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Influence of molecular weight on the fracture properties of aliphatic polyketone terpolymers

W.C.J. Zuiderduin*, D.S. Homminga, H.J. Huétink, R.J. Gaymans

Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

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Abstract

The influence of polymer molecular weight on the mechanical properties of aliphatic polyketones was investigated. The molecular weight varied from 100,000 to 300,000 g mol^{-1}. The crystallinity was found to be independent of polymer molecular weight, as was the glass transition temperature. The yield strength and stiffness of the aliphatic polyketone terpolymers were also found to be independent of molecular weight. The post yield behaviour showed strong dependency on polymer chain length. The draw stress was increased significantly with higher molecular weight material. The impact resistance was increased with molecular weight, resulting in ductile fractures with large energy consumption upon fracture. The brittle-to-ductile transition temperature was lowered with increasing chain length. The difference in material deformation was linked to the higher mechanical connectivity and more stable post yield behaviour of the polymers with an increased molecular weight.

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Keywords: Molecular weight; Entanglements; Mechanical properties

1. Introduction

Aliphatic polyketones are a family of polymers prepared by the polymerisation of α-olefins and carbon monoxide in a perfectly 1:1 alternating sequence using palladium catalysts [1].

Aliphatic polyketones (Fig. 1) are a group of engineering plastics with an unique combination of thermal, mechanical, barrier and chemical resistance properties. Polyketones posses excellent properties like fast crystallisation, good tensile strength, good chemical and wear resistance, very low permeability and good impact behaviour over a broad temperature range [2,3]. These properties give them significant commercial potential in a broad range of engineering, barrier packaging, fibre and blend applications [1,4].

Perfectly alternating aliphatic polyketones based on ethylene and carbon monoxide, $-[CH_2CH_2C(O)]_n-$ (PK-E), have a relatively high melting point of 257 °C [5,6]. This is about 125 °C higher than the T_m of polyethylene and reflects the strong polar group contribution, resulting from the high regularity repeating ketone unit. At elevated temperatures (e.g. during melt processing) polyketones can undergo intermolecular and intramolecular aldol condensation reactions [7,8]. The intermolecular degradation reactions (crosslinking) lead to an increase of the melt viscosity, this limits the melt-processing window of this type of polymers [9]. These reactions are catalysed by impurities, such as salts (ions) and catalyst residues [10].

During processing degradation can be avoided by reducing the melting temperature of the copolymer. The melting temperature can be lowered by incorporating propylene groups into the polymer chain, which reduces the chain regularity of these terpolymers.

In PK-EP-6 for example 6 mol% of the ethylene groups are replaced by propylene groups. This lowers the crystallinity of the polymer and consequently also lowers the melting temperature (from 257 to 225 °C) [11–13].

There have been a number of papers on the subject of aliphatic polyketones, especially the crystallisation behaviour and crystal structure have been a subject of interest [13–16], however, to our knowledge no papers have been reported that deal with the molecular weight and its influence on the mechanical properties of aliphatic polyketones.

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* Corresponding author. Tel.: +31-534894347; fax: +31-534893823.
E-mail address: w.c.j.zuiderduin@ct.utwente.nl (W.C.J. Zuiderduin).

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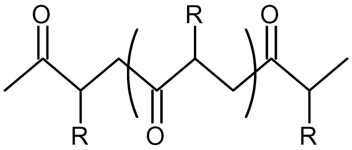

Fig. 1. Molecular structure of an aliphatic polyketone copolymer R=H or R=CH_3.

The fracture resistance of a thermoplastic polymer depends critically upon its relative molecular weight [17, 18]. The fracture energy falls rapidly when the chains are too short to form effective entanglements [19]. Very short polymer chains are held together only by van der Waals forces and are unable to form stable crazes [20].

Entanglements restrict the mobility of polymer molecules in the bulk and in concentrated solutions and are the basis of the unique dynamic properties of polymers [21]. The molecular weight between two entanglements (M_e) can be obtained from the storage modulus [22]. It is in fact the M_e which underlies many of the theoretical treatments of diffusion and viscoelasticity of molten polymers [23,24]. In addition the large strain and failure properties of solid polymers such as the natural draw ratio [25] and crazing [26], are profoundly affected by the M_e. Failure properties, such as toughness, depend critically upon the ratio of the molecular weight to its M_e [27]. Hui and Kramer [28] showed that the fracture toughness of glassy polymers is strongly depending on the ratio of M_e/M_n.

Mikos and Peppas [29] also suggest such a relation for the fracture strength of notched samples.

The molecular weight between entanglements (M_e) for polyketone terpolymer is 1700 g mol^{-1}. The molecular weights of the series used here (100,000–300,000 g mol^{-1}) are well above the M_e. The entanglement density is not influenced by molecular weight at these high molecular weights (with $M_w \gg M_e$), as is described by Lomellini [22].

Stress–strain properties of semi-crystalline polymers such as PE and PP depend on M_w similar to amorphous polymers [30]. Unoriented crystalline materials are found to deform by a complex process involving initial breakdown and subsequent reorganisation of crystalline regions as described by Peterlin [31–33]. After an initial stage of plastic deformation in the spherulites, the latter begin to breakdown. Lamellae packets oriented normal to the applied stress may separate along the amorphous boundary region, while others begin to rotate toward the stress axis. The crystals themselves are now broken into smaller blocks, but the chains remain folded. As this phase of deformation continues, these small bundles become aligned, forming microfibrils. Since many blocks are torn from the same lamellae, they remain connected by a number of tie-molecules created by unfolding chains. The combination of many more fully extended tie molecules and the orientation of the bundles within each fibril contributes toward a rapid increase in stiffness and strength; strain hardening. Therefore, an important parameter in semi-crystalline materials is the tie-chain density, the entanglement density between crystals in the solid state. As described by Mikos et al. [29] and Brown et al. [21] a higher tie-chain density increases the amount of effective tie chains. A higher tie-chain density also increases the mechanical connectivity of the polymer system.

Especially, at a higher strain the mechanical connectivity becomes important. Another aspect that can have a large influence is the chain endgroup concentration. When the molecular weight increases the amount of chain endgroups is decreased. The chain ends do not participate in the mechanical connectivity, which is formed by the amorphous entanglements and the crystalline domains. The chain ends are, therefore, weak spots in the mechanical connectivity of the polymer network [34]. This is also expressed in the strain hardening responds of polymers; the strain hardening responds are increased with higher molecular weight [35]. The fracture energy increases with molecular weight, and the most important factor for this increase is the increased mechanical connectivity of the polymer system [29].

1.1. Aim

The influence of molecular weight on the fracture and deformation behaviour of aliphatic polyketone terpolymers will be studied. The impact properties of polymers with different molecular weights are studied in an instrumented single edge notched tensile set-up. The impact resistance is studied as a function of temperature, to obtain the brittle-to-ductile transition temperatures. The thermal properties of the different polymers are studied, as well as the tensile properties. The structure property relations of the terpolymers with different molecular weight are evaluated.

2. Experimental

2.1. Materials

The different polyketone terpolymers were kindly supplied by the SHELL Research and Technology Centre Amsterdam (SRTCA). The materials specifications are described in Table 1. These polyketones are perfect alternating terpolymers, polymerised from ethylene and

Table 1
Material properties

Polymer	[η] (dl g^{-1})	Molecular weight M_w (g mol^{-1})	Propylene content (mol%)
A	1.21	100,000	6
B	1.57	150,000	6
C	1.68	170,000	6
D	2.20	220,000	6
E	2.36	240,000	6
F	2.84	296,000	6

carbon monoxide; a small percentage (6 mol%) of the ethylene is replaced by propylene compared to PK-E to lower the melting temperature. The commercial polyketone (PK-EP-6) has a glass transition temperature of approximately 15 °C and a melting temperature of 225 °C with a crystallinity of 35 wt%.

2.2. Specimen preparation

Compounding of the materials was done using a Berstorff (ZE 25 × 33D) twin screw (co-rotating) extruder. In the extrusion step, barrel temperatures were set at 240 °C and a screw speed of 140 rpm and a throughput of 4 kg h^{-1}. A screw speed of 140 rpm was used. The *L*/*D* ratio of the screws was 33, and $D = 25$ mm. To avoid undesirable degradation reactions, the extruder was thoroughly cleaned prior to the experiments, non-ionic water was used as a cool medium and a nitrogen-flow was maintained over the melt in the extruder. During the extrusion process stabilisers were added, 0.2 wt% calcium-hydroxy-apatite (melt stabilisation), 0.3 wt% Nucrel (ethylene–methacrylic acid copolymer, processing aid) and 0.2 wt% naugard 2-2′-oxamidobis(ethyl-3(3,5 di-*t*-butyl-4-hydroxyphenyl)propionate), anti oxidant).

The dried polymer was injection moulded into rectangular bars (74 × 10 × 4) impact test specimen (ISO 180/1A) and Dumbbell shaped specimen (ISO R527-1) using an Arburg Allrounder 221-55-250 injection moulding machine. The barrel had a flat temperature profile of 20 °C above the melt temperature (240 °C), the mould temperature was kept at 70 °C with an injection pressure of 55 bar, holding pressure was kept at 45 bar. Total cycle time was approximately 23 s. A single edge 45° V-shaped notch with a tip radius of 0.25 mm and a depth of 2.0 mm was milled in the bars.

2.3. Conditioning

The test bars were dried at 80 °C under vacuum for 15 h, and kept under vacuum at room temperature after this drying step. Because of the physical ageing behaviour of this type of polyketone (T_g around room temperature), every 10th day the test bars were heated to 80 °C for half an hour to rejuvenate the physical ageing. After this treatment, the test bars were cooled down in a controlled manner in the oven and kept under vacuum. The test bars are not used in the first two days after a heat treatment since the physical ageing process is very fast in this period.

2.4. DSC

DSC spectra were recorded on a Perkin Elmer DSC7 apparatus, equipped with a PE7700 computer and Tas-7 software. Five to six milligram of dried sample was heated at a rate of 20 K min^{-1}. The peak temperature of the second scan was taken as the melting temperature of the polymer; the peak area was used to determine the melting enthalpy.

2.5. Notched Izod impact test

Notched Izod impact tests were carried out using a Zwick pendulum. To vary the test temperature, the specimens were placed in a thermostatic bath. 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 carried out in ten-fold. The T_{bd} was taken on the slope of the S-shaped curve of fracture energy as a function of temperature, on the value $E_{(1/2)} = (E_{max} - E_{min})/2$.

2.6. Dynamic mechanical analysis

A Myrenne ATM3 torsion pendulum was used at a frequency of approximately 1 Hz. The storage modulus G' and the loss modulus G'' were measured. The samples (50 × 8.8 × 2.2 mm^3) were first cooled to -100 °C and subsequently heated to a temperature were the storage modulus G' would drop below 15 MPa, this temperature is defined as the flow temperature (T_{flow}). During cooling and heating, 1.0 °C min^{-1}, a measurement was done every 5 °C. The initial amplitude of the torsion was set at 0.1% strain.

2.7. Tensile tests

Tensile tests were conducted on dumbbell shaped specimens (ISO R527-1) with a Zwick tensile Z02 tester; all tests were carried out in five folds. Test speed was constant at 60 mm min^{-1} (which correlates to an apparent strain rate of 12.5×10^{-3} s^{-1}), the modulus was determined in the strain regime of 0.1–0.25% strain, while the yield stress was taken at the first point were $d\varepsilon/d\sigma = 0$. The strain was monitored with extensometers attached on the specimen.

2.8. Single edge notched tensile experiments

The fracture behaviour was studied by a tensile test on notched bars, referred to as single edge notch tensile test (SENT). Tests were carried out on a Schenck VHS servohydraulic tensile machine. The specimen length between the clamps is 35 mm, thus accordingly at a clamp speed of 1 m s^{-1} the macroscopic apparent strain rate is 28.5 s^{-1}. At these high strain rates 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 pad in order to reduce harmonic oscillations [36], because of this damping no filtering is required afterwards. This method has been used successfully by others for the study of the impact behaviour of polycarbonate, polypropylene, styrenic–acrilonitrilic and polyamide polymer systems [37–39]. The clamp displacement was assumed to equal the piston displacement, which is measured with a LVDT. The force is measured with a piezo-electric force transducer located between the upper clamp and the crosshead. Force, time and piston displacement are recorded using a transient recorder with a maximum sample rate of 2 MHz per channel. After completion of the test the results are sent to a computer. The strain rate of 28.5 s^{-1} corresponds well to the strain rate in the notched Izod impact test.

The tensile machine was equipped with a temperature chamber. The temperature chamber is heated or cooled with a nitrogen flow, which passes a heating unit. The heating unit is driven by an Eurotherm controller. A thermocouple inside the chamber registers the temperature. Calibration was carried out using a specimen with an embedded thermocouple.

Fig. 2 gives a typical stress–displacement curve for a ductile fracture obtained by a SENT test. In order to characterise the fracture process, it may be divided into a crack initiation part and a crack propagation part.

The crack initiation stage starts from zero displacement, and crack initiation is assumed to take place at the point of maximum stress. For low strain rates this was verified with the aid of the time records and optical determined the onset of crack initiation. For low strain rates the onset of crack initiation always coincides with the point of maximum stress. At high strain rates it is not possible to optically check the point of crack initiation, but it is assumed that crack initiation occurs at the maximum stress.

The displacement after the maximum load contributes to the crack propagation part of the fracture process. Brittle fracture is characterised by zero propagation displacement and energy. With ductile fracture the propagation displacement contributes significantly to the fracture displacement.

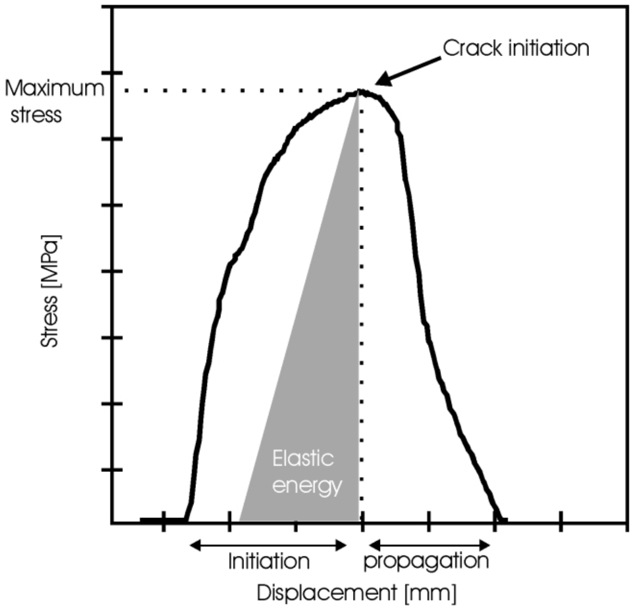

Fig. 2. Typical stress–displacement curve obtained by a SENT test.

2.9. Parameter definitions

Crack initiation is assumed to occur at maximum load. The point of maximum stress is, therefore, chosen as the boundary between crack initiation and crack propagation. The following parameters are used to describe the fracture process:

Maximum stress	force maximum on the force displacement curve, divided by the initial cross sectional area behind the notch (32 mm^2). Stress concentrations are neglected.
Initiation displacement	clamp displacement between the first point of force rise and the point of maximum force.
Initiation energy	area under the force-displacement curve up to the force maximum.
Crack propagation displacement	clamp displacement between the point of maximum force and the first point of zero force after force fall.
Crack propagation energy	area under the force-displacement curve after maximum force.
Fracture displacement	total displacement during the fracture process.

Fracture energy: total area under the force-displacement curve during the fracture process.

In case of brittle fracture the force falls almost instantaneously from the maximum force to zero. Therefore, brittle fracture is characterised by a very low propagation displacement and very low propagation energy. The onset of propagation energy and displacement are taken as the marker for ductility. Ductile fracture is defined here as a fracture, which requires additional energy to propagate a crack through the specimen. All measurements were performed in five-fold.

2.10. Infrared thermography

The temperature rise during fracture of specimens of thickness 4 mm was monitored using an infrared camera. With the infrared camera, only temperatures at the surface of the specimen can be determined. The spot size of about 100 μm is relatively large. The temperature indicated in one spot is an average temperature over the entire spot size. The temperature can, therefore, not be determined directly at the fracture surface, where it is expected to be highest. The temperature resolution of the camera was 0.15 °C, and the temperature range −20–300 °C. The spectral range was 8–14 μm and the image frequency 30 s^{-1} the spatial resolution was 0.1 mm spot size.

3. Results and discussion

The materials (aliphatic polyketones with 6% polypropylene) with different polymer molecular weight were melt processed and subsequently injection moulded into test specimen. The influence of polymer molecular weight on the mechanical, thermal and rheological properties are discussed.

3.1. Thermal properties

The materials were characterised with dynamical mechanical analysis (DMA) and differential scanning calorimetry (DSC). The thermal properties are summarised in Table 2.

The melting temperature obtained from DSC measurements remains constant with increasing molecular weight. The enthalpy necessary to melt the crystalline domains is also unaffected by the chain length. Consequently the crystallinity measured with DSC is constant in this molecular weight series and is approximately 34%. The small difference between the first and second heating sequence, shows that these types of aliphatic polyketones are fast crystallising materials. This also explains the minor influence of molecular weight on the crystallinity of these polymers. From the DMA experiments a T_{flow} was determined, which is the temperature were the storage modulus drops below 15 MPa (Fig. 3). This temperature is an indication for the melting temperature. The T_{flow} remains constant with increasing molecular weight at a value of 220 °C. The glass transition temperature is taken at the maximum of the curve of loss modulus (G'') versus temperature. The T_g is unaffected by the molecular weight and is situated at 14 °C. This is logical since the T_g is determined at low strains and, therefore, one would not aspect an influence of molecular chain length on the glass transition temperature.

The dependence of the storage modulus and the loss modulus on temperature are presented for the aliphatic polyketone terpolymers with different molecular weight.

The storage modulus at 20 °C is measured to be 660 MPa. This corresponds well to the modulus found in the tensile test which is 2 GPa, ($E_{\text{young}}/3G'$). Above the glass transition the moduli of the higher molecular weight materials is somewhat lower, this might be due to a lower crystallinity of the high molecular weight materials, but this was not supported by the data from the DSC measurements.

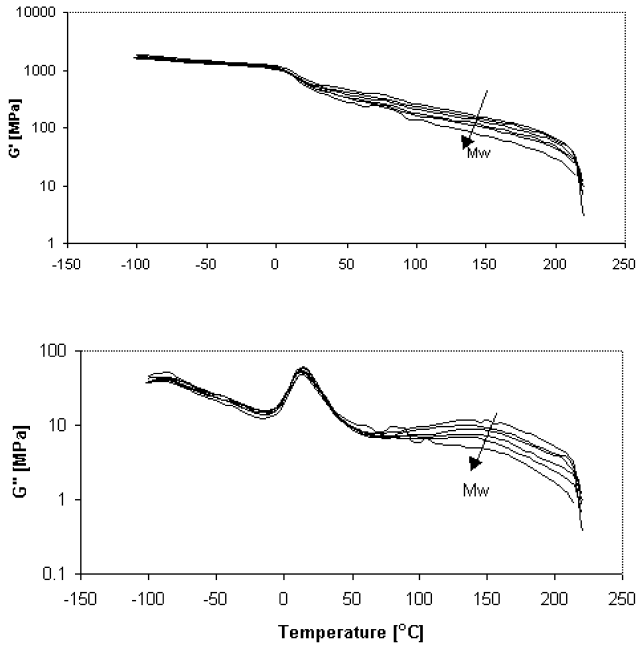

Fig. 3. Storage and loss modulus for polyketone terpolymers with varying molecular weight, the arrow indicates direction of increasing molecular weight.

The lowest transition in the spectrum is located at approximately −85 °C, and is related to the local chain motion of the amorphous material. This is sometimes regarded as a secondary glass transition (T_γ).

3.2. Tensile properties

Aliphatic polyketones are semi-crystalline polymers and deform with neck formation. The tensile properties were determined from standard engineering stress–strain curves; the post yield properties are, therefore, clouded by the well-known inhomogeneous deformation in the neck of polymers.

The yield stress measured was high and remained unaffected upon increasing polymer molecular weight

Table 2
Thermal properties of aliphatic polyketones determined with DSC and DMA

Polymer	Molecular weight (g mol^{-1})	T_m First heating (°C)	ΔH First heating (J g^{-1})	T_m Second heating (°C)	ΔH Second heating (J g^{-1})	Crystallinity[a] (%)	T_g (°C)	T_{flow} (°C)
A	100,000	227	68	222	78	34	14	220
B	150,000	227	75	222	78	34	14	220
C	170,000	228	82	222	80	35	14	220
D	220,000	228	77	223	77	34	13	220
E	240,000	226	76	221	78	34	14	220
F	296,000	228	78	224	79	35	14	220

[a] Calculated with the enthalpy for 100% crystalline polyketone terpolymer, $\Delta H_{100\%} = 227\ \text{J g}^{-1}$.

(Table 3). This has also been reported in literature for polypropylene on several occasions [37,38]. Above the glass transition temperature the yield stress is dominated by the crystal domains and is a low strain property. Chain length usually does not influence the mechanical properties in the low strain regime. The strain necessary to activate the yield process was also measured as a function of molecular weight (Table 3). The yield strain for the PK-polymers is remarkably high and showed an increase with molecular weight. The yield strain measured on standard dumbbell shaped samples is difficult to determine, due to the inhomogeneous manner of deformation. From infrared thermography experiments it has been shown (Fig. 4) that well before the yield point is reached ($\varepsilon = 7\%$) the materials start to develop heat (approximately 6–8 °C). This heat development must have its origin in some sort of plastic deformation of the polymer. The yield strain may also be influenced by the manner of localisation of deformation, although usually localisation processes are thought to occur after the yield point. The post yield behaviour of the polyketone terpolymer showed some characteristic features. The drop of stress from the yield stress to the draw stress is defined here as strain softening. This drop of stress from yield stress to draw stress showed large influence of molecular weight. The yield stress and the draw stress are plotted versus polymer chain length in Fig. 5.

The draw stress is increased with molecular weight, the draw stress is determined by the mechanical connectivity of the polymer, the yield stress clearly is not. The softening occurring after the yield stress is significantly decreased when the polymer chains are longer. The tendency for localisation of the plastic process is, therefore, lower when the polymer molecular weight is higher. The strain softening decrease with higher molecular weight is probably due to the stronger strain hardening responds of the high molecular weight materials. Strain hardening stabilises the localisation of the deformation in the neck. One important other feature influencing the softening is the temperature development in the samples due to plastic deformation. This is shown in Fig. 6, the drawing of a propagating neck was recorded with an infrared camera.

The temperature that is reached in the propagating neck is reduced when the polymer chain length is increased. The profile of the neck shape is also different, the localisation/softening is reduced as a consequence the local strain rate is lowered and the adiabatic heating is decreased. Also one can see that as the temperature is less increased the softening is further reduced. A self-amplified process is taking place, less localisation—lower temperature rise—even less localisation etc. The temperature at a distance from the propagating neck is raised in all cases to the same extend, approximately 6–8 °C. This indicates that plastic deformation processes are operative before the yield stress is reached.

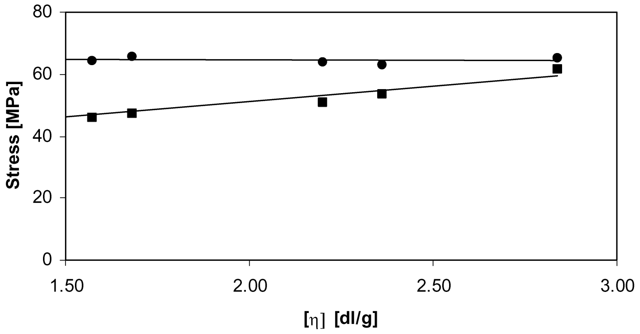

Fig. 4. Infrared recordings of aliphatic polyketones with different molecular weight; tensile, $12.5 \times 10^{-3}\ s^{-1}$, 20 °C.

The decrease in temperature in the neck with molecular weight cannot fully account for the decrease in softening behaviour of the different materials. The ΔT in the neck is 20 °C between the lowest and highest molecular weight. This accounts for a lowering in stress of approximately, 6.5 MPa. The differences in draw stress are somewhat stronger (16.5 MPa).

The modulus of the different materials are unaffected by the molecular weight. The highest molecular weight material shows an increase in modulus but this is regarded as a statistical deviation. The tensile data are summarised in Table 3.

The fracture stress increases with increasing chain length, the fracture stress equals the draw stress in all cases, this indicates that the polymers fracture during neck propagation. This is a statistical process and the number of defects or flaws in the material determines the fracture strain. The higher molecular weight PK-materials are more difficult to process and show, therefore, a lower fracture strain, in the engineering stress–strain curve.

Table 3
Tensile properties of aliphatic polyketones

Polymer	Modulus (Gpa)	Yield stress (MPa)	Yield strain (%)	Draw stress (MPa)	Fracture stress (MPa)	Fracture strain (%)	Strain softening (MPa)
A	2.0	64.9	16.8	45.2	45.2	122.0	19.7
B	1.9	64.5	16.8	46.0	46.0	206.1	18.4
C	2.0	65.6	17.3	47.2	47.2	212.6	18.4
D	1.9	63.9	18.7	50.7	50.7	182.1	13.1
E	1.9	62.9	19.4	53.4	53.4	96.0	9.5
F	2.3	65.3	19.8	61.7	61.7	67.6	3.7

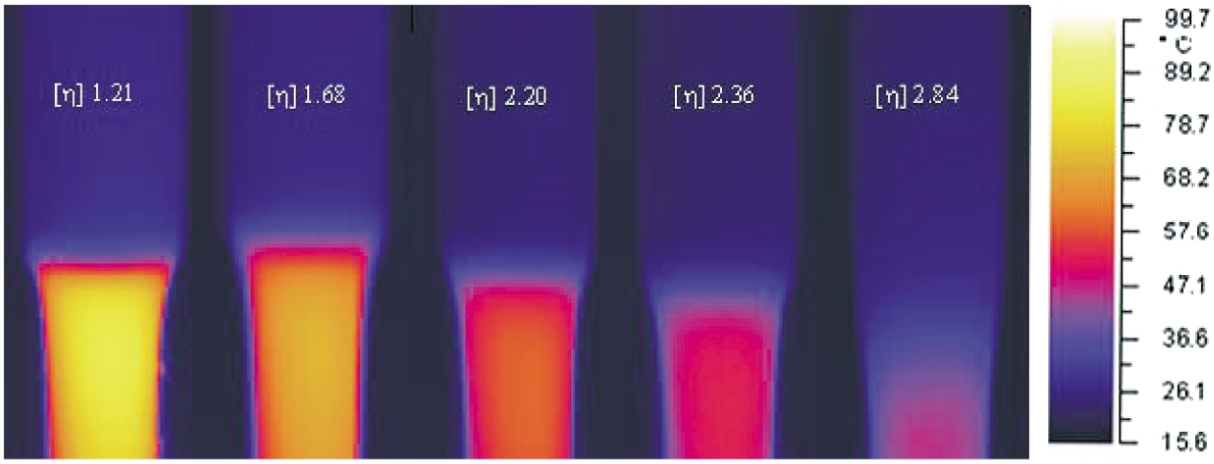

Fig. 5. Stress as a function of molecular weight, $12.5 \times 10^{-3}\ s^{-1}$, 20 °C; (●), yield stress; (■), draw stress.

3.3. Notched Izod impact

The impact resistance has been measured in notched Izod impact as a function of temperature to obtain the brittle-to-ductile transition temperature. The experimental data are given in Fig. 7.

The fracture energy increases with temperature for all materials up to the brittle to ductile transition (T_{bd}).

The impact resistance is increased strongly with molecular weight; the materials with longer polymer chains show very high fracture energies up to 60–70 kJ m^{-2}. The T_{bd} is shifted to lower temperatures when the polymer chain length is increased. A secondary effect is that the transition becomes increasingly sharp when the molecular weight is increased. The impact resistance of the lower molecular weight samples do not show a clear brittle-to-ductile transition in this temperature range. With this notch radius, it seems that the transition will not shift below 0 °C. At low temperatures the impact energy of the different materials converges to a single line, and this behaviour is similar to polypropylene [38]. The fracture energy in the ductile area increases with molecular weight, this was also shown for polyamide [37]. This is an effect of delocalisation of the deformation due to the more stable post yield behaviour of materials with a higher molecular weight. The increased hardening response due to the increased mechanical connectivity enlarges the plastic zone size during fracture and consequently the energy absorption upon fracture increases. This was validated with infrared thermography for samples at an apparent strain rate of $28.5 \times 10^{-3}\ s^{-1}$ in the single edge notched tensile set-up (Fig. 8).

Plastic deformation is an energy dissipating process, therefore, heat is generated during an impact experiment. The zone, which shows a temperature rise, is an indication of the process zone where plastic processes occur. The plastic zone size is clearly increased with polymer molecular weight; the amount of material, which is participating in the shear yield process is increased. The temperature at this relative low strain rate was raised to 100 °C. The localisation of the visco-plastic processes

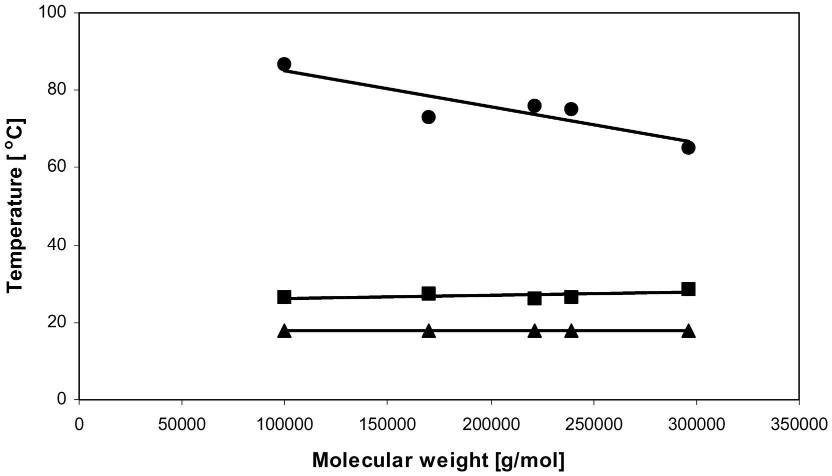

Fig. 6. Temperature during tensile deformation for different molecular weight polymers, $12.5 \times 10^{-3}\ s^{-1}$; (▲), initial temperature; (■), temperature outside necked region; (●), temperature in propagating neck.

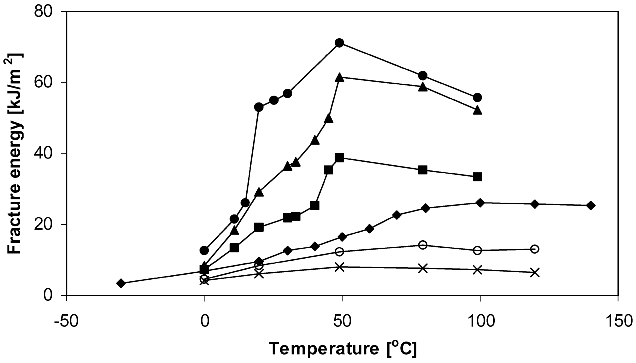

Fig. 7. Notched Izod impact strength for polyketone terpolymers with different molecular weight; x, [η] 1.21; (○), [η] 1.56; (◆), [η] 1.70; (■), [η] 2.2; (▲), [η] 2.36; (●), [η] 2.84.

behind the notch tip raises the local strain rate tremendously. The non-isothermal heating is as a consequence considerably large even at these moderate strain rates.

3.4. Single edge notched tensile (SENT)

The materials with different molecular weight are evaluated with the single edge notched tensile test. This is a very useful method to investigate the fracture process of polymers. The SENT experimental set-up is discussed in Section 2. The maximum stress has been measured as a function of temperature and molecular weight at a constant test speed of 1 m s^{-1} corresponding to an apparent strain rate of 28.5 s^{-1} (Fig. 9).

The maximum stress decreases with temperature for all materials, this is expected because the yield stress as well as the fracture stress decrease with temperature. At room temperature the stress is increased with molecular weight of the polymer. The yield stress of the different materials was found to be unaffected by polymer chain length. This indicates, that is not the yield stress that determines the maximum stress in the brittle region but that the fracture stress is more important. In the brittle region (low temperatures) the differences in stress are quite large. In the ductile regime (high temperatures) the differences in stress are smaller, and are converging to one line for all materials. The fracture stress is highly dependent on polymer chain length and the yield stress is not.

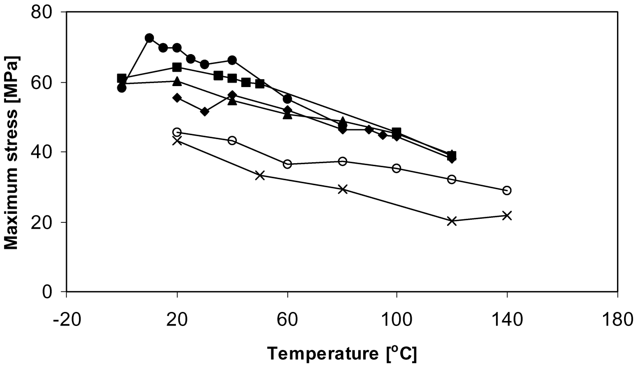

Fig. 9. Maximum stress as function of temperature for materials with different molecular weight in SENT, 28.5 s^{-1}, x, [η] 1.21; (○), [η] 1.56; (□), [η] 1.70; (■), [η] 2.2; (▲), [η] 2.36; (●), [η] 2.84.

3.5. Crack initiation

In the first part of the force-displacement curve elastic energy is stored and also deformation can take place behind the notch. No crack is present during this stage of the deformation process. When the stress–displacement curve reaches a maximum, a crack is initiated. This has been experimentally validated for low strain rates, however, for high strain rates this is very difficult and it is assumed that the crack is initiated at the point of maximum stress at high strain rates as well. Furthermore, it is not logical that a crack is initiated before the point of maximum stress because it would then be necessary for the remaining ligament to bear a higher load although the ligament is decreasing. When there are no geometric effects present, such as necking, the crack will also not initiate at a later stage then at the point of maximum stress. The crack initiation can be given in displacement or as energy values. The displacement results were found to be more sensitive to structural changes and are used here.

The displacement necessary to initiate a crack is

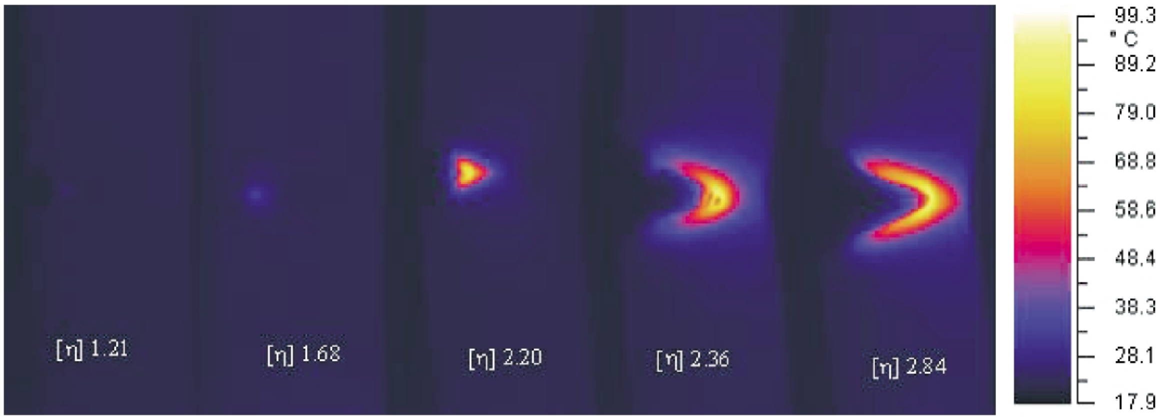

Fig. 8. Infrared images of polymers with different molecular weight in SENT, 28.5×10^{-3} s^{-1}.

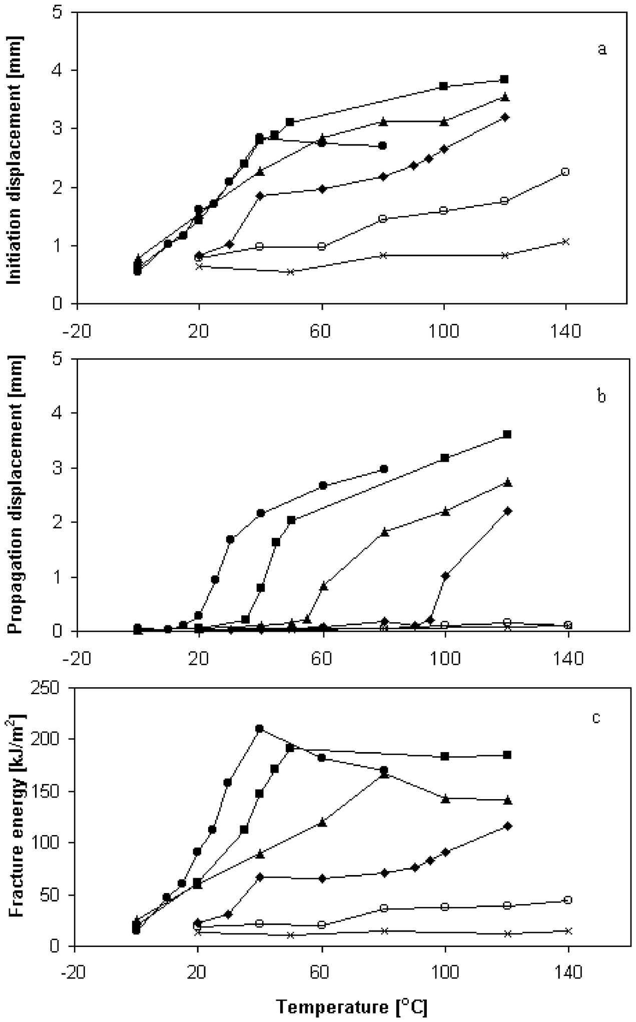

Fig. 10. Initiation-, propagation displacement and fracture energy for polyketones with different molecular weight, SENT 28.5 s^{-1}; x, [η] 1.21; (○), [η] 1.56; (◆), [η] 1.70; (■), [η] 2.2; (▲), [η] 2.36; (●), [η] 2.84.

increasing with molecular weight and temperature (Fig. 10(a)). The mobility of the polymer chains increases with temperature and, therefore, the material can react more easily upon an applied load. The yield stress also decreases with temperature, which results in more plastic deformation and more delocalisation of the deformation behind the notch. Both give rise to crack blunting and more material is deformed before a crack is initiated at elevated temperatures. The effect of molecular weight on the resistance to crack formation is also remarkable. The initiation displacement (and energy) increases with longer polymer molecules. Even in the ductile regime, where the maximum stresses are equal, the materials with longer polymer chains give rise to an increased initiation strain (and energy). This stems from the enlarged mechanical connectivity of materials with higher molecular weight. The slopes of the lines are also higher with a higher molecular weight. This is probably caused by the delocalisation of the deformation, which causes the plastic deformation zone to grow into two directions. Delocalisation of the deformation is very important, the notch will is blunted to a larger extend and more energy will be dissipated upon fracture. This is caused by the larger amount of strain hardening with a higher molecular weight, the higher draw stresses in tensile are an indication for this (Fig. 5).

3.6. Crack propagation

Once a crack is initiated in the material, the crack propagation process is started. The amount of energy absorbed during crack propagation is a measure for the ductility of the material. The onset of propagation displacement (and energy) is taken as a marker for the transition from brittle to ductile. In Fig. 10(b) the propagation displacement is given. The crack propagation displacements show the same dependency on temperature for all molecular weights. At low temperatures the displacement necessary to propagate a crack is close to zero. At a certain temperature the crack propagation displacement starts to rise strongly with temperature. This is due to the onset of ductility of the fracture. More energy needs to be supplied to the system to propagate a crack in this temperature range. The two lowest molecular weight materials, however, have no transition in the studied temperature range. The onset of ductility starts at lower temperatures for materials with a longer chain length. The largest molecular weight is starting to perform ductile at room temperature. Compared to other neat polymers a room temperature ductility in a notched test is remarkable.

3.7. Fracture energy

The combined crack initiation and crack propagation energy result in the fracture energy (Fig. 10(c)). The fracture energy of the specimen strongly increases with molecular weight, the shape of the curves are very similar to those of the notched Izod impact experiments (Fig. 7). The deformation is delocalised by a strain hardening mechanism. This leads to a large quantity of material taking part in the deformation process with as a result very high fracture energies of 210 kJ m^{-2} for the largest molecular weight in single edge notched tensile.

From the onset of propagation displacements the brittle-to-ductile transitions have been determined (Fig. 11). The brittle-to-ductile transition temperature strongly decreases with molecular weight; the transition is shifted about 80 °C from the lowest to the highest molecular weight. This is quite remarkable, since the entanglement density of the system is not changed in this molecular weight range. Also it is not expected that the tie-chain density is changed in this region, especially since the crystallinity remained constant. The end-to-end distance of the molecules is increased with longer molecules and of course the end-group concentration is lowered. It can, therefore, be argumented that the mechanical connectivity was raised, and that the post

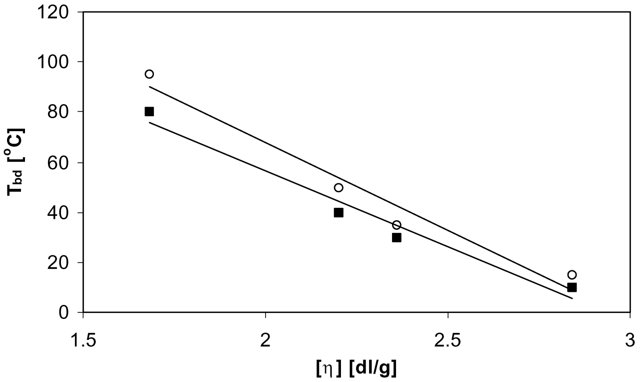

Fig. 11. T_{bd} as function of molecular weight, (○), SENT 28.5 s^{-1}; (■), notched Izod.

yield behaviour was stabilised in this molecular weight range by an increase in the strain hardening responds. This was also found for neat polypropylene and nylons [37,38].

The notched Izod impact test and the single edge notched tensile test are in good agreement with each other. The brittle-to-ductile transition temperature is lowered to the same extend for both experiments. The test speed of 1 m s^{-1} in tensile corresponds to the 3.2 m s^{-1} in bending/tensile in the Izod test.

4. Conclusions

The influence of molecular weight of PK-terpolymers on yield and fracture is studied. The PK-terpolymers are semi-crystalline materials and the crystallinity was found to be independent of molecular weight, as was the glass transition temperature (T_g). The yield strength and the stiffness of the polyketone terpolymers were also found to be independent of polymer molecular weight. The post yield behaviour showed strong dependency on polymer chain length. The draw stress was increased significantly with larger molecular weight material. The impact resistance was increased with molecular weight, resulting in ductile fractures with large energy consumption. The brittle-to-ductile transition temperature was lowered considerably with increasing chain length.

The mechanical connectivity consisting of entanglements in the amorphous phase and the tie chains between crystal domains is more connected when the polymer chain length increases. This is due to the decreased end group concentration and secondly by the larger end-to-end distance of longer polymer molecules. Consequently more material has to be fractured and deformed to propagate a crack through the material. The temperature development in aliphatic polyketone terpolymers during fracture was also strongly influenced by chain length. Higher molecular weight material shows less localisation of the deformation and consequently less adiabatic heating of the material.

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