Table II).

The much stronger pressure sensitivity of the yield stress of ductile semicrystalline polymers compared to metals can be easily understood considering the nature of the intermolecular interactions, which is of the van der Waals type, i.e., very weak, and owing to their low density that allows some compressibility. However, the much different pressure sensitivity of polymers having similar kinds of molecular interactions, such as polyethylene (PE) and polypropylene, is quite puzzling. The yield stress dependence on pressure is notably twice as large for PP than for PE at room temperature, i.e., $\mu \approx 0.10$ for PE and $\mu \approx 0.20$ for



Figure 3 Scanner image of the incipient neck of a PP sheet drawn up to the yield point: $T = 20^{\circ}$ C ($\dot{\varepsilon} = 10^{-3}$ s⁻¹).

PP in both cases of compressive and tensile deformation modes (see refs. 9 and 10 for tension and ref. 20 together with Table I for compression).

Molecular Grounds of the Plastic Flow in PP

Table II reports the two characteristic parameters of the yield criterion of eq. (1), i.e., τ° and μ , that have been computed from the $\sigma_{\rm YC}$ and $\sigma_{\rm YT}$ data of Table I using eqs. (2) and (3). The drop of τ° by about $\frac{1}{2}$ between 20° and 60°C results from reduction of intermolecular elastic interactions.²¹ As a matter of fact, a similar drop of storage modulus¹³ as well as shear modulus²² occurs in the same range of temperature. This is the domain of the crystalline mechanical relaxation, i.e., the temperature range of thermal activation of chain mobility in the crystal that entails a loss of mechanical stiffness. Considering that the amorphous phase is rubbery above 0°C, this finding emphasizes the major contribution of the crystalline phase in the slip process.

The friction coefficient also drops by a factor $\frac{1}{2}$ in the same temperature range (Table II). This can be ascribed to the high thermal expansion coefficient in the α relaxation temperature domain, as has been reported for a number of semicrystalline polymers.²³ This results in a quick increase of the intermolecular spacing and reduces the molecular friction in the crystalline phase. An amorphous phase contribution may be also involved due to free volume changes under pressure, as suggested by Duckett and Joseph.²⁴ But one should expect a pressure dependence from this contribution rather than a normal stress dependence, in the temperature range 20–60°C.

Notwithstanding, the unusually large value of the friction coefficient at 20°C is relevant to a strong dilatation effect associated with the plastic process itself.

In a dislocation-based approach of the plastic flow of PE, we have proposed a mechanism of 180° chain twist to account for the thermally activated nucleation and propagation of screw dislocations through the crystalline lamellae.²⁵ The leading idea was that such a conformational defect involves a local c/2 compressive strain, which can move along the crystalline chain stem, resulting in a c/2 translation of this stem. The dislocation line, which lies along the chain stem, sweeps a dense crystallographic plane in the direction normal to the chain axis by nucleation and propagation of new conformational defects in the neighbor



Figure 4 Sketch of the dislocation-based crystal slip: (a) nucleation, (b) propagation, and (c) exit from the crystal of a screw dislocation.

stems. This process results in an overall slip of the crystal with an elementary step of c/2 on the crystal folding surface, as depicted in Figure 4. The twist defect is precisely the process that has been proposed for the α mechanical relaxation in PE crystals and for the crystal thickening during annealing. It is a fundamental link between viscoelasticity and plasticity.

Regarding PP, little is known on the molecular grounds of the crystalline mechanical relaxation. Three-fold rotational jump combined with a c/3 translation in the 3/1 helix is the shortest and less energy-consuming pathway for a chain to move between two consecutive crystallographic positions. However, the conformational defect that is able to provide such a jump is still unknown. Borrowing from Boyd's review 26 on molecular relaxation processes in crystalline polymers, we recently proposed a mechanism of worm-like motion of the chains through the crystal thickness owing to mobile conformational defects.¹³ The suggested chain motion results from a compressive strain that builds up in the chains of a crystallographic plane bearing a resolved shear stress close to the critical value for crystal slip. The compressive strain is accommodated by a thermally activated conformational defect that locally reduces the pitch of the 3/1 PP helix, and that propagates along the chain axis under the effect of the stress field as sketched in Figure 5. The worm-like motion of the compressive conformational defect in the chain allows its translation through the crystal thickness.

Such a mechanism is suspected to be accompanied by a permanent or transient structural disordering of the crystalline phase, due to the large distance required by the chain to turn back into a crystallographic register after recovery of the sta-



Figure 5 Schematic model of a compressive strain in a helix chain propagating in a worm-like motion along the chain.

ble helical conformation. Indeed, at temperatures lower than 70°C, i.e., below the peak temperature of the α relaxation, the low conformational mobility in the crystal stems may lead to an accumulation of such plasticity defects as the plastic strain increases. The chain may then benefit from a metastable settlement into the potential energy wells of the smectic phase, which consists of a regular stacking of parallel chains with little lateral ordering. We actually did not observe significant amounts of the smectic phase at the yield point, either by thermal analysis or by X-ray diffraction. Notwithstanding, our assumption is supported by Saraf et al.^{27,28} who showed the straininduced transformation into the smectic form of monoclinic PP in plane strain compression, as well as Nakamura et al.²⁹ in the case of solidstate extrusion. This phase transformation has been, however, reported by Osawa and Porter to permanently occur for compression ratios CR > 1, i.e., far beyond the yield point, for unloaded samples.³⁰ The former authors have put forward an attractive interpretation for the order-disorder transition on the basis of improved ductility. This proposal allows us to strongly suspect that the first features of strain-induced phase change occur at the threshold of the plastic flow in undetectable amounts of frozen-in dislocation defects,³¹ or as transient local phenomena.³²

In addition to bringing improved ductility, such a phase change involves a dilatation effect, due to the lower density of the smectic phase, which makes the plastic deformation very sensitive to the normal stress on the slip plane. According to the model for the thermal activation of plasticity in glassy polymers under pressure proposed by Escaig,¹⁵ the above mechanism is anal-

ogous to the glide of a Somigliana dislocation having a Burgers vector component out of the slip plane. The latter component works against the normal stress, and the ratio of the normal component to the parallel component of the Burgers vector equals the friction coefficient of the Coulomb criterion. In the present instance of PP, the transverse expansion effect of the smectic-like defects moving in the slip plane acts as a normal component to the slip process. It thus provides an explanation to the unusually large value of the PP friction coefficient at 20°C, notably in comparison with PE. In this connection, it is to be mentioned that PE may undergo a strain-induced transformation of the stable orthorhombic form into the monoclinic form. However, this phenomenon is a martensitic-like transition that is not dislocation governed, but relies on a coherent shear. Besides, the two phases have very close specific volumes so that little pressure effect results from the phase change.

CONCLUSION

The large difference between the compressive and tensile yield stresses of isotactic polypropylene reveals a strong sensitivity of the slip process to the normal stress component. Compressive deformation under hydrostatic pressure corroborates this strong dependency that argues in favor of a Coulomb plasticity criterion.

A molecular model based on a worm-like motion of the chain stems in the crystal occurring due to the migration of a mobile conformational defect is proposed to account for the plasticity of polypropylene through the thermal activation of screw dislocations. The dilatation effect of such defects and the partial phase transformation of the stable monoclinic form into the less dense smectic form is responsible for the stronger pressure sensitivity of PP compared to PE.

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