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Fracture of polypropylene 1. The effect of molecular weight and temperature at low and high test speed

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The fracture behaviour of polypropylene was studied as a function of the molecular weight and the temperature. The molecular weight (M_w) ranged from 164 to 657 kg/mol. The fracture behaviour was studied by the notched Izod impact test and by a tensile test on notched Izod bars at low (1 mm/s) and high (1 m/s) test speed. The process of strong energy absorption during crack propagation, referred to as ductile deformation, is associated with the formation of shearlips. At 1 mm/s, the ductile deformation is initiated by necking during crack initiation; at 1 m/s ductile deformation precedes necking. The brittle/ductile transition temperature (T_{bd}) decreases with increasing molecular weight. The T_{bd}–molecular weight curve shifts by about 40°C towards higher temperatures if the test speed is increased from 1 mm/s to 1 m/s. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Above its glass transition temperature (about 10°C) polypropylene exhibits ductile behaviour, and cold drawing (necking) is observed at room temperature[1]. Like most polymers polypropylene is notch sensitive. Under impact conditions, un-notched polypropylene features a clear brittle/ductile transition between 0 and 20°C[2], whereas notched polypropylene is characterised by a brittle/ductile transition temperature of about 100°C[3].

The brittle/ductile transition of polymers is described by the Ludwik–Davidenkov–Orowan criterion[4]. This criterion states that the fracture type changes from brittle to ductile if the yield stress drops below the fracture stress. With increasing temperature or decreasing test speed, the yield stress decreases more rapidly than does the fracture stress; consequently, the fracture type changes from brittle to ductile[4].

The effect of the test speed, however, is probably more complicated since, with increasing test speed, the plastic deformation process may change from isothermal to adiabatic. Adiabatic plastic deformation at the crack tip leads to a localised temperature rise. Infrared thermography[5] was used to study the temperature rise during fracture of pure polypropylene and PP–EPDM blends as a function of test speed (10^{-4}–10 m/s). A significant temperature rise was measured during crack initiation and during crack propagation. The temperature rise increases almost linearly with the logarithm of the test speed.

The effect of the temperature and the test speed on the fracture behaviour of polymers can easily be studied by carrying out a tensile test on notched specimens. A high-speed tensile machine offers test speeds ranging from typical test speeds of simple tensile tests to test speeds applied during impact tests. If notched Izod specimens are used, the tensile test may be compared to the frequently used Izod impact test.

In the present paper the effect of the molecular weight and the temperature on the fracture behaviour of polypropylene homopolymer is studied at low (1 mm/s) and high test speed (1 m/s). The fracture behaviour is determined by a tensile test on notched Izod specimen. Special attention was paid to the brittle/ductile transition.

EXPERIMENTAL

Materials

A series of commercially available polypropylene homopolymers (Vestolen P grades) with a range of molecular weights were kindly supplied by Vestolen GmbH. *Table 1* lists the molecular weight characteristics of the polypropylene series. It should be noted that the molecular weight distribution (M_w/M_n) of P9000 is wider than that of the other materials.

Specimen preparation

Rectangular bars and dumbbell-shaped specimens were injection moulded on a 221-55-250 Arburg Allrounder. The barrel temperature and the screw speed were 230°C and 200 rpm, respectively. The mould temperature was 40°C.

Table 1 Molecular weight characteristics of the polypropylenes

Grade	MFI[a] (dg/min)	M_w^b (g/mol)	M_v^b (g/mol)	M_n^b (g/mol)	M_w/M_n (—)
P9000	0.3	657 000	556 000	77 800	8.4
P8000	1.1	427 000		82 000	5.2
P7000	2.4	362 000	313 000	63 300	5.7
P6000	5.5	316 000	274 000	52 800	6.0
P2000	37.5	164 000	141 000	34 700	4.7

[a] 230°C, 21.6 N; data sheet Vestolen (11.94)
[b] Private communication, Vestolen GmbH

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The geometry of the rectangular bars (74×10×4 mm) corresponds to the ISO 180/1A specifications, and that of the dumbbell-shaped specimen (10×3×115 mm) corresponds to the ISO R527-1 specifications. A single-edge 45° V-shaped notch (tip radius 0.25 mm, depth 2 mm) was milled in the bars. The bars were prepared in three batches. One batch was used for the notched Izod impact test (3.4 m/s) (batch 1), one for the SEN tensile test at 1 mm/s (batch 2), and one for the SEN tensile test at 1 m/s (batch 3). These batches differ in terms of injection moulding time. The injection moulding time of batches 2 and 3 were similar and considerably exceed the injection moulding time (cooling time) of batch 1. Longer cooling gives less deformed samples on demoulding. The data should not be affected by the longer cooling cycle.

D.s.c.

Differential scanning calorimetry (d.s.c.) was carried out on a Perkin-Elmer DSC 7. Samples (about 10 mg) were taken from the core of dumbbell-shaped specimens. Scans were recorded at a heating rate of 20°C/min. The melting temperature was defined as the peak temperature. The peak area was taken as the melting enthalpy. Measurement were performed in twice.

Spherulite size

Samples for the spherulite size determination were taken from the core of the bars used for the Izod impact test. Thin sections (about 2.5 μm) were microtomed at room temperature with a diamond knife and were studied under a polarised light microscope equipped with a photo camera. The spherulite size was determined manually from the photos using a graphic tablet.

Tensile test

Tensile tests were carried out on the dumbbell-shaped specimens. The tensile test used to compare the tensile properties of the different polypropylenes was carried out on an Instron tensile machine (50 mm/min). The force was measured by a load cell (500 kg) and recorded by a computer. The clamp displacement was calculated by multiplying the test time with the clamp speed.

The tensile test at various temperatures was carried out on a Schenck VHS servo-hydraulic tensile machine. This apparatus is especially designed for high-speed testing, clamp speeds ranging from 10^{-5} to 12 m/s. A pick-up unit is used to allow the piston to reach the desired test speed before loading the specimen. All moving parts are made of titanium in order to diminish inertia effects. The contact between the pick-up unit and the lower clamp is damped by a rubber damping pad. The force is measured using a piezo-electric force transducer located between the upper clamp and the cross head. Force and piston displacement are recorded using a transient recorder (sample rate 2 MHz). After completion of the test, the results are sent to a computer. The tensile machine was equipped with a temperature chamber. The temperature chamber is heated or cooled by a cooled nitrogen stream which passes a heating unit. The heating unit is driven by a Eurotherm controller. A thermocouple inside the chamber registers the temperature. Calibration was carried out using a specimen with an embedded thermocouple. The clamp displacement was assumed to equal the piston displacement.

The strain in the gauge section of the dumbbell was calculated by dividing the clamp displacement by the initial length. The initial length was calculated to be 100 mm, assuming unidirectional stress in the dumbbell. The stress was calculated by dividing the force by the initial cross-sectional area of the gauge section (30 mm^2). The modulus was determined at the initial linear part of the stress–strain curves. The yield stress was defined as the first maximum in the stress–strain curves. All tests were performed five times.

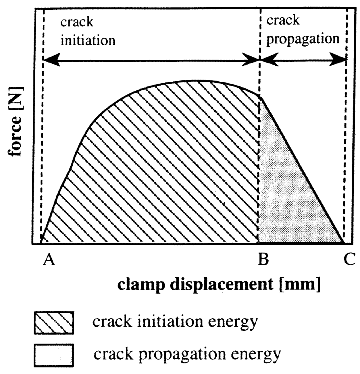

Figure 1 Schematic representation of the force–displacement curve obtained by an SEN tensile test

SEN tensile test

The fracture behaviour was studied by a tensile test on the notched bars, referred to as a single-edge notch (SEN) tensile test. These tests were carried out on a Schenck servo-hydraulic tensile machine described in detail in the previous section. *Figure 1* shows schematically a force displacement curve obtained by this test. The samples tested at high test speeds often show a discontinuity in the stress–strain curve before the maximum stress is reached. The origins of this discontinuity are thought to be a dynamic effect of the SEN-test at these high test speeds.

The fracture process (A → C, *Figure 1*) may be divided into a crack-initiation stage (A → B, *Figure 1*) and a crack propagation stage (B → C, *Figure 1*). Crack propagation is assumed to start at or just past the maximum stress. In the brittle samples the materials fracture at or just past the maximum stress. In the neighbourhood of the brittle/ductile transition the maximum stress for the ductile and the brittle fracturing samples is about the same. The following parameters are used to describe the fracture process:

Maximum stress:	force maximum on the force displacement curve, divided by the cross-sectional area behind the notch (32 mm^2)
Crack initiation displacement (CID):	difference in clamp displacement between points B and A on the force displacement curve (*Figure 1*)
Crack initiation energy (CIE):	difference in supplied energy between points B and A, as shown in *Figure 1*
Crack propagation displacement (CPI):	difference in clamp displacement between points C and B on the force displacement curve (*Figure 1*)
Crack propagation energy (CPE):	difference in supplied energy between points C and B, as shown in *Figure 1*
Fracture displacement:	total displacement
Fracture energy:	total energy

The clamp displacement was assumed to equal the piston displacement. The stress was calculated by dividing the force by the initial cross-sectional area behind the notch (~32 mm^2). The supplied energy was calculated by integrating the force displacement curve. The clamp distance was 45 mm. All measurements were done five times.

Notched Izod impact test

Notched Izod impact tests were carried out using a Zwick

Table 2 D.s.c. results at the first heating stage for the polypropylenes

Grade	$T_{m,1}$ (°C)	$\Delta H_{m,1}$ (J/g)
P9000	167	90
P8000	169	91
P6000	167	92
P2000	168	96

Table 3 Tensile modulus and tensile yield stress at 5 mm/min for the polypropylenes

Grade	*E* modulus (MPa)	Yield stress (MPa)
P9000	1095	39.5
P8000	903	32.4
P6000	925	33.8
P2000	1005	32.7

pendulum equipped with a 4 J hammer. To vary the test temperature, the specimens were placed in a thermostatic bath. A temperature calibration curve was obtained at the testing time as a function of the thermostatic bath temperature. The impact strength was calculated by dividing the absorbed energy by the initial cross-sectional area behind the notch (~32 mm^2). All measurements were performed five times.

RESULTS AND DISCUSSION

Materials

The spherulite size of all the tested polypropylenes is almost identical and equals 40 ± 3 μm (weight average size). The melting temperature and the melting enthalpy were determined by d.s.c. at 20°C/min. *Table 2* lists the melting temperature and melting enthalpy at the first heating stage. The melting temperature of all tested polypropylenes is almost equal. The melt enthalpy slightly increases with decreasing molecular weight. At a heat of fusion of 207 J/g for 100% crystalline polypropylene[6], the crystallinity of the tested polypropylenes is about 45 wt.%.

Tensile test

Table 3 lists the tensile modulus and the tensile yield stress at 5 mm/min. The P9000 has the highest modulus and yield stress despite showing the lowest crystallinity. This discrepancy may be due to the orientation in the dumbbell-shaped specimens caused by the injection moulding process. In this case the highest orientation is encountered in the P9000 specimens.

The values shown in *Table 3* represent the tensile properties of the bars used for the SEN tensile test at 1 m/s, since these bars were injection moulded under the same conditions as the dumbbell-shaped specimens. The bars used for the SEN tensile test at 1 mm/s and for the notched Izod impact test were injection moulded under different conditions than the dumbbell-shaped specimen, so that their tensile properties may differ from those shown in *Table 3*.

The tensile modulus and the tensile yield stress of P7000 as a function of the temperature were determined at 50 mm/min; the results are shown in *Figure 2*.

SEN tensile test

The fracture behaviour was studied at low test speed (1 mm/s) and at high test speed (1 m/s) by carrying out a tensile test on notched specimens (SEN tensile test). The specimens were injection moulded. The notch may either be milled or injection moulded. The material properties at the tip of injection-moulded notches may differ from the material properties in the bulk of the specimen, due to the difference in morphology between core and the skin of injection-moulded specimens[7]. The notch was therefore milled in the material.

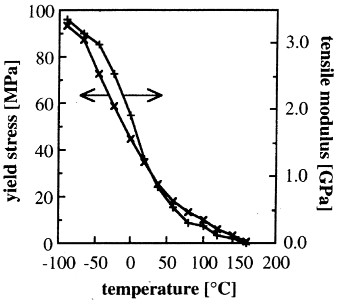

Figure 2 The tensile yield stress (×) and tensile modulus (+) of P7000 *versus* the temperature at 50 mm/min

In order to interpret the SEN tensile test results correctly, the stress, the stress state and the strain rate in front of the notch tip and in front of the tip of a running crack (referred to as crack tip in the sequel) are analysed:

Stress concentration factor. The stress concentration at the notch tip can be calculated using the equation describing the stress at the equator of an elliptical inclusion in a loaded body[8]:

$$\sigma_c = \sigma_\infty \left(1 + 2\sqrt{\frac{a}{\rho}}\right) \quad (1)$$

where, σ_c is the local stress at the equator of the elliptical inclusion, σ_∞ the applied remote stress, $2a$ the length of the inclusion and ρ the radius of curvature of the inclusion at the equator. In a notched Izod specimen, the notch length (a) is 2 mm and the notch tip radius (ρ) equals 0.25 mm. Using equation (1) this gives a stress concentration of 6.6 at the notch tip. This analysis is restricted to elastic deformation. in the case of plastic deformation at the notch tip blunting, of the notch tip occurs, reducing the stress concentration.

The tip radius of the crack is unknown, but the crack tip radius is expected to be considerably smaller than the notch tip radius. The stress concentration at the crack tip is therefore considerably higher than at the notch tip.

Strain rate. In the case of linear elastic deformation, the strain rate at the notch tip and at the crack tip equals the applied strain rate multiplied by the stress concentration factor. In the case of plastic deformation, the relation between the applied strain rate and the strain rate at the notch and the crack tip is much more complicated, due to blunting of the notch tip and the crack tip and due to the fact that plastic deformation may be inhomogeneous.

Stress state. To obtain plane strain conditions the ASTM E399 norm requires that the specimen should be thicker than 2.5 $(K_{Ic}/\sigma_y)^2$. The K_{Ic} for polypropylene equals approximately 3 MPa[9], the thickness of the Izod specimen is 4 mm, which means that the yield stress (σ_y) had to exceed 120 MPa to afford plane strain conditions. The yield stress of polypropylene as a function of the temperature at 50 mm/min (strain rate 0.0083 s^{-1}) is shown in *Figure 2*. The yield stress of polypropylene as a function of the test speed is given elsewhere[5]. Comparison of the effect of the

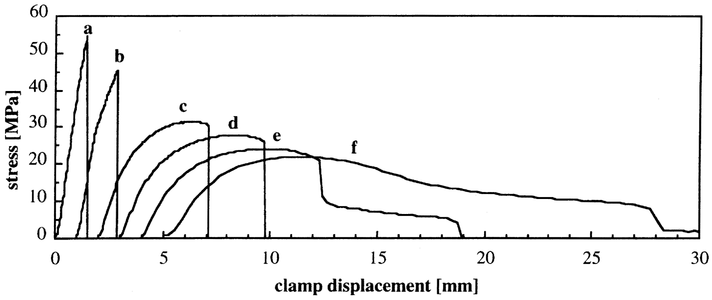

Figure 3 Stress–displacement curves obtained by SEN tensile tests at 1 mm/s and at various temperatures for P9000. Temperature (°C): (a) − 40; (b) − 20; (c) 20; (d) 40; (e) 50; (f) 60

test speed and the effect of the temperature on the yield stress shows that an increase in the test speed by a factor of 10^4 corresponds to a temperature decrease by approximately 40°C. Thus, in the temperature range studied in this section (− 50–140°C), the yield stress of polypropylene is lower than that required for plane strain conditions, even in the SEN tensile test at 1 m/s.

Due to the absence of plane strain conditions, fracture of polypropylene in the SEN tensile test may be accompanied by large scale yielding. Fracture mechanics, by the J-integral approach[10], offers a method of analysing fracture accompanied by large-scale yielding. However, the J-integral approach has only been used sporadically and interpretation is not generally known. We therefore used a different approach.

In this context, the fracture process was characterised, among others, by the crack initiation and the crack propagation energy. Since the stress concentration at the notch tip is relatively low, a significant part of the crack initiation energy is absorbed by the bulk of the specimen. This is especially the case when notch tip blunting due to plastic deformation occurs. In the case of crack propagation, the energy is more concentrated than during crack initiation, due to the smaller crack tip radius.

SEN tensile test: 1 mm/s

The fracture behaviour at low test speed was investigated by a single-edge notch (SEN) tensile test at 1 mm/s. Stress–displacement curves for P9000 at different temperatures, obtained by a SEN tensile test at 1 mm/s, are shown in *Figure 3*. The curves displayed are characteristic of all tested polypropylenes. The fracture process may be divided into a crack initiation and crack propagation stage. During crack initiation, stress builds up at the notch tip but is too low to enable crack propagation. It is assumed that crack propagation starts at the transition in the stress displacement curve near the stress maximum. Consequently, at low temperature, crack propagation starts at maximum stress (*Figure 3*, −20 and −40°C). At higher temperatures, crack propagation starts beyond the maximum stress, and crack propagation is preceded by yielding during crack initiation (*Figure 3*).

The sharp drop in stress at low temperatures (*Figure 3*) indicates that no additional energy is needed for crack propagation. This type of fracture is referred to as brittle fracture. At high temperature, additional energy is needed for crack propagation (*Figure 3*). This type of fracture is referred to as ductile fracture.

Maximum stress. 'Maximum stress' is defined as the maximum stress during a SEN tensile test. This stress is the net cross-sectional stress neglecting stress concentration at the crack tip. *Figure 4* shows the maximum stress *versus* temperature. At higher temperatures (≥ 0°C), crack propagation is preceded by yielding during crack initiation (*Figure 3*). This suggests that the maximum stress at high temperatures is dominated by the yield stress or even equals the net cross-sectional yield stress. This explains the decrease in maximum stress with increasing temperature and the independence of the molecular weight at higher temperatures (*Figure 4*).

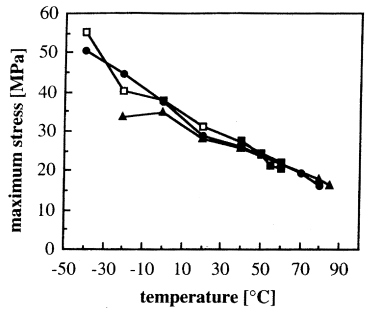

Figure 4 Maximum stress during SEN tensile tests at 1 mm/s as a function of the temperature for the polypropylenes. (□) P9000; (■) P7000; (●) P6000; (▲) P2000. The stress is the net cross-sectional stress, neglecting stress concentration at the notch tip

Figure 5 shows the crack initiation, crack propagation and fracture displacement as a function of the temperature. *Figure 6* shows the crack initiation, crack propagation and fracture energy as a function of the temperature. Crack propagation is assumed to start at the transition in the stress displacement curve near the stress maximum. However, in the case of ductile fracture no clear transition was observed and determination of the beginning of crack propagation was somewhat arbitrary.

Crack initiation. Below 0°C the CID is almost independent of the temperature and the molecular weight. Above 0°C, the CID increases with increasing temperature and increasing molecular weight. The behaviour of the CIE with the temperature is comparable to that of the CID.

Crack propagation. With increasing temperature, the crack propagation displacement (CPD) and the CPE increase sharply from their zero level. With increasing molecular weight, the CPD– and CPE–temperature curves shift towards lower temperatures.

Fracture surface. *Figure 7* shows P9000 specimens fractured during a SEN tensile test at 1 mm/s and at various

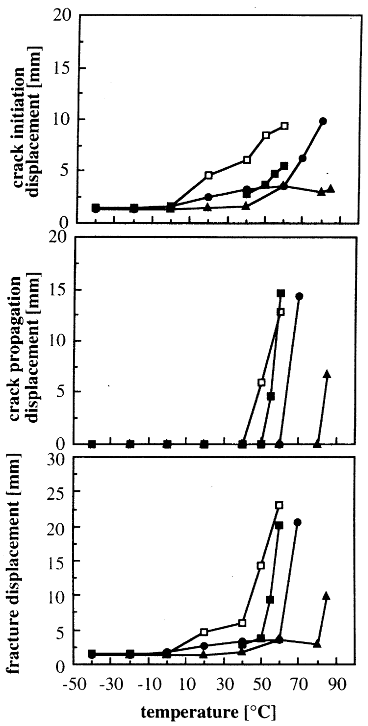

Figure 5 Displacement during SEN tensile tests at 1 mm/s as a function of the temperature for the polypropylenes. (□) P9000; (■) P7000; (●) P6000; (▲) P2000

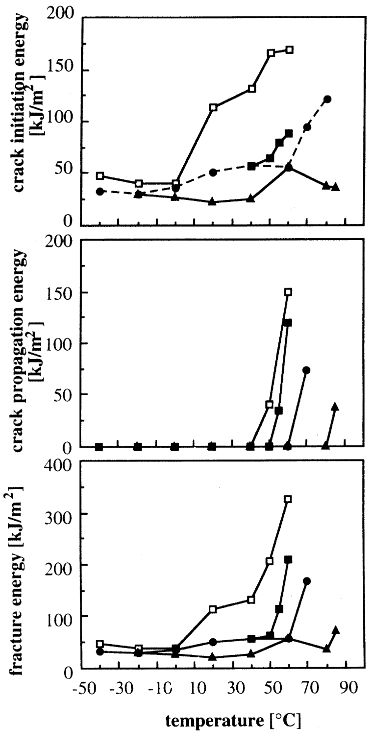

Figure 6 Supplied energy during SEN tensile tests at 1 mm/s as a function of the temperature for the polypropylenes. (□) P9000; (■) P7000; (●) P6000; (▲) P2000

temperatures. Some of the related stress displacement curves are shown in *Figure 3*: 0°C, the entire fracture surface has a transparent brittle appearance; 20°C, the fracture surface just behind the notch tip is stress whitened, and yielding is observed at the notch tip; 40°C, the entire fracture surface is stress whitened, and an intensely stress-

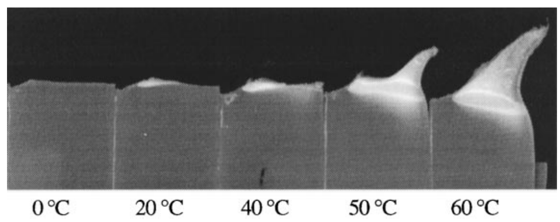

Figure 7 P9000 specimen fractured during a SEN tensile test at 1 mm/s and at various temperatures

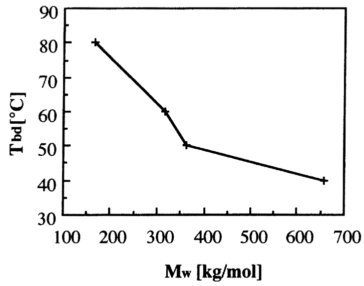

Figure 8 The brittle/ductile transition temperature (T_{bd}) in an SEN tensile test at 1 mm/s *versus* the weight-average molecular weight (M_w)

whitened yield zone is formed at the notch tip (*Figure 7*) (infrared thermography measurements show that this yield zone is formed during crack initiation[5]); 50°C, the yield zone at the notch tip encompass the entire cross-sectional area resulting in necking of the specimen during crack initiation (*Figure 7*). At and above 50°C, the material is considerably deformed during crack propagation. The deformed material is intensely stress whitened (*Figure 7*).

At 50°C, P9000 starts to exhibit pronounced plastic deformation as a result of crack propagation. As illustrated in *Figure 6*, at this temperature crack propagation energy starts to increase. In other words, ductile deformation is due to pronounced plastic deformation during crack propagation.

Brittle/ductile transition. In this context, the brittle/ductile transition is defined as the onset of ductile deformation. The energy absorption during crack propagation is a measure of the toughness of fracture. The crack propagation energy depends on the CPD and on the stress experienced during crack propagation. The stress and the CPD are independent of each other, and an increase in the CPD may be accompanied by a decrease in the stress. As a consequence, the energy may decrease as the CPD increases. For this reason, the CPD seems to be a more accurate measure of the toughness of fracture than the crack propagation energy. In this context, the CPD is therefore used as a measure of the toughness of fracture. The brittle/ductile transition temperature (T_{bd}) was determined by extrapolating the CPD temperature curve (*Figure 5*) to zero. The T_{bd} decreases with increasing weight-average molecular weight (*Figure 8*).

SEN tensile test: 1 m/s

The fracture behaviour at high test speed was studied by an SEN tensile test at 1 m/s. Stress displacement curves for P9000 at various temperatures, obtained by an SEN tensile test at 1 m/s, are shown in *Figure 9*. These curves are characteristic of all tested polypropylenes. Crack propagation is assumed to start at the transition in the stress

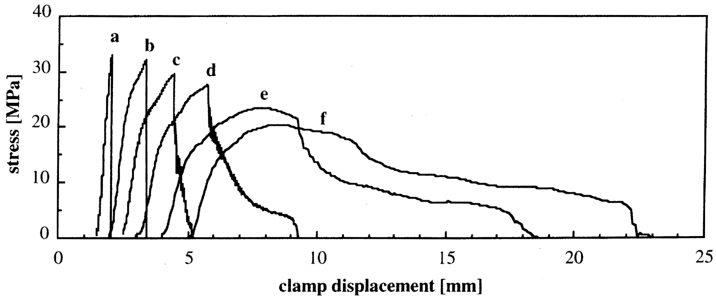

Figure 9 Stress–displacement curves obtained by SEN tensile tests at 1 m/s and at various temperatures for P9000. Temperature (°C): (*a*) 20; (*b*) 40; (*c*) 60; (*d*) 80; (*e*) 90; (*f*) 100

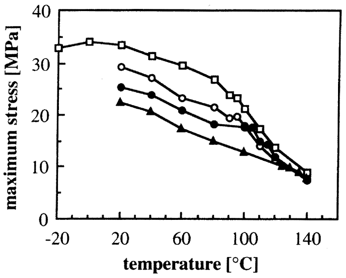

Figure 10 Maximum stress during SEN tensile test at 1 m/s *versus* the temperature for the polypropylenes. (□) P9000; (■) P7000; (●) P6000; (▲) P2000. The stress is the net cross-sectional stress, neglecting stress concentration at the notch tip

displacement curve near the stress maximum. At low temperatures ($\leq$ 80°C), the crack propagation starts at the maximum stress (*Figure 9*). At higher temperatures ($>$ 80°C), crack propagation starts beyond the maximum stress, and crack propagation is preceded by yielding during crack initiation (*Figure 9*).

Maximum stress. *Figure 10* shows the maximum stress as a function of the temperature. This stress is the net cross-sectional stress, neglecting stress concentrations at the notch tip. The maximum stress decreases with increasing temperature. The slope of the maximum stress–temperature curve changes at higher temperatures.

This change in slope occurs with decreasing molecular weight at 80, 95, 105 and 130°C, respectively. Prior to this change in slope, crack propagation starts at maximum stress; beyond this point crack propagation starts after the maximum stress is reached (*Figure 9*). Thus, the changing slope accompanies transformation of the stress maximum from fracture stress to yield stress.

Prior to the change in slope, the maximum stress is a fracture stress and increases with increasing molecular weight (*Figure 10*), due to an increase in the amount of tie chains[11]. Beyond the change of slope, the maximum stress turns into a yield stress and is almost independent of the molecular weight (*Figure 10*). It should be noted that P9000 has a slightly higher yield stress than the other polypropylenes (*Table 3*).

Figure 11 shows the crack initiation, crack propagation and fracture displacement as a function of the temperature. *Figure 12* shows the crack initiation, crack propagation and fracture energy as a function of the temperature. Determination of the beginning of crack propagation is described at 1 mm/s.

Crack initiation. Below 20°C, the CID remains almost

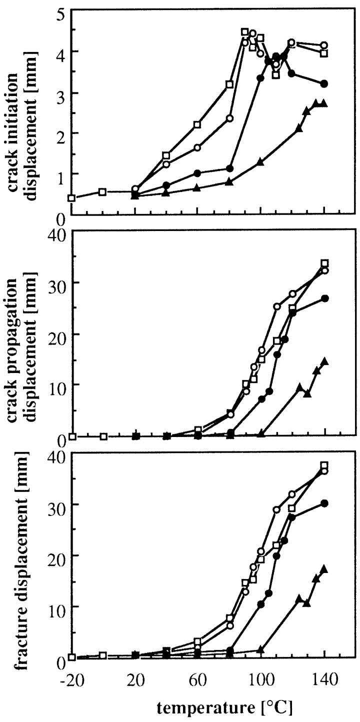

Figure 11 Displacement during SEN tensile tests at 1 m/s as a function of the temperature for the polypropylenes. (□) P9000; (■) P7000; (●) P6000; (▲) P2000

constant, irrespective of the temperature. Above 20°C, the CID increases with increasing temperature and increasing molecular weight. The CID at 1 m/s is much smaller than the CID at 1 mm/s. The CIE shows a maximum with respect to temperature and increases with increasing molecular weight. The CIE is approximately proportional to the product of maximum stress and CID. Before reaching the maximum CIE the increase in CID with increasing temperature is relatively stronger than the decrease in maximum stress with increasing temperature, and the CIE increases with increasing temperature. After reaching the maximum CIE, the CID remains almost constant, and the CIE decreases with increasing temperature, due to the decrease in maximum stress. The CIE increases with increasing molecular weight, due to the increasing maximum stress and increasing CID.

Crack propagation. With increasing temperature the CPD and the CPE increase sharply from their previous zero level. Initially, the increase in CPD and CPE is not as sharp as at 1 mm/s, but subsequently the slope of the

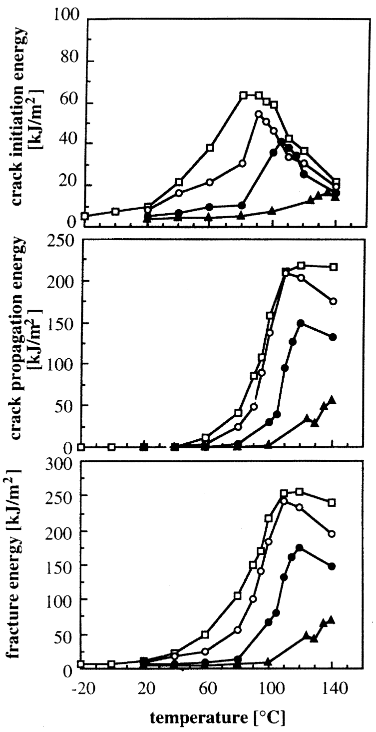

Figure 12 Supplied energy during SEN tensile tests at 1 m/s as a function of the temperature for the polypropylenes. (□) P9000; (■) P7000; (●) P6000; (▲) P2000

CPD–temperature curve is almost similar to that at 1 mm/s. At higher temperatures, P8000 and P6000 exhibit a change in slope in the CPD–temperature curve accompanied by a maximum in the CPE–temperature curve. This change in slope and this maximum were not observed at 1 mm/s. The CPE increases with increasing molecular weight. Analogous to the crack initiation energy the CPE is approximately proportional to the product of the maximum stress and the CPD. Before reaching the maximum CPE the increase in CPD with increasing temperature relatively exceeds the decrease in maximum stress with increasing temperature, and the CPE increases. After reaching the maximum CPE, the increase in CPD becomes relatively smaller than the decrease in maximum stress, and the CPE decreases.

Total fracture process. As the temperature increases, the fracture energy passes through a maximum, which is primarily attributed to a corresponding maximum in the crack propagation energy. At 1 mm/s, no maximum is observed in the fracture energy curve.

Fracture surface. *Figure 13* shows P9000 specimens fractured during a SEN tensile test at 1 m/s and at various temperatures. The related stress–displacement curves are shown in *Figure 9*. At 60°C, shearlips appear at the back part of the fracture surface (*Figure 13*). With increasing temperature, the size of the shearlips increases and the shearlips extend over the fracture surface (*Figure 13*) until they ultimately cover the entire fracture surface. Necking during crack initiation occurs at temperatures higher than approximately 100°C. Plastic deformation at the fracture zone is accompanied by stress whitening (*Figure 13*), which disappears with increasing plastic strain and increasing temperature (*Figure 13*).

Figure 14 shows the P9000 fracture surface at 90°C. The thickness of the shearlips increases towards the back of the specimen. As the two shearlips meet, the plastic deformation becomes homogeneous.

P9000 starts to form shearlips at 60°C. As illustrated by *Figure 12*, at this temperature the CPE begins to increase. This means that ductile deformation is associated with the formation of shearlips. The other materials show similar ductile deformation behaviour. Ductile deformation starts at temperatures below the temperature at which necking of the specimens during crack initiation occurs, which demonstrates that, at 1 m/s, ductile deformation is not initiated by necking during crack initiation, as it is at 1 mm/s.

Brittle/ductile transition. The brittle/ductile transition temperature (T_{bd}) is determined by extrapolating the linear part of the CPD–temperature curve to zero. For P8000 and P6000, the linear part preceding the change in slope was extrapolated and for P2000 the part of CPD–temperature curve between 130 and 135°C. As aforementioned the slope of this linear part is almost similar to that of the CPD–temperature curve at 1 mm/s. *Figure 15* exhibits the T_{bd} *versus* weight-average molecular weight (M_w). The T_{bd} decreases with increasing M_w.

Notched Izod impact test

The notched Izod impact strength *versus* temperature is shown in *Figure 16A*. The impact strength increases with the temperature passing through a transition followed by a maximum in strength. The impact strength increases with increasing molecular weight. At temperatures above the transition temperature, the specimens were partly fractured, while below this temperature they were completely fractured.

This indicates that the transition is a brittle/ductile transition. The decrease in impact strength after the brittle/ductile transition is partly due to incomplete fracture of the specimens, since the impact strength was calculated for the entire cross-sectional area behind the notch. However, this decrease in impact strength was also observed during the SEN tensile test at 1 m/s (*Figure 12*), although in this test the specimens were completely fractured. This suggests that the decrease in the notched Izod impact strength is, as is as incomplete fracture, due to a decrease in the intrinsic impact strength. As discussed for the SEN tensile test at 1 m/s, the decrease in intrinsic impact strength is due to the decrease in stress with increasing temperature.

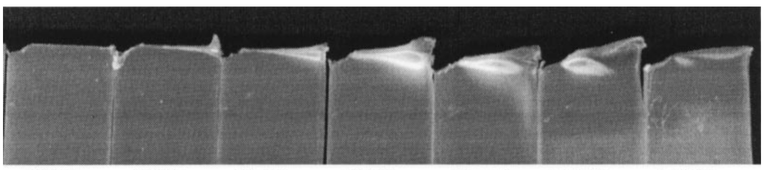

Figure 13 The P9000 specimen fractured at various temperatures by an SEN tensile test at 1 m/s

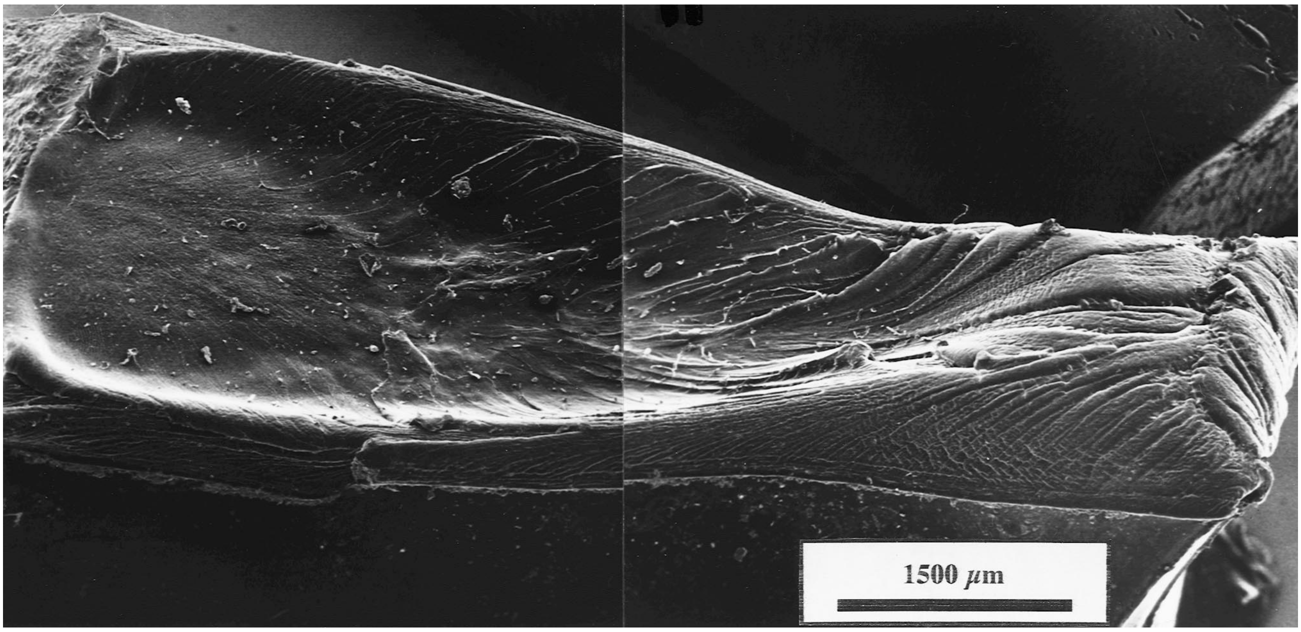

Figure 14 SEM micrographs of the fracture surface of a P9000 specimen fractured at 90°C by an SEN tensile test at 1 m/s

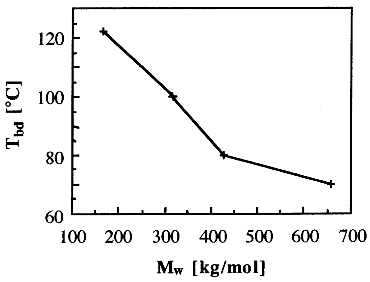

Figure 15 The brittle/ductile transition temperature (T_{bd}) in an SEN tensile test at 1 m/s as a function of the weight-average molecular weight (M_w) for polypropylene

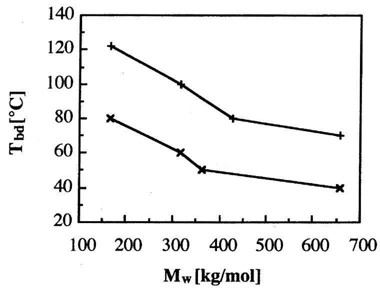

Figure 17 The brittle/ductile transition temperature (T_{bd}) *versus* the weight-average molecular weight (M_w) in an SEN tensile test at 1 m/s (+) and at 1 mm/s (×), for polypropylene

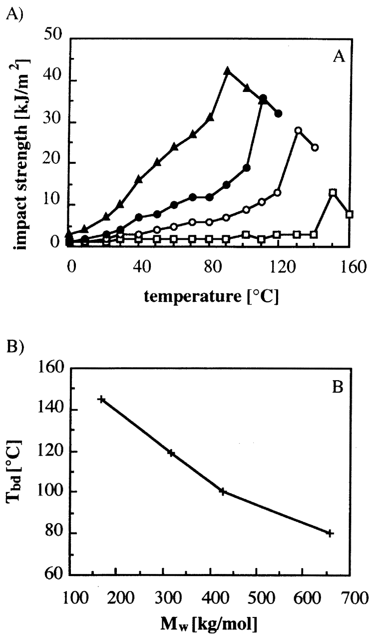

Figure 16 (A) Notched Izod impact strength *versus* temperature for the polypropylenes. (□) P9000; (■) P7000; (●) P6000; (▲) P2000. (B) The brittle/ductile transition temperature (T_{bd}) in a notched Izod impact test *versus* the weight-average molecular weight (M_w)

The transition temperature in the impact strength temperature curve is considered to be the brittle/ductile transition temperature (T_{bd}). The T_{bd} decreases almost linearly with increasing weight-average molecular weight (*Figure 16B*).

DISCUSSION

Low versus high test speed

Ductile deformation at low and high speed is due to pronounced plastic deformation during crack propagation. At 1 mm/s, ductile deformation is initiated by necking during crack initiation, while at 1 m/s ductile deformation precedes necking. The difference in ductile deformation behaviour at 1 mm/s and 1 m/s may be attributed to the difference in temperature rise during fracture[5].

However, the relation between the temperature rise and the fracture process is very complicated and further studies are needed to elucidate the difference in ductile deformation behaviour in relation to the difference in temperature rise.

Figure 17 depicts the T_{bd} as a function of the weight-average molecular weight (M_w) at 1 mm/s and at 1 m/s. The effect of the molecular weight on the T_{bd} at 1 mm/s and 1 m/s seems to be similar, despite the difference in ductile deformation behaviour. Increase of the test speed from

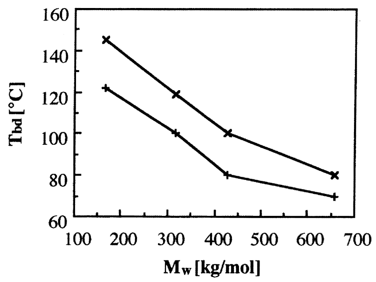

Figure 18 The brittle/ductile transition temperature (T_{bd}) *versus* the weight-average molecular weight (M_w) in an SEN tensile test at 1 m/s (+) and in a notched Izod impact test (×), for polypropylene

1 mm/s to 1 m/s shifts the T_{bd}–M_w curve by approximately 40°C towards higher temperatures.

Brittle/ductile transition

Ductile deformation at 1 m/s is due to the formation of shearlips. Plastic deformation during crack propagation is possible when the yield stress behind the crack tip is lower than the fracture stress behind the crack tip. As a consequence, the brittle/ductile transition may be attributed to a certain competition between the fracture stress and the yield stress. With increasing temperature, the yield stress decreases relative to the fracture stress, and at T_{bd} the yield stress drops below the fracture stress. With increasing molecular weight, the fracture stress increases and the T_{bd} decreases.

Ductile deformation at 1 mm/s is also due to the formation of shearlips, although ductile deformation is initiated by necking during crack initiation. Necking gives rise to orientation, which enhances the fracture stress; the yield stress drops below the fracture stress, resulting in ductile deformation. The effect of the temperature and the molecular weight on the brittle/ductile transition at 1 mm/s has to be described by the effect of these parameters on the necking during crack initiation.

Notched Izod impact test versus SEN tensile test

The equivalent strain rate (time to yield) is for the notched Izod test, 1.5 ms and for the SEN tensile test at 1 m/s is 4 ms[12]. Increasing the test speed from 1 mm/s to 1 m/s increases the equivalent strain rate from 4 ms to 4 s, thereby increasing the T_{bd} by approximately 40°C (*Figure 17*). Thus, the T_{bd} increases by 40°C if the test speed (or strain rate) increases by a factor of 10^3. The difference between the T_{bd} in the Izod impact test and the T_{bd} in the SEN tensile test at 1 m/s, due to difference in strain rate, is therefore expected to be less than 1°C. The applied strain rates for the Izod impact test and at the SEN tensile test at 1 m/s are thus comparable. *Figure 18* compares the T_{bd} obtained by a notched Izod impact test to the T_{bd} obtained by an SEN tensile test at 1 m/s. The T_{bd} determined by an SEN tensile test at 1 m/s is about 20°C lower than the corresponding value derived from a notched Izod impact test. This difference may be due to the fact that the stress during a notched Izod impact test is more triaxial than the stress in an SEN tensile test, caused by the bending moment in the notched Izod impact test. The von Mises yield criterion[13] demonstrates that the applied stress at which yielding occurs increases with increasing triaxiality. Consequently, the T_{bd} increases with increasing stress triaxiality.

CONCLUSIONS

Ductile deformation of polypropylene is associated with the formation of shearlips. Ductile deformation at 1 mm/s is initiated by necking during crack initiation; at 1 m/s ductile deformation precedes necking. This points to a difference in the ductile deformation behaviour at 1 mm/s and at 1 m/s.

The brittle/ductile transition temperature (T_{bd}) decreases with increasing (weight-average) molecular weight; the effect of molecular weight on the T_{bd} at 1 mm/s and at 1 m/s seems to be similar. Increasing the test speed from 1 mm/s to 1 m/s increases the T_{bd} by about 40°C.

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REFERENCES

1. Jang, B. Z., Uhlmann, D. R. and Van der Sande, J. B., *Polym. Eng. Sci.*, 1985, **25**, 98.
2. Ramsteiner, F., *Polymer*, 1979, **20**, 839.
3. Faulkner, D. L., *J. Appl. Polym. Sci.*, 1988, **36**, 467.
4. Ward, I. M., in *Mechanical Properties of Solid Polymers*, Ch. 12. John Wiley & Sons, London, 1971.
5. Van der Wal, A. and Gaymans, R. J., PP-EPDM blends 3, *Polymer*, in press.
6. Cheng, S. Z. D., Janimak, J. J., Zhang, A. and Hsieh, E. T., *Polymer*, 1991, **32**, 648.
7. Jang, B. Z., Uhlmann, D. R. and VanderSande, *J. Appl. Polym. Sci.*, 1984, **29**, 4377.
8. Inglis, C. E., *Trans. Inst. Naval Archit.*, 1913, **55**, 219.
9. Mai, Y. W. and Williams, J. G., *J. Mater. Sci.*, 1977, **12**, 1376.
10. Williams, J. G., in *Fracture Mechanics of Polymers*, Ch. 8. Ellis Horwood, Chichester, UK, 1984.
11. Huang, Y.-L. and Brown, N., *J. Mater. Sci.*, 1988, **23**, 3648.
12. Reed, P. E., in *Developments in Polymer Fracture*, ed. E. H. Andrews. Appl. Sci. Publishers, 1979, p. 121.
13. Ward, I. M., in *Mechanical Properties of Solid Polymers*. John Wiley, Chichester, 1983.