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Influence of copolymerisation on fracture behaviour of aliphatic polyketones

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Abstract

High strain rate tensile impact properties of aliphatic polyketone terpolymers were investigated and related to the polymer chain structure. Aliphatic polyketones were used as a model system, by changing the termonomer content and type. Aliphatic polyketone is a perfectly alternating copolymer and the structure was changed with the addition of a few mol% of termonomer: propylene, hexylene and dodecene. Studied were the thermal properties with DSC and DMTA, tensile behaviour, notched tensile impact behaviour, notched Izod properties and the temperature development during deformation. The perfectly alternating copolymer had a melting point of 257 °C, a T_g at 15 °C, a high crystallinity (48%), a high yield stress (77 MPa) and yield strain (31%) but a relatively low fracture strain (85%) and an impact strength (notched Izod) of 13 kJ/m^2. Increasing the propylene content to 6%, lowered the melting temperature to 224 °C, without changing the T_g. The modulus and yield stress were lowered but the impact strength improved. Increasing the length of the termonomer while keeping the T_m at 224 °C lowered the T_g, the modulus, the yield stress but strongly improved the impact resistance. The longer termonomers, with a lower yield stress, reduced the necking behaviour. The temperature increase in front of the notch was about 85 °C. By adding termonomers to aliphatic ketones, the notched impact behaviour improved significantly at the cost of modulus and yield stress.

Keywords: Crystallinity; Polyketone; Impact behaviour

1. Introduction

Aliphatic 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 [1–3]. These properties give them significant commercial potential in a broad range of engineering, barrier packaging, fibre and blend applications [4,5]. The strong polar intermolecular forces, combined with the flexible polymer backbone result in a semi-crystalline polymer with a glass transition temperature of 15 °C. The chemistry of these type of terpolymers perfectly controls the chain structure of the resulting terpolymer, this makes these polymers suitable to function as model materials to gain insight in the structure property relations of copolymers [2–4].

Perfectly alternating aliphatic polyketones based on ethylene and carbon monoxide, –[CH2CH2C(O)]$_n$– (PK-E), have a relatively high melting point of 257 °C and a T_g of 15 °C [6–9]. This material is highly crystalline and difficult to process without degradation [11–13]. The intermolecular degradation reactions (cross-linking) lead to an increase of the melt viscosity, this limits the melt processing window [14,15]. In order to improve the processability, the melting temperature is lowered by *tert*-polymerisation. The physical properties like T_m, T_g and crystallinity can be influenced by introduction of a third monomer like propylene (PK-EP) or a higher α-olefin [16,17]. The incorporation of 6 mol% of propylene in the polymer backbone (PK-EP-6) results in a reduction of T_m from 257 to 225 °C, without changing the T_g. This strong lowering of the T_m with only 6% of termonomer is due to the very controlled copolymerisation of these systems [4].

Next to propylene also higher olefines can be introduced, thereby forming longer side branches in the polymer chain. These side branches do not fit into the crystal lattice and

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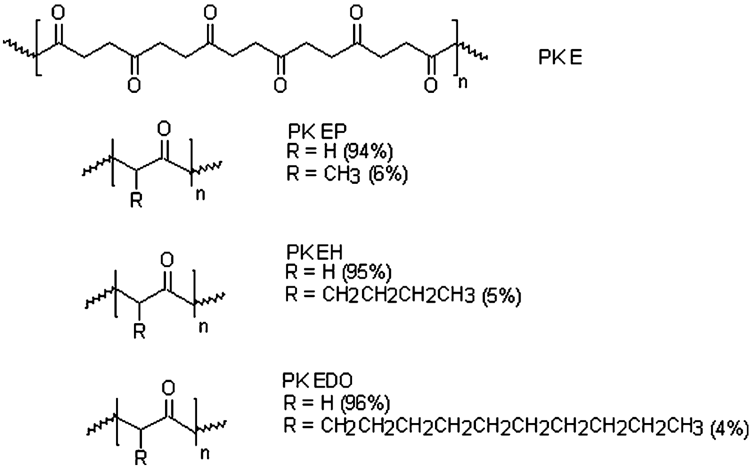

Fig. 1. Aliphatic polyketone terpolymers with different termonomers; m=4–6 mol%.

therefore the introduction of a higher olefin disturbs the crystallisation process [2,9,10]. This lowers the crystallinity of the polymer and also lowers the melting temperature. The introduction of side branches into the polymer backbone, also change the amorphous phase of the polymer [2,9,11, 14]. The effect of side groups is twofolds. The introduction of a side group reduces the conformation possibilities and this leads to a stiffening effect, however, longer side groups also reduce the chain interaction by increasing the distance between chains and this effect leads to a reduction in stiffness. It depends on which mechanism is dominant whether the T_g of the polymer increases or decreases.

The fracture behaviour depends on the crystalline structure, the crystallinity and the amorphous structure of polymers. The yield stress and stiffness increase with crystallinity. It was found for various other materials that an increase in crystallinity led to a reduction in impact resistance [18–21]. In particular, the brittle-to-ductile transition is very sensitive towards changes in crystallinity. The brittle-to-ductile transition temperature of polypropylene, as measured with the notched Izod impact test, increases from 40 to ±120 °C when the crystallinity is increased from 30 to 55 wt% [18].

In this paper the influence of amount of propylene termonomer and the length of the termonomer incorporated in the polyketone backbone on the thermal and fracture properties have been studied. Materials have been selected without a termonomer (PK-E) and with different termonomers: propylene (0–6 mol%) (PK-EP), hexylene (4 mol%) (PK-EH) and dodecene (4 mol%) (PK-Edo). For the series with different termonomer length, it was chosen to keep the melting temperature as constant as possible, by adjusting the amount of termonomer incorporated in the polymer chain. The molecular weight was kept constant in order to reduce the influence of chain length. It was shown that the fracture behaviour of these terpolymers show a large dependency on molecular weight [23]. The polymer structures are shown in Fig. 1.

2. Experimental

2.1. Materials

Different polyketone terpolymers were kindly supplied by the SHELL Research Centre Amsterdam (SRTCA). The material specifications are described in Table 1. These polyketones are perfect alternating terpolymers, polymerised from ethylene and carbon monoxide; a small percentage (4–6 mol%) of the ethylene is replaced by a higher olefin to lower the melting temperature.

2.2. Specimen preparation

Compounding of the materials was done using a Berstorff (ZE 25×33D) twin screw (co-rotating) extruder. In the

Table 1
Material specifications

Material	Termonomer		Content (wt%)	[η] (dl/g)
	Type	mol%		
PK-E	None	0	0	1.5
PK-EP-3	Propylene	3	2.3	1.8
PK-EP-6	Propylene	6	4.5	1.7
PK-EH	Hexylene	4	5.8	1.9
PK-Edo	Dodecene	4	11.0	1.8

extrusion step, barrel temperatures were set at 20 °C above the melt temperature as measured with DSC, a screw speed of 140 rpm and a throughput of 4 kg/h was used. The *L*/*D* ratio of the screws was 33, with $D=25$ mm. During the extrusion process stabilisers were added, 0.2 wt% calcium-hydroxy-apatite (for melt stabilisation), 0.3 wt% Nucrel (ethylene-methacrylic acid copolymer, as processing aid) and 0.2 wt% naugard 2-2′-oxamidobis(ethyl-3(3,5 di-*t*-butyl-4-hydroxyphenyl)propionate), anti oxidant). The polymer was injection moulded into rectangular bars ($74\times10\times4$ mm^3) for impact test specimen (ISO 180) and Dumbbell shaped specimen (ISO527) using an Arburg Allrounder 221-55-250 injection moulding machine. The barrel had a flat temperature profile of 20 °C above the melt temperature (T_m+20 °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 for the notched Izod impact test and the single edge notched tensile (SENT) test.

2.3. Notched Izod impact test

Notched Izod impact tests were carried out using a Zwick pendulum, according to ISO 180. 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 tenfold.

2.4. Differential scanning calorimetry (DSC)

DSC spectra were recorded on a Perkin–Elmer DSC-7 apparatus, equipped with a PE7700 computer and Tas-7 software. 3–6 mg of dried sample was heated at a rate of 20 K/min. The peak temperature of the second scan was taken as the melting temperature of the polymer; the peak area was used to determine the enthalpy.

2.5. Dynamic mechanical thermal 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 at a strain of 0.1%. The samples ($50\times8.8\times2.2$ 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, a measurement was done for every 5 °C.

2.6. Tensile tests

Tensile tests were conducted on dumbbell shaped specimens with a Zwick tensile Z02 tester; according to ISO527, all tests were carried out in fivefolds. Test speed was constant at 60 mm/min (apparent strain rate 1.25×10^{-3} s^{-1}). The modulus was determined in the strain regime of 0.1–0.25% strain, the yield stress was taken at the first point were $\mathrm{d}\varepsilon/\mathrm{d}\sigma=0$. The strain was monitored with extensometers attached on the specimen.

2.7. Single edge notched tensile experiments

The fracture behaviour was studied by a tensile test on notched bars, referred to as SENT test. Tests were carried out on a Schenck VHS servohydraulic tensile machine. With this apparatus it is possible to achieve clamp speeds ranging from 10^{-5} to 12 m/s. the specimen length between the clamps was 35 mm, thus accordingly the macroscopic apparent strain rate can be varied from 2.8×10^{-4} to 285 s^{-1}. The piston displacements used here were 10^{-3} and 1 m/s, which correspond to 2.8×10^{-2} and 28.6 s^{-1}. 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. A rubber pad damps the contact between the pick-up unit and the lower clamp in order to reduce harmonic oscillations [22]. The tensile machine was equipped with a temperature chamber. Fig. 2 shows a typical stress–displacement curve for a ductile fracture obtained by a SENT test. In order to characterise the fracture process, it is divided into a crack initiation part and a crack propagation part.

2.8. Parameter definitions

The point of maximum stress is the boundary between crack initiation and crack propagation, this was confirmed

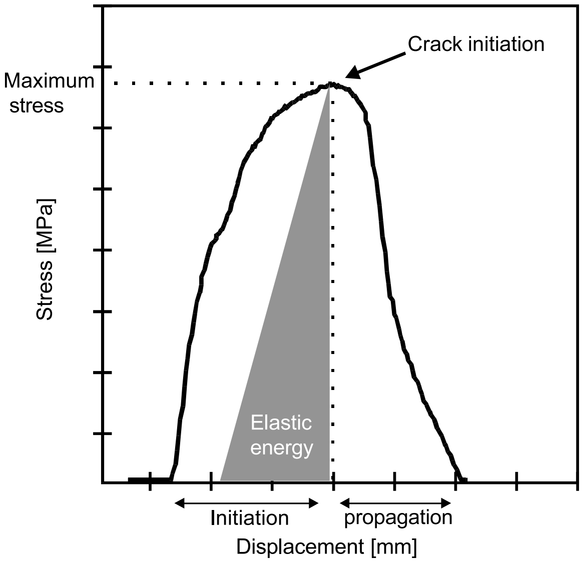

Fig. 2. Typical stress–displacement curve obtained by a SENT test.

and described previously [23]. 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.
Crack initiation displacement:	clamp displacement between the first point of force rise and the point of maximum force.
Crack 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 fivefold.

2.9. 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 used was 100 μm. The temperature indicated in one spot is an average temperature over the entire spot size. The temperature resolution of the camera was 0.15 °C, and the temperature range -20 to -300 °C. The spectral range was 8–14 μm and the image frequency 30 s^{-1}. Calibration was performed with samples of known temperature, with embedded thermocouples.

3. Results and discussion

The aliphatic polyketones with propylene incorporated into the backbone, are terpolymers with methyl groups attached to the main chain of the polymer. The polymers with higher olefins incorporated into the backbone, are terpolymers with longer side branches. These side branches give rise to changes of properties of the amorphous phase and they influence the degree of crystallisation of the polymer. Studied have been PK polymers with different amounts of propylene and PK polymers with different type of termonomers.

3.1. Aliphatic polyketones with different propylene content

A series of aliphatic polyketones was selected: no termonomer incorporated in the backbone of the polymer (PK-E), 3 mol% propylene (PK-EP-3) and 6 mol% propylene (PK-EP-6) were used as termonomer.

3.1.1. Differential scanning calorimetry

The results of the differential scanning calorimetry experiments are summarised in Table 2.

The melting temperature is lowered with propylene content. It is expected that at these low termonomer contents most of the termonomer will be present in the amorphous phase [9,10,14]. Therefore, it seems logical that the crystal lattice of the different polymers is little affected. This leads to the conclusion that the strong lowering of the melting temperature with only a few percent of propylene content is due to the decreasing crystal/amorphous ratio, and perhaps thinner crystal lamellae. The crystallinity decreases with propylene content from 48 wt% down to 34 wt% with introduction of only 6 mol% propylene in the polymer backbone. Obviously the methyl-group disturbs the crystallisation process. The T_c is lowered with increasing propylene content. However, the undercooling ($T_m - T_c$) is unaffected by incorporation of propylene at the expense of ethylene in the polymer backbone. The glass transition is the same for all three polymers and the melting temperature is lowered, consequently the window for crystallisation ($T_m - T_g$) is decreased significantly.

3.1.2. Dynamical mechanical thermal analysis

The dependence of the storage modulus and the loss modulus on temperature are shown in Fig. 3 for aliphatic polyketone terpolymers with different propylene content. The storage modulus decreases with temperature over the entire temperature range. Two major transitions can be observed, a glass transition near 15 °C and a melting temperature. The storage modulus (G') is lowered with increasing propylene content. The PK-E material has a significant higher modulus, which reflects its higher crystallinity. With propylene content the flow temperature (T_{flow}) decreases (Table 2). This correspond well with the trend in melting temperatures (T_m) found with DSC.

Table 2
Physical and mechanical properties of aliphatic polyketones

Polymer	Propylene content (mol%)	T_m (°C)	T_g (°C)	T_c (°C)	T_m-T_c (°C)	T_m-T_g (°C)	ΔH_m (J/g)	χ_c (wt%)	E (GPa)	σ_{yield} (MPa)	ε_{yield} (%)	σ_b (MPa)	ε_b (%)
PK-E	0	258	15	191	67	243	110	48	2.3	77	31	63	85
PK-EP-3	3	241	15	175	66	226	91	40	2.0	70	23	49	242
PK-EP-6	6	224	15	164	60	209	77	34	1.8	65	17	47	300

The loss modulus (G'') shows a peak at the glass transition. The glass transition temperature (T_g) is not significantly changed with increasing propylene content (Table 2). The methyl side branch of the propylene group lowers chain interactions and also decreases conformational possibilities. As the glass transition temperature remains practically unchanged, these two effects have apparently cancelled out.

3.1.3. Tensile properties

The tensile properties are shown in Table 2 for the series with different propylene content. All samples showed the characteristic necking behaviour of thermoplastics. The modulus decreases with increasing amount of propylene in the polymer backbone. The T_g is not significantly influenced by the introduction of propylene termonomer therefore the amorphous phase does not contribute largely to the change in modulus. The lowered stiffness is mainly due to the decreased crystallinity with increasing amount of propylene incorporated in the polymer chain. The yield stress is also decreased with increasing amount of propylene. This effect is also due to the lowering of the crystallinity. The yield strain is lowered with increasing propylene content. The fracture strain is increased when a larger amount of propylene is incorporated in the polymer backbone. The higher crystallinity of the PK-E material makes it more sensitive towards early fracture; this is caused by the enhanced yield stress, as plastic processes are suppressed, the crazing mechanism becomes operative.

The fracture stress is determined by the draw stress and decreases with increasing amounts of propylene in the polymer chain. The natural draw ratio was not reached for these polymers during the tensile test and therefore the fracture stress equals the draw stress.

3.1.4. Notched Izod impact

The notched Izod impact test is used to study the effect of temperature on the fracture energy under impact conditions. The notched Izod fracture energy is plotted as a function of temperature in Fig. 4. The impact energy increases with temperature for all materials up to a temperature of 70 °C. This reflects the larger mobility of the polymer molecules at elevated temperatures. At temperatures above 70 °C the impact energies start to decrease again, this effect is caused by incomplete fracture at elevated temperatures due to the lowered stiffness. The notched Izod impact energy is raised with propylene content. The yield stress was lowered with propylene content due to the lowered crystallinity. The glass transition was not changed with propylene content, thus the crystalline phase has a strong effect on the fracture behaviour. Below the glass transition temperature the differences in fracture energy between these polymers become negligible. The materials with a higher propylene content deform more easily upon loading. All fractures developed in a brittle manner, no shear yielding or stress whitening was observed. The fracture energy is raised

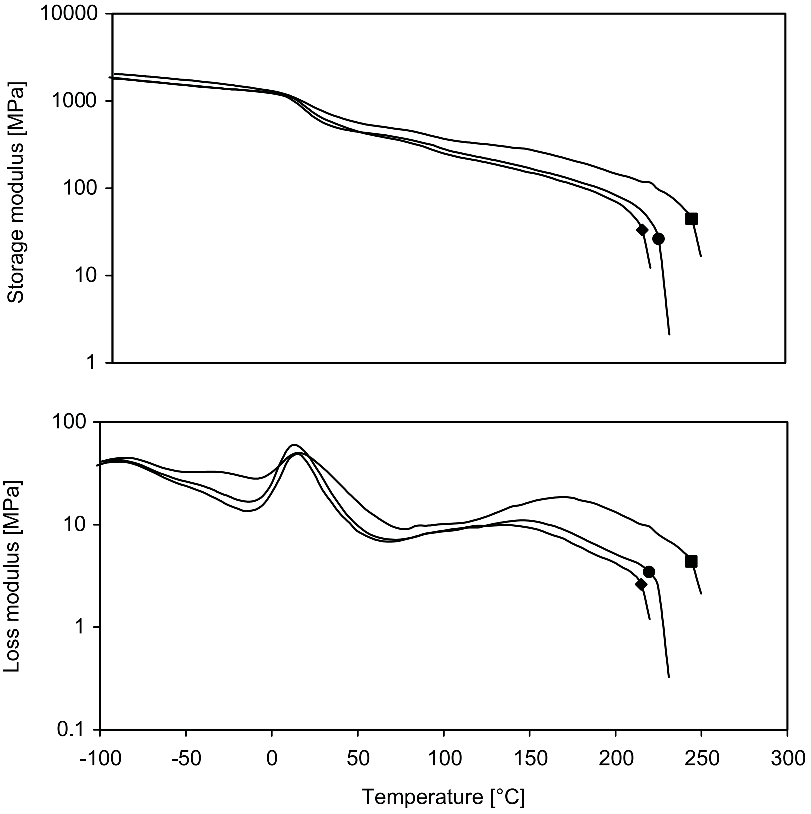

Fig. 3. Storage and loss modulus for aliphatic polyketones with different amounts of propylene in the polymer chain: ■, PK-E; ●, PK-EP-3; ♦, PK-EP-6; frequency 1 Hz, strain 0.1%, torsion mode.

because of the local deformation ahead of the notch tip, which increases with propylene content.

3.1.5. Single edge Notched tensile properties

The polymers with different propylene content have been evaluated in the SENT test. The maximum stress during the SENT test is shown in Fig. 5 as a function of temperature. The maximum stress decreases with increasing temperature for all these polymers. The yield stress of these polymers is significantly decreased when the temperature is raised. However, the yield stress is not always the dominant stress in the SENT test [23]. The trend in Fig. 5(a) is that the maximum stress is increased with propylene content. The yield stress was decreased with propylene content, which shows that the yield stress is not controlling the maximum stress. The crazing stress is more important together with the strain hardening responds of these polymers. The notch tip may also be more blunted before crack initiation by a local shear yielding zone. A blunted notch gives rise to a lower stress concentration ahead of the notch during crack initiation and therefore a higher macroscopic stress is needed to initiate a crack. The terpolymers with a higher propylene content, have lower yield stresses, which makes notch blunting more plausible.

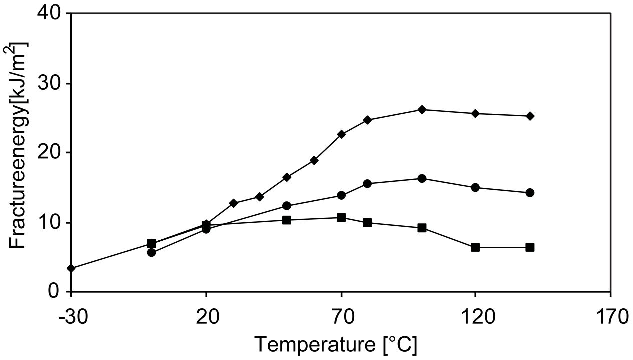

Fig. 4. Notched Izod impact values for aliphatic polyketones with different propylene content in polymer chain: ■, PK-E; ●, PK-EP-3; ♦, PK-EP-6.

3.1.5.1. Crack initiation. The crack initiation- and propagation displacements are given in Fig. 5. The initiation and propagation energy are not given, they hold no additional information because they are integrated from stress and displacement. The fracture energy is also given in Fig. 5(d).

The crack initiation displacement of the PK-E material is hardly effected by temperature (Fig. 5(b)). The PK-E polymer shows very brittle behaviour and therefore no brittle-to-ductile transition was observed. In the entire temperature range tested no energy to propagate a crack through the sample was observed for this material. The PK-EP-3 and PK-EP-6 polymers do show an increase in crack initiation displacement with temperature. The relative mobility of the polymer chains increases with temperature

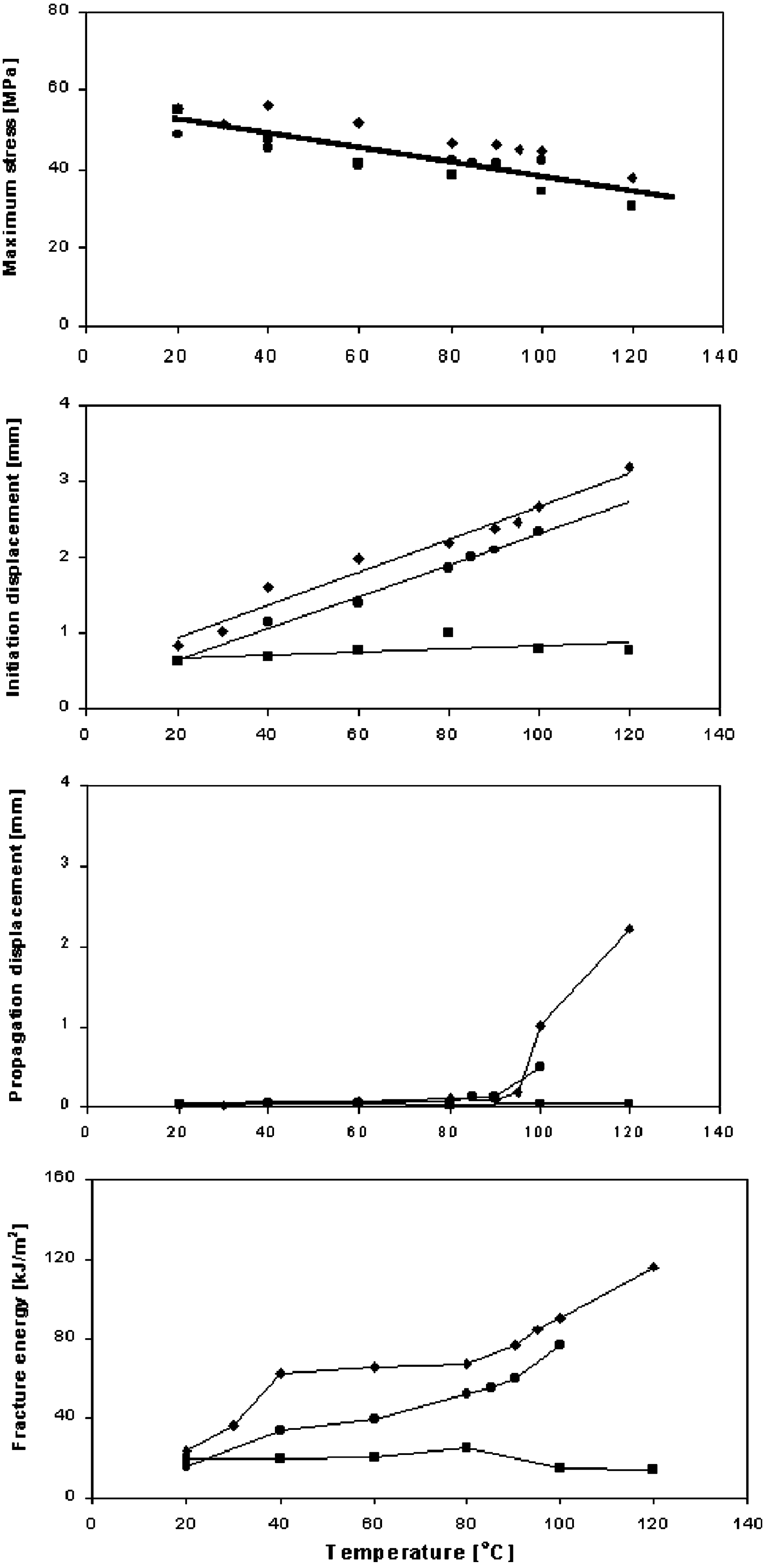

Fig. 5. Maximum stress, initiation- and propagation displacement and fracture energy for polyketones with different propylene content; SENT, strain rate 28.6 s^{-1}; ■, PK-E; ●, PK-EP-3; ◆, PK-EP-6.

and therefore the material can react more easily upon an applied load. The yield stress decreases with temperature, which results in more plastic deformation and more delocalisation of the deformation behind the notch, this raises the materials resistance towards crack initiation. The resistance versus crack initiation is increased with propylene content. This is due to the lowered crystallinity of the PK-EP materials. It was also shown in previous studies that the crystallinity decreases the resistance to crack formation [24,25].

3.1.5.2. Crack propagation. The crack propagation displacement of PK-E is close to zero over the entire temperature range (Fig. 5(c)). This polymer is not showing a transition from brittle to ductile behaviour. The polymer fractures in a completely brittle fashion at these conditions. The PK-EP-3 and PK-EP-6 material do show an increase in crack propagation displacement. The onset of ductility is approximately at the same temperature, but the PK-EP-6 polymer is clearly more ductile.

3.1.5.3. Fracture energy. The fracture energy is plotted as a function of temperature in Fig. 5(d). The fracture energy is strongly dependent on propylene content. The fracture energy increases with increasing propylene content. This is due to the lowered crystallinity of the PK-EP-3 and PK-EP-6 polymers. The lowered crystallinity leads towards a lower yield stress and this makes the plastic deformation more pronounced. When the plastic processes behind the notch tip are more delocalised the fracture energy is increased significantly. A remarkable difference with the notched Izod fracture energies is that at elevated temperatures the fracture energy is not decreased. In SENT the fractures are always complete, in Izod the samples may not fully be broken but partially bended due to the lowered modulus at elevated temperatures. Another parameter is the initiation part of the fracture process, which consumes more energy in the Single Edge Notched Tensile experiments compared to the notched Izod tests. It is remarkable that only a few percent of propylene as termonomer has such a strong effect on the toughness of these aliphatic polyketones.

3.2. Aliphatic polyketones with different termonomer length

The polymers with higher olefins incorporated into the backbone, are terpolymers with side branches. These side branches give rise to changes of properties of the amorphous phase and they influence the crystallisation process of the polymer. The altered properties may influence the fracture and deformation behaviour properties of the aliphatic polyketones. Therefore a polymer without a third monomer is investigated (PK-E) as well as polymers with different termonomer length (polymers with propylene, hexylene and dodecene units incorporated in the main chain). It was chosen to keep the crystallinity and melting temperature constant and therefore it was necessary to adept the amount of termonomer built in to the polymer chain. The termonomer concentration varied between 4 and 6 mol% (4.5–11.0 wt%, Table 1).

3.2.1. Differential scanning calorimetry

The results of the differential scanning calorimetry are summarised in Table 3.

The melting temperatures of the terpolymers with different branch length (at different concentrations) are equal and they have approximately the same crystallinity (T_m 224 °C and χ_c 34 wt%). The polymer without any branch attached to the backbone (PK-E), shows a higher melt temperature (257 °C) and a significant higher crystallinity (48 wt%).

The distance between the melting temperature and the glass transition is quite large compared to other polymers. Polypropylene has a similar T_g but a lower T_m (170 °C) which comes down to a ratio of T_g/T_m of 0.65. Nylon-6 has a ratio of 0.67 and PET has a ratio T_g/T_m of 0.68. This reflects the extraordinary crystal packing of polyketones in relation to their flexible backbone [8].

3.2.2. Dynamical mechanical thermal analysis

The dependence of the storage modulus and the loss modulus on temperature are presented for aliphatic polyketone terpolymers with different termonomer length in Fig. 6.

The storage modulus decreases with temperature over the entire temperature range. This decrease is somewhat faster when the material is passing its glass transition. The PK-E material shows a significant higher modulus, which reflects the higher crystallinity, due to the fact that there are no side branches present in this material. The storage modulus (G') is lowered with increasing termonomer length. The terpolymers have the same crystallinity, but a longer side branch lowers the storage modulus. This must be due to the increased mobility of the amorphous phase. The flow temperature of the PK-E polymer is high compared to the other materials. The loss modulus shows a peak at the glass transition. The glass transition temperature (T_g) decreases with increasing termonomer length. The PK-E and the PK-EP show equal T_g values. The methyl side branch of the PK-EP polymer is too small to lower the chain interactions significantly. The decreased chain interactions are cancelled out by the decreased conformational possibilities and the glass transition temperature is practically unchanged.

3.2.3. Tensile test

All samples showed the characteristic necking behaviour of thermoplastic materials. The tensile results are given in Table 3. The T_g as well as the crystallinity are given to characterise the different polymers.

The most important properties that are changed with the chain structure of the polymers are the young's modulus and the yield stress. Both the modulus and the yield stress decrease with increasing branch length. A higher T_g gives

Table 3
Physical and mechanical properties of aliphatic polyketones with different termonomers

Polymer	Termonomer	T_m (°C)	T_g (°C)	T_c (°C)	T_m-T_c (°C)	T_m-T_g (°C)	ΔH_m (J/g)	χ_c (wt%)	E (GPa)	σ_{yield} (MPa)	ε_{yield} (%)	σ_b (MPa)	ε_b (%)
PK-E	–	257	15	191	67	243	110	48	2.3	77	31	64	85
PK-EP	Propylene	224	15	164	60	209	77	34	1.8	65	17	47	300
PK-EH	Hexylene	224	10	180	44	214	79	35	1.6	62	31	55	86
PK-Edo	Dodecene	225	2.5	172	53	222.5	74	33	1.1	51	31	62	344

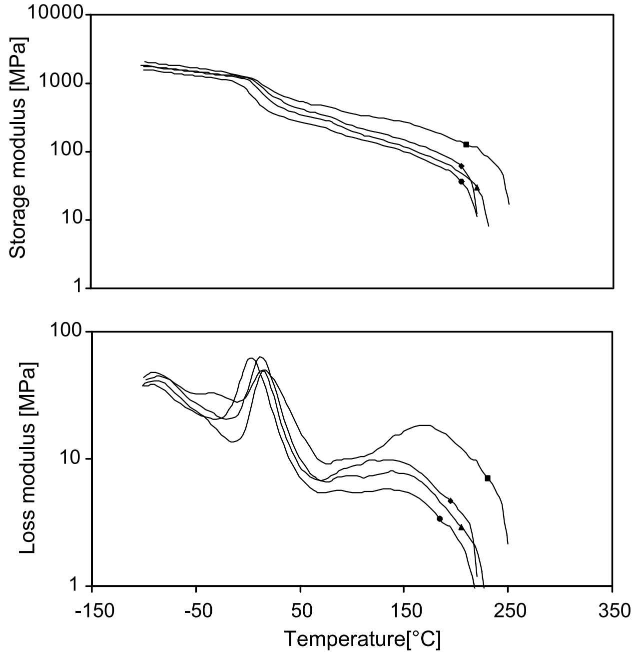

Fig. 6. Plots of storage and loss modulus as a function of temperature for different aliphatic polyketones: ■, PK-E; ♦, PK-EP; ▲, PK-EH; ●, PK-Edo; frequency 1 Hz, strain 0.1%, torsion mode.

rise to a higher yield stress and modulus. The effect of introducing a side branch onto the polymer backbone on the yield stress and modulus is shown in Fig. 7.

The material's tensile properties can thus be influenced significantly by the introduction of a third monomer. A higher olefin as termonomer will lower the yield stress and stiffness of the polymer.

3.2.4. Notched Izod impact test

The Izod impact energy is plotted as a function of temperature in Fig. 8. The impact energy increases with temperature for all materials up to a temperature of 70 °C. At temperatures above 70 °C the impact energies start to decrease again; this effect is caused by incomplete fracture at elevated temperatures due to the lowered stiffness. The general trend observed in Fig. 8 is that the impact resistance is strongly raised for polymers with higher olefins as termonomer. These materials deform more easily upon loading. This is mainly due to the lowered yield stress of these types of terpolymers. The deformation of the material takes place in a more delocalised manner and consequently the plastic processes behind the notch tip absorb more energy upon fracture.

3.2.5. Single edge notched tensile (SENT) test

The maximum stress is plotted as a function of temperature in Fig. 9(a). The polymers with different olefins used as termonomer do not show large differences in terms of maximum stress. The stress is lowered with increasing

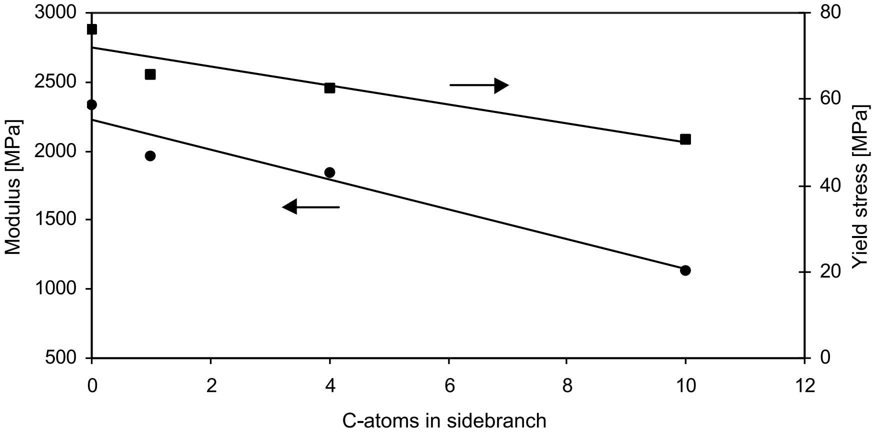

Fig. 7. Yield stress and modulus as a function of branch length, 60 mm/min, $T=20$ °C.

temperature as can be expected. The yield stress and the fracture stress are both lowered with increasing temperature.

3.2.5.1. Crack initiation. The crack initiation displacement and crack propagation displacement are plotted as a function of temperature in Fig. 9(b). The energy data give the same trends and therefore only the displacement values are given here. The PK-E material has significant lower crack initiation displacements over the entire temperature range. The PK-E polymer shows very brittle behaviour and no transition from brittle to ductile behaviour was observed. An increase in crack initiation displacement with temperature was found for the materials with higher olefins built in the polymer chain. The yield stress decreases with temperature, which results in more plastic deformation and more delocalisation of the deformation ahead of the notch, this raises the materials resistance towards crack initiation.

3.2.5.2. Crack propagation. When the fracture process develops in a brittle manner the crack propagation displacement is close to zero. The onset of propagation displacement is regarded as a marker for the brittle-to-ductile transition (Fig. 9(c)). The PK-E polymer shows no increase in propagation displacement in this temperature regime. The other materials show a clear brittle to ductile transition temperature. The T_{bd} is decreased with increasing branch length. This is a consequence of the greater mobility of the amorphous phase, which lowers the yield stress of the polymer. A second effect is the greater amount of material participating in the plastic processes ahead of the notchtip.

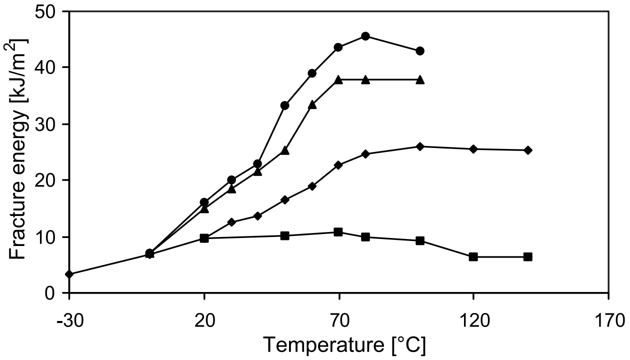

Fig. 8. Notched Izod impact energy as a function of temperature for polyketones with different side branch length: ■, PK-E; ◆, PK-EP; ▲, PK-EH; ●, PK-EDo.

3.2.5.3. Fracture energy. The PK-E material shows very low fracture energy in the entire temperature range, no ductile fracture behaviour was observed (Fig. 9(d)). This material has a higher crystallinity. The higher crystallinity leads to an increased stiffness and yield stress and lowers the resistance to fracture. For the other three materials the difference in fracture energy was small in the brittle regime. The crack initiation data were very similar for these polymers. When the fracture starts developing in a ductile manner, above the T_{bd}, the fracture energy depends strongly on the crack propagation energy (Fig. 10).

The T_{bd} is clearly decreased with termonomer length. The large step from the PK-E polymer towards the PK-EP polymer is due to the higher crystallinity of the PK-E material. Based on the glass transition the T_{bd} of the PK-E polymer would be lower and just slightly higher than that of the PK-EP material. (T_g PK-E: 16 °C, PK-EP: 15 °C).

Fig. 11 shows the efficiency of toughening the aliphatic polyketone polymer by two methods; by altering the chemical structure of the terpolymer and by the addition of a cavitating rubber phase. The lowering of the brittle-to-ductile transition temperature is plotted as function of the reduction of modulus. A reduction of stiffness leads towards more tough polymers in both cases. The toughening with addition of cavitating rubber particles is, however, much more effective compared to copolymerising the polyketone polymer. The modulus is less compromised by addition of

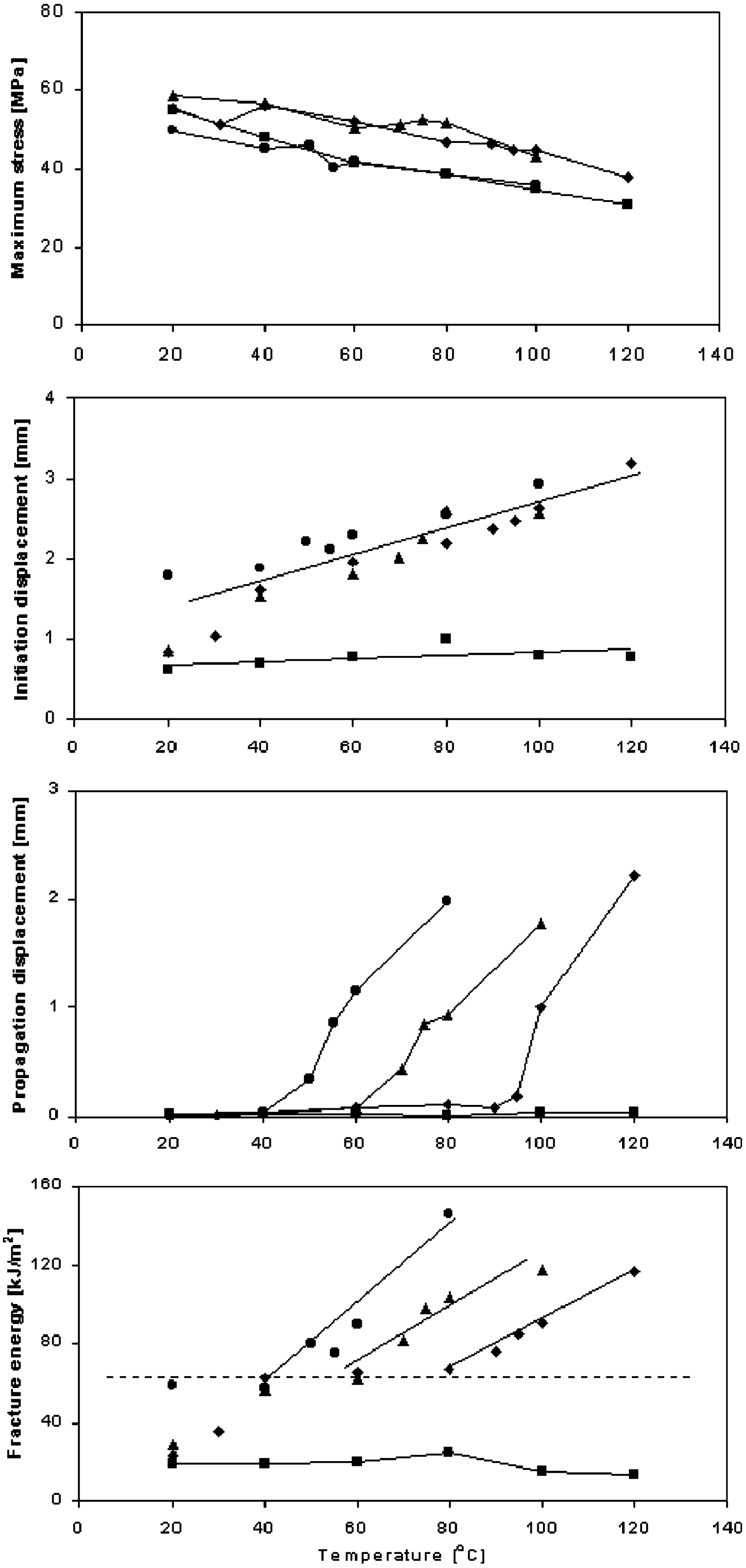

Fig. 9. Maximum stress, initiation- and propagation displacement and fracture energy as function of temperature; SENT, 28.6 s^{-1}; ■, PK-E; ♦, PK-EP; ▲, PK-EH; ●, PK-Edo.

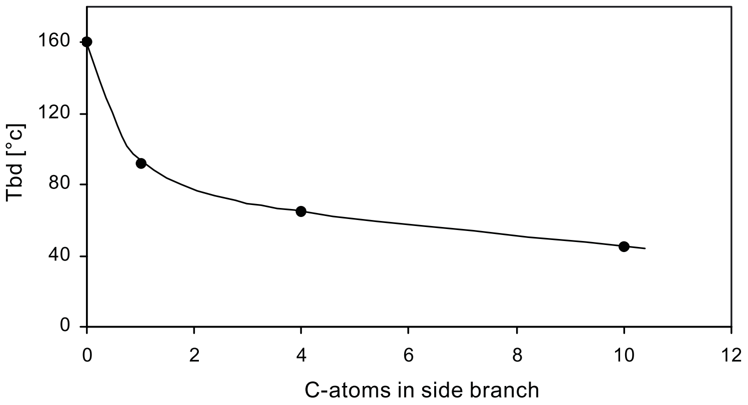

Fig. 10. The brittle-to-ductile transition temperature as function of branch length. Data from SENT test, strain rate 28.6 s^{-1} (test speed 1 m/s).

rubber particles at the same level of toughening. The addition of a rubber phase leads towards a change in fracture mechanism in polyketone terpolymers [26] whereas the copolymerisation does not.

3.3. Infrared thermography

It is known that when polymers are subjected to high strain rates, the deformation process may become (partly) adiabatic. The plastic processes may in that case give a strong temperature rise of the material. This can have large consequences for the fracture process in terms of strain softening and thermal blunting. To monitor the temperature development during fracture an infrared camera was used. Fig. 12 shows the neck profile for the polyketone terpolymers with different side branch length in a tensile test. The PK-Edo does not show significant necking behaviour. The deformation develops more or less homogeneously. The temperature rise at these moderate strain rates is quite high, the temperature is raised to 70 °C for the PK-EP polymer. The temperature of the polymers with a longer side branch is somewhat lower (60 °C). The localisation of the plastic process is reduced for these polymers. This behaviour is characterised in the shape of the neck that develops in an engineering tensile test. When softening is reduced the local strain rate is reduced. The heat that is generated is fairly unchanged but the cooling factor increases due to the increased time scale. The stresses that are developed during the tensile test are also lower for the polymers with longer side branches, due to the lowered yield stress.

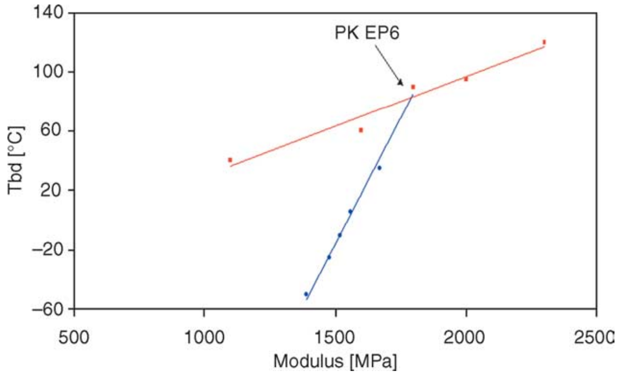

Fig. 11. The brittle-to-ductile transition temperature as function of modulus; ■, PK-terpolymers; ●, rubber toughend polyketone polymers.

Also studied was the temperature development in a SENT sample for the different terpolymers. The effect of a lower glass transition temperature is clearly visible, the yield stress is decreased and the softening behaviour is reduced. As a consequence the plastic zone size ahead of the notch tip is increased and the material displays more ductile behaviour (Fig. 13). The delocalised fracture behaviour contributes largely to the increased fracture energy. The temperatures are not significantly different (PK-EH: 106 °C and PK-EDo: 104 °C). The PK-EP polymer shows a somewhat lower temperature of the plastic zone but this is mainly due to the lack of deformation during the fracture process in this material.

4. Conclusions

Polyketone terpolymers were studied as model copolymer systems to gain insight in the structure property relations of polymers. The thermal and mechanical properties of aliphatic polyketones can be adjusted by incorporation of only a few mol percent of termonomer in the polymers main chain. The crystallinity, the yield stress and modulus were lowered with increasing propylene content. The notched impact resistance was increased strongly. The larger deformability due to the lowered crystallinity causes the fracture energy to increase significantly. The terpolymers with higher olefins showed a lower glass transition temperature (T_g) compared to the copolymer of ethylene and carbon monoxide. The T_g decreased with increasing length of the termonomer. The yield stress and modulus were lowered with longer side branches. Since the crystallinity was kept constant, this lowering must be attributed to larger

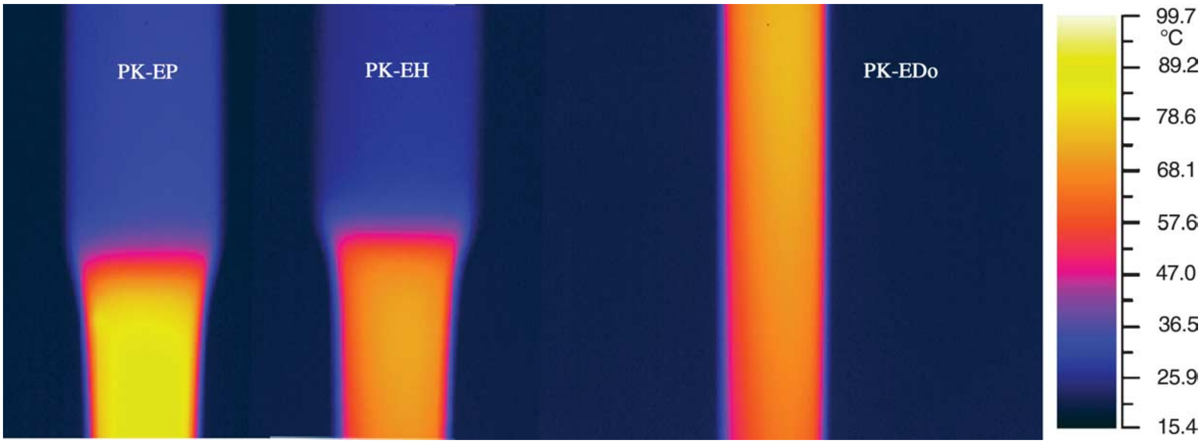

Fig. 12. Neck profiles for different polyketone terpolymers, PK-EP; PK-EH and PK-Edo; ambient temperature 20 °C, strainrate 1.25×10^{-3} s^{-1}, (test speed 60 mm/min).

flexibility of the amorphous phase, a larger free volume. The impact resistance was strongly increased with higher olefins as the termonomer. The brittle-to-ductile transition temperature lowered significantly with increasing length of the termonomer. Thus by adding termonomers to aliphatic ketones, the notched impact behaviour can be improved significantly but by sacrificing the modulus and yield stress.

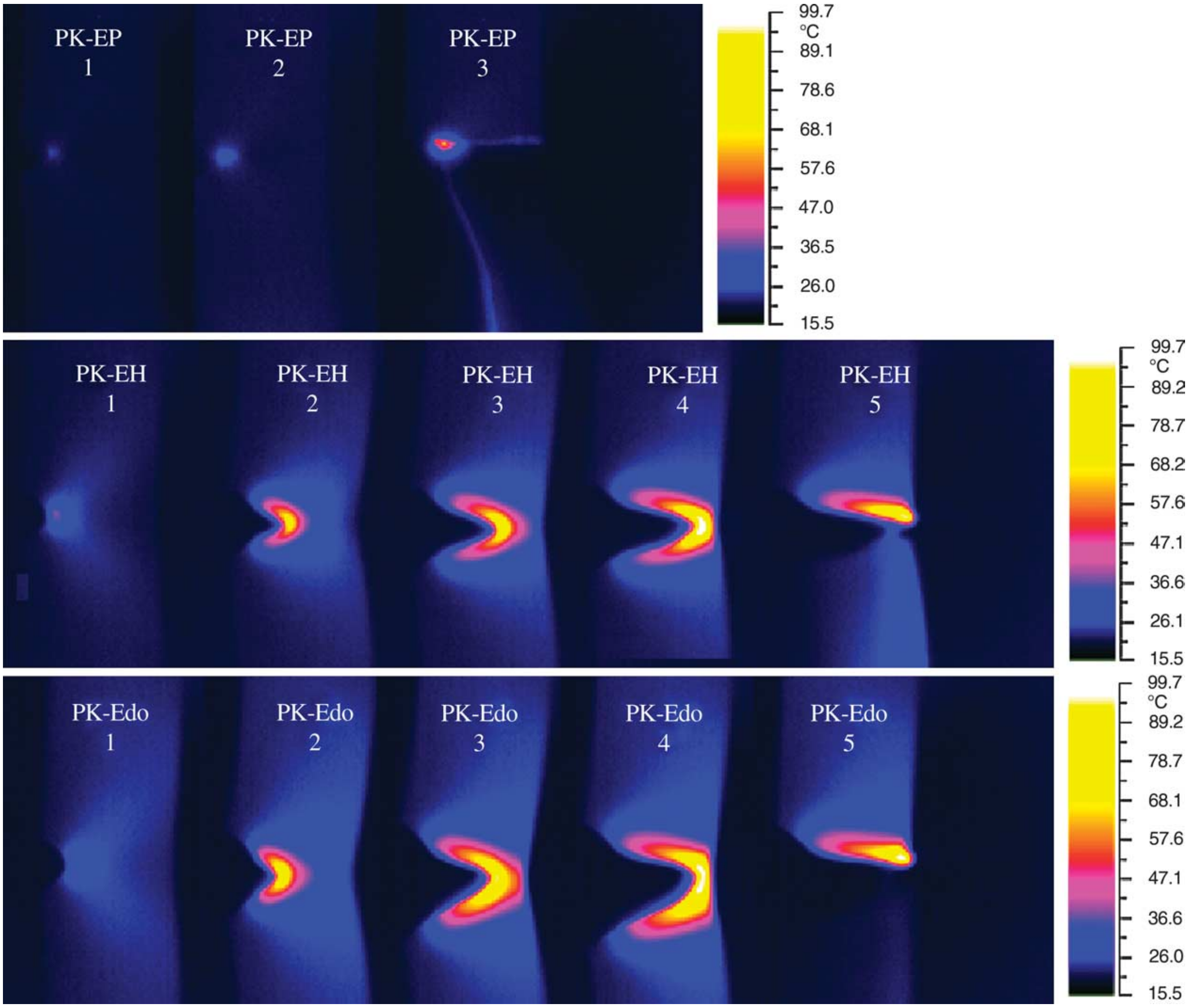

Fig. 13. Infrared images of single edge notched tensile samples of different PK-terpolymers; strain rate 2.9×10^{-2} s^{-1} (test speed 10^{-3} s^{-1}), ambient temperature 20 °C.

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