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The effect of random branching on the balance between flow and mechanical properties of polyamide-6

Paul Steeman*, Atze Nijenhuis

DSM Research, SRU-PM, P.O. Box 18, 6160 MD Geleen, The Netherlands

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ABSTRACT

The rheological and mechanical properties of a series of linear and randomly branched polyamide 6 samples, with varying molar mass and varying degree of moderate branching, have been investigated.

As expected, it was found that random long-chain branching has a pronounced effect on the rheological behaviour of the materials in both shear and extensional flow. The zero shear viscosity increases with branching while the flow curve becomes more shear thinning. Randomly branched materials have an enhanced melt strength in elongational flow. Although branched, the materials show perfect melt stability in their rheology.

The mechanical properties show minor differences between the linear and the moderately branched samples and are mainly dependent on the weight average molar mass. A small increase in modulus, yield stress and failure stress and a decrease in the strain at break are found, which is probably due to increased molecular orientation in the plane of injection moulding. The IZOD impact strength is similar to what is normally found for linear polyamide-6, and independent of branching. Also the fracture toughness K_{IC} is not affected by the incorporation of random branching. However, it is clearly dependent on the weight average molar mass.

By using random branched polyamide-6, molecular weights and related mechanical properties can be obtained that are out of reach for linear polyamide-6.

1. Introduction

It is well established that branching of polymeric chains has a large influence on the rheological properties of their melts [1,2]. Short chain branching often results in a decrease of the zero shear viscosity because of the more compact polymer chains. In literature the use of dendritic and hyperbranched poly(ether)amides to lower the viscosity of polyamide 6 has been reported [3,4]. By contrast, long chain branching results in an increase of the zero shear viscosity, accompanied by elastic effects due to the slower stress relaxation of the branches [5,6]. Moreover, long chain branching results in strain hardening during extensional flow. These rheological effects have been confirmed by a large number of experimental studies on the behaviour of star-like, comb-like and randomly branched polymers [7–15]. Especially for polyolefines, many studies have reported on well-designed long-chain branched polymeric chains, synthesized using metallocene catalysts. Linear polypropylene is known to have a low melt strength which can be enhanced by blending with long chain branched polypropylene [16,17], tough issues with limited miscibility of linear and long-chain branched polypropylenes have been reported [18]. For shaping of a product its rheological properties are very important. However, for practical end use good mechanical properties are a prerequisite. Therefore, a good balance between processability and mechanical properties of the solid material is required. Upon optimising the processability of polymeric materials often a loss in mechanical properties results. For instance, in reducing the molar mass to obtain a lower viscosity, also a drop in fracture toughness occurs. In the literature some studies have reported on the effect of molecular architecture, especially branching, on the mechanical properties. Han et al. [19,20] studied the effect of molecular topology on the crazing mechanisms in glassy polymers. They found that the drawing behaviour of linear and star polystyrenes is independent of molecular weight and molecular topology at temperatures below the glass transition. At higher temperatures the transition from chain scission to disentanglement crazing is slightly affected by the topology. However, in all cases brittle fracture due to crazing occurs. In an IUPAC study [21] of linear and branched polycarbonate of equal weight average molar mass it was concluded that the brittle–ductile transition temperature of

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* Corresponding author. Tel.: +31 464761629; fax: +31 464767569.
E-mail address: paul.steeman@dsm.com (P. Steeman).

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branched materials is higher than that of the linear type. It is concluded that branching of amorphous polymers, at equal molar mass, results in more brittle materials.

In the case of semi-crystalline materials it is to be expected that the influence of molecular weight and chain branching on modulus and yield stress is indirect, because of the semi-crystalline morphology involved. For polypropylene it has been reported that the presence of a fraction of long chain branched polymeric chains results in enhanced flow induced crystallization with increased orientation in the flow direction [22] and a morphology showing finer and more numerous spherulites [18]. Consequently, the solid-state mechanical properties are affected. E.g. dynamic mechanical properties have been reported to show broadened and more complex relaxation behaviour [23,24] while the large strain mechanical properties showed a higher tensile modulus and yield stress [25]. Finally, upon using long chain branched polyolefin elastomers as impact modifier for polypropylene copolymers an enhanced toughening effect has been reported [26].

For star-branched polymers it has been shown that a significantly lower viscosity in the melt and in solution can be obtained. However, the solid-state mechanical properties of these materials have only been very limited reported [27]. It is known [1] that star-branched polymers do not give enhanced performance in elongational flow because their behaviour at large strains is comparable to that of linear chains. Arm retraction is not hindered by the presence of a single branch point, thus resulting in fast stress relaxation. By contrast, the shear viscosity is strongly affected by the presence of star-branched chains [28]. An improvement of the elongational flow behaviour can only be obtained with multiple branch points in the polymeric chain.

In the case of industrially synthesized polycondensates such as polyamide 6 it is only very limited possible to make well-designed/regular branched polymeric chain architectures because of the intrinsic random nature of the polycondensation process and the risk of gelation. However, *random* branching can be introduced via the addition of multi-functional monomers to the reaction mixture. It was the purpose of this work to investigate and report the effect of such random branching on the balance between processability and mechanical properties of polyamide-6.

2. Experimental

2.1. Polymerisation

Polymerisations were carried out in a 20-L autoclave. Seven different grades, consisting of 3 linear polymers and 4 branched polymers, were made in batches of 10 kg. Each grade was polymerised twice resulting in a combined 20 kg of virgin polymer.

At 95 °C the autoclave was charged (amounts are listed in Table 1), put under vacuum and subsequently purged with nitrogen. This vacuum/nitrogen cycle was repeated 3 times after which the autoclave was sealed. The stirred reaction mixture was kept for 1 h at 95 °C until it was molten. At this point the reaction mixture was heated over a 3 h period to 270 ± 10 °C. During the heating period the pressure increases to a final 0.5 MPa (5 bar). In 2 h the pressure was let down to 0.1 MPa (1 bar or atmospheric pressure). The polymerisation at 270 °C was stopped when the stirrer torque reached 50 N m (on average 5 h after the start of the reaction). The polymer was discharged at an over-pressure of 0.6 MPa (6 bar). The melt was quenched in a water bath and the obtained string was granulated.

After washing the polymer under running water of 95 °C some 17 kg per grade remained. The polymers were post-condensated during 12 h in a 170 L tumble dryer at 190 °C under vacuum with a small nitrogen-purge.

Table 1
Composition of the different charges. The base load of each charge was 10 kg of caprolactam and 0.1 kg of aminocaproic acid and initially 100–200 g water as initiator for the caprolactam polymerisation. (BA = benzoic acid, HMDA = hexamethylene diamine, TCAM = paste of 50w/w% water and 50w/w% tris-caproic acid melamine available as Irgacor L190 from CIBA).

Material	BA (g)	HMDA (g)	TCAM (g)	Estimated number average number of branch points/chain[a]
Linear 1	54.45	0	0	0
Linear 2	27.22	0	0	0
Linear 3	0	0	0	0
Branched 1	54.45	25.89	208.86	0.37
Branched 2	21.78	10.35	83.54	0.21
Branched 3	36.30	25.89	208.86	0.48
Branched 4	27.22	19.41	156.65	0.38

[a] The estimated average number of branch points per chain was calculated from the monomer composition and corrected for the conversion as estimated from the measured M_w using the Macosko/Miller theory.

2.2. Materials

Branched polymers were obtained by adding the specified amounts (Table 1) of 1.6-hexane diamine and tri-functional 6,6′,6″-(1,3,5-triazine-2,4,6-triyltriimino)tri-hexanoic acid [80584-91-4] (TCAM) as branching agent in an exact 1:1 M ratio at the start of the polymerisation. The amounts of HMDA and TCAM used in the recipes theoretically introduce (at full conversion) on average 0.5 (branched 1 and 2) and 0.75 (branched 3 and 4) branch points per polymeric chain. Molar mass control and melt stability was obtained by using mono-functional benzoic acid as chain stopper. The third linear material was prepared without chain stopper in order to achieve the highest possible molecular weight/melt viscosity.

After post condensation and drying the granules of the materials were stored in sealed laminated bags. SEC, DSC and rheological experiments were performed on these granules. For the mechanical evaluation, sample plates (100 × 100 × 1.8 mm) and K_{IC} compact tension specimen were injection moulded using standard polyamide-6 conditions. In order to study the effect of flow orientation on the mechanical properties the test specimen for tensile and IZOD testing were machined from the sample plates both parallel and perpendicular to the flow direction of injection moulding.

2.3. Characterisation

The molar mass distributions of the materials were determined with size exclusion chromatography (SEC). The measurements were performed in HFIP (hexafluorisopropanole) at 35 °C. A Hewlett Packard 1090 chromatograph, equipped with a HP1047A refractive index (RI) detector and a Viscotec H502 differential viscosimeter (DV) was used at a flow rate of 0.4 ml/min. The universal calibration method was applied, with an internal DSM calibration standard for polyamide-46. Electrolyte effects were suppressed by adding an appropriate amount of potassium-trifluoracetate salt.

DSC measurements were performed under nitrogen with a Perkin Elmer DSC-7 according to the ISO-DIS standard 11357-2/3, with a scan speed of 10 °C/min in the temperature interval between 50 °C and 250 °C. The peak melting temperature and the heat of fusion were extracted from the second heating curve. Prior to the measurements the materials were dried at 80 °C in vacuum.

The rheological properties of the materials were studied with various techniques. Dynamic mechanical measurements on the melt were performed with a Rheometric Scientific RMS800 dynamic mechanical analyser equipped with a 25 mm diameter parallel plate geometry. Granules of the materials were loaded into the rheometer and molten to a 1.8–2 mm thick sample. After 5 min melting and equilibration in the rheometer at 230 °C (about 10 °C above the melting temperature), frequency scans were performed at angular frequencies between 0.1 and 100 rad/s. The frequency scans were repeated after 10 and 15 min residence time in the melt and confirmed the expected very good melt stability. Capillary extrusion experiments were performed with a Göttfert Rheograph 2002 equipped with a 30/1 (mm/mm) round die capillary, again at a melt temperature of 230 °C. Finally, the behaviour of the melts in uniaxial flow at 230 °C was studied by melt spinning with a Göttfert Rheotens, installed below the die exit of a Rheograph 2000, equipped with a 30/1 (mm/mm) capillary and running at an extrusion speed of 5.3 mm^3/s. The lower detection limit of this instrument for the drawing force is about 0.2 cN.

The solid-state mechanical properties of the materials were determined at room temperature. Tensile measurements were performed on standard ISO 527-1A specimen with a Zwick 1455 tensile tester. The modulus was determined with a test speed of 1 mm/min, at strains between 0 and 1%. The large strain properties were determined using a test speed of 20 mm/min. The IZOD notched impact strength was determined according to the ISO 180 notch 1A standard with a 2.75 J hammer. The specimen dimensions were 80 × 10 × 2.7 mm. Finally, the fracture toughness of the materials was determined by measuring the critical stress intensity factor K_{IC} on injection moulded compact tension blocks, according to the ESIS protocol of October 1989. The thickness of the blocks was 19 mm and the width 37 mm. The samples were pre-cracked with a razor blade, which was pushed slowly into the sample with a vice.

3. Results

3.1. Polymerisation

All polymerisations went smoothly. The time to reach a torque of 50 N m (at 270 °C) was on average significantly shorter for the branched polymers as compared to the linear polymers (3.5 h vs. 5.5 h).

3.2. Molecular characterisation

Table 2 contains some characteristic moments of the molar mass distribution of the various materials as determined with SEC-DV. Compared to the linear polymers the branched samples show a clearly broadened molecular weight distribution, both in M_w/M_n and in the high molecular weight tail as can be seen from the M_z/M_w values. The M_w range of the linear samples covers the M_w range of the branched materials, thus enabling a study of the effect of random branching. Table 2 also contains the Mark–Houwink coefficient obtained from the slope of the viscosity vs. molar mass curve (DV detector) and the intrinsic viscosity $[\eta]$ of the polymer as a whole as calculated from the DV results by summing over the various fractions. It can be noted that the branched samples have lower values for Mark–Houwink coefficient and a lower intrinsic viscosity in comparison with the linear materials of equal M_w. This cannot be attributed to the broadening of the molecular weight distribution and shows that the molecules of the branched materials have a smaller hydrodynamic volume in comparison with the linear materials of comparable M_w. It is concluded that indeed significant branching is present in the polymeric chains of the branched recipes.

Table 2
Moments of the molar mass distributions, the Mark–Houwink coefficient a, and the intrinsic viscosity $[\eta]$ of the polyamide 6 samples.

Material	M_w [kg/mol] ±5%	M_w/M_n ± 7%	M_z/M_w ± 10%	a Mark–Houwink	$[\eta]$ ± 5%
Linear 1	25	2.5	1.8	0.68	1.14
Linear 2	36	2.8	2.0	0.68	1.50
Linear 3	54	2.5	2.0	0.68	1.82
Branched 1	40	3.4	2.3	0.48	1.31
Branched 2	52	3.3	2.3	0.48	1.68
Branched 3	56	3.9	2.6	0.44	1.61
Branched 4	56	3.5	2.4	0.48	1.64

3.3. Thermal analysis

Table 3 contains the thermal properties of the samples as determined from the second heating run. The DSC trace was integrated with a linear base line between 80 °C and 235 °C.

Within the accuracy of the measurements – comparing materials of equal molar mass – no effect of branching on either the melting point or the heat of fusion can be detected. It is concluded that the low amount of branching incorporated does not significantly affect the crystallinity of the materials. Based on the amount of co-monomer and assuming complete exclusion of the co-monomer from the crystalline phase a decrease of the melting point of at most 0.5 °C is expected. Clearly, the molecular weight has a significant influence on T_m.

3.4. Rheological properties: shear rheology

In Fig. 1 the results of the dynamic mechanical analysis on the samples are depicted as a function of the angular frequency ω. Both the dynamic viscosity η_d (solid lines) and the phase angle δ (dashed lines) were included.

Three groups of flow curves can be clearly distinguished: *Firstly:* the lowest molar mass sample linear 1, *secondly:* the medium molar mass sample linear 2 and the branched sample 1 and *thirdly:* the highest molar mass sample linear 3 and the branched samples 2–4. The phase angle curves clearly display the differences in viscoelastic behaviour amongst the materials. The linear samples show at the lowest frequencies a Newtonian plateau in the viscosity where the phase angle approaches 90° (liquid behaviour). As expected, this plateau shifts to lower frequencies with increasing molecular weight. The branched material with the lowest molecular weight (sample branched 1) shows from its phase angle viscoelastic behaviour similar to the highest molecular weight linear material (sample linear 3), although with a lower viscosity. The other branched materials (samples branched 2–4) display an even more viscoelastic behaviour (lower phase angles) which seems to be composed of two relaxation processes and a transition between these two in the frequency range from 1 to 10 rad/s.

The branched materials are clearly much stronger shear thinning than the linear materials, which also sets in at lower frequencies. Thus, with equal zero shear viscosity (e.g. branched 1 vs. linear 2), the branched material has a much lower viscosity at

Table 3
2nd heating run melting temperature and heat of fusion of the polyamide 6 samples.

Material	T_m ± 0.5 [°C]	ΔH ± 3 [J/g]
Linear 1	221.6	89
Linear 2	220.1	91
Linear 3	218.6	79
Branched 1	220.1	88
Branched 2	219.4	88
Branched 3	219.2	81
Branched 4	218.8	78

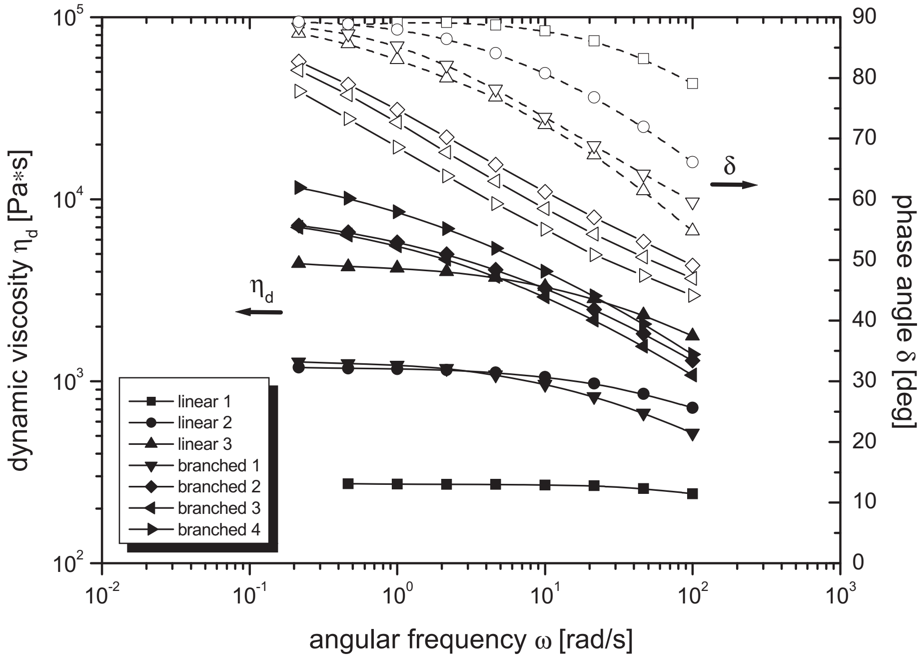

Fig. 1. The dynamic viscosity and the phase angle of the linear and branched polyamide samples at 230 °C as a function of the angular frequency.

high shear rates, as important for processing. Similarly, a branched material with comparable viscosity at high shear rates has a much higher zero shear viscosity (e.g. branched 4 vs. linear 3) which is e.g. advantageous in those cases when stability against sagging under gravity is required. These observations are confirmed from the flow curves at high shear rates (Fig. 2) determined with capillary rheometry. Also at high rates the branched materials are much more shear thinning than the linear materials.

Table 4 contains the values of the dynamic viscosity at $\omega = 1$ rad/s (from dynamic measurements), the steady state viscosity at $\dot{\gamma} = 10^4\ \text{s}^{-1}$ (from capillary rheometry) and their ratio. The enhanced shear thinning as discussed can be clearly observed.

3.5. Rheological properties: extensional rheology

The behaviour of the materials in uniaxial flow was investigated by melt spinning the material exiting the die of the capillary rheometer. A curve of the melt extension rate versus the force is obtained. Table 5 contains the maximum draw ratio and the melt strength determined for the polyamide samples. The melt strength is the force on the melt at break.

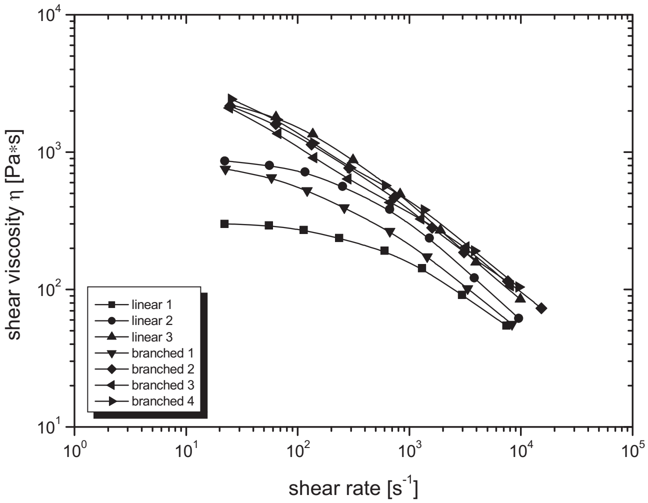

Fig. 2. The steady state viscosity of the linear and branched polyamide samples at 230 °C as a function of the shear rate.

The maximum draw ratio of the materials could not be determined because the materials tended to wrap around the wheels of the melt-spinning device. However, in all cases a plateau force was obtained before these problems emerged. From the data is it found that the melt strength increases with molar mass (increasing viscosity) and is significantly enhanced by random branching. The latter is most probably due to the well known strain hardening effect because of long chain branching, as has been reported for LDPE [2].

3.6. Mechanical properties: deformation behaviour

The deformation behaviour of the polyamide-6 materials was studied by stress–strain measurements in tension. Fig. 3 shows a set of five measurements on the linear polyamide-6 of the highest molar mass, parallel to the direction of injection moulding. These results are representative for the results on all samples. The materials yield at a strain of 4–5% after which solid-state flow occurs while the samples deform uniformly. Up to 15–20% strain the curves are well reproducible. Above this strain range the deformation localises and finally the sample fails.

Because of the localisation, the engineering stress and strain (as determined from the initial test bar dimensions) are not representative for the true stress and strain of the material in the

Table 4
The dynamic viscosity at 1 rad/s, the steady shear viscosity at 10^4 s^{-1} and their ratio at 230 °C.

Material	M_w ± 5% [kg/mol]	η_d [1 rad/s] ± 5% [Pa s]	η_s [10^4 s^{-1}] ± 5% [Pa s]	Shear thinning ratio η_d/η_s
Linear 1	25	270	46	6
Linear 2	36	1200	60	20
Linear 3	54	4200	84	50
Branched 1	40	1200	50	25
Branched 2	52	5800	96	60
Branched 3	56	5600	92	61
Branched 4	56	8500	100	85

Table 5
The maximum draw ratio and melt strength of the polyamide 6 samples.

Material	Draw ratio [−]	Melt strength ± 0.1 [cN]
Linear 1	>30	<0.2
Linear 2	>30	0.2
Linear 3	>30	0.4
Branched 1	>30	<0.2
Branched 2	>30	0.6
Branched 3	>30	0.9
Branched 4	>30	1.0

localised region. The reproducibility of this part of the engineering curves is bad, mainly due to the differences of the neck location as compared to gauge location (in, out, overlap), and detection of accurate failure parameters (stress and strain at break) impossible. It is believed that the material behaviour itself is reproducible. As an indication of the *onset of failure* we determined the failure point from the intercept between to straight lines, one drawn through the flow plateau (after yielding) and the other through the (down-curved) part after localisation occurred.

Table 6 contains the tensile modulus of the linear and branched materials, both perpendicular and parallel to the flow direction of injection moulding, as determined between 0 and 1% deformation. The tensile modulus of the branched polyamide-6 materials is 10–15% higher than the modulus of the linear materials, and becomes slightly dependent on the direction. For the branched materials the tensile modulus perpendicular to the flow direction of injection moulding is higher than parallel, which might result from the fountain flow. These effects are small but significant within the accuracy of the measurements.

Table 7 contains the yield stress and strain of the linear and branched materials, both perpendicular and parallel to the flow direction of injection moulding. The yield stress of the branched polyamide-6 materials is again significantly higher than the value for the linear materials, with a minor loss in yield strain. Both parameters are hardly direction dependent.

Finally, Table 8 contains the ‘onset of failure’ stress and strain of the linear and branched materials, both perpendicular and parallel to the flow direction in injection moulding. The ‘onset of failure’ stress of the branched polyamide-6 materials is again up to 15% higher than the value for the linear materials, accompanied by a loss in ‘failure’ strain. Within the accuracy of the measurements, both parameters are hardly direction dependent.

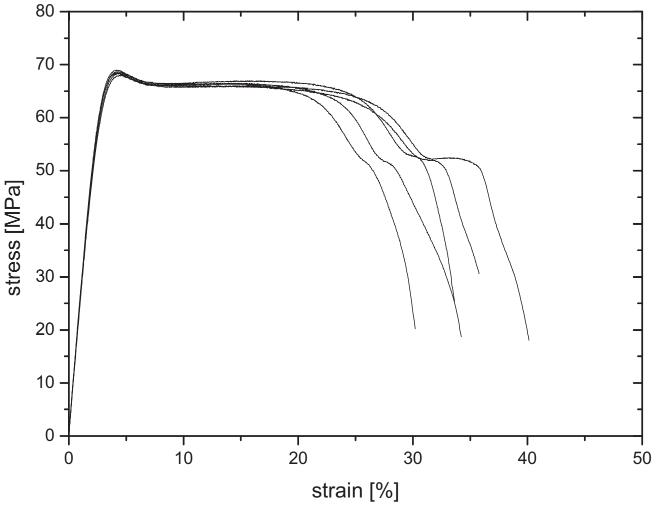

Fig. 3. A series of five stress–strain curves obtained for the sample linear 3, which shows the typical variations in the results as observed for all linear and branched polyamide-6 materials.

Table 6
The tensile modulus parallel and perpendicular to the flow direction in injection moulding, respectively.

Material	M_w ± 5% [kg/mol]	$E_{//}$ ± 0.1 [GPa]	$E_{\perp}$ ± 0.1 [GPa]
Linear 1	25	2.7	2.7
Linear 2	36	2.7	2.7
Linear 3	54	2.6	2.7
Branched 1	40	2.8	2.7
Branched 2	52	3.0	3.2
Branched 3	56	3.2	3.4
Branched 4	56	3.0	3.4

3.7. Mechanical properties: failure behaviour

The failure behaviour of the material has been studied via notched impact (IZOD) and K_{IC} fracture toughness measurements. The IZOD tests were performed both parallel and perpendicular to the flow direction in injection moulding. The fracture toughness tests were performed on a moulded compact tension test piece, specially designed to minimise orientation effects of injection moulding and to maximise the test validity. Table 9 contains the results of both failure tests. Within the accuracy of the IZOD test it is hardly possible to draw conclusions. All materials are brittle, as is well known for non-impact modified and dry polyamide-6. The notched IZOD impact strength is within measurement accuracy independent of the molar mass. For the branched materials, parallel to the flow direction in injection moulding, it is slightly higher than the IZOD of the linear materials, while in the perpendicular direction the opposite is the case. On the average there are no significant differences in notched IZOD values between the linear and the branched materials. Within the accuracy of the measurements also the fracture toughness K_{IC} is not affected by branching. However, it does depend on the molar mass and increases with increasing molar mass. The differences amongst the materials are dominated by differences in average molar mass.

4. Discussion

4.1. The zero shear viscosity of the melts

Fig. 4 shows the zero shear viscosity of the materials (determined by fitting the Cross equation to the dynamic flow curve) as a function of the weight average molar mass. The data points for the linear samples fit to a power law relationship, with an exponent of 3.6 ± 0.2. This value is slightly higher than the value of 3.4 usually observed for linear polymers, but agrees well with the value of 3.5 as reported by Laun [29]. Due to the limited number of data points and the narrow molar mass range covered the accuracy of our value is limited.

The branched polymers (2–4) have a higher zero shear viscosity than the highest molar mass linear polymer (3). This polymer has a mass comparable to that of these branched polymers. This effect is well known from literature and usually attributed to the length of the branches, i.e. the presence of long chain branching [5,6]. By design the molecular weight of the branches, or the distance between branch points (depending on the exact molecular architecture), is larger than a least two times the molecular weight between entanglements M_e. Therefore, the branched segments have become part of the entanglement network. Because the branches are on one end fixed to the polymer backbone, their stress relaxation can not occur via reptation and proceeds in a much slower fluctuation mode [1]. This causes an increase of the zero shear viscosity. These findings are confirmed by the results in elongational flow. The latter three branched materials have

Table 7
The yield stress and strain parallel and perpendicular to the flow direction in injection moulding, respectively.

Material	M_w ± 5% [kg/mol]	$\sigma_{y//}$ ± 1 [MPa]	$\sigma_{y\perp}$ ± 1 [MPa]	$\varepsilon_{y//}$± 0.2 [%]	$\varepsilon_{y\perp}$ ± 0.2 [%]
Linear 1	25	74	74	4.8	4.8
Linear 2	36	74	73	4.6	4.7
Linear 3	54	70	72	3.8	4.1
Branched 1	40	75	74	4.6	4.9
Branched 2	52	78	81	4.3	4.6
Branched 3	56	80	81	4.2	4.6
Branched 4	56	78	87	4.4	4.5

enhanced melt strength in comparison with a linear material of comparable molar mass. This is again attributed to the presence of branched segments of sufficiently high molar mass in the branched samples 2–4. The lower molar mass branched polymer 1 shows nor enhanced melt strength nor a higher zero shear viscosity, which indicates that the branches in this material are probably of lower molecular weight and therefore less entangled. Tough these results are very strong indicators for the presence of long chain branches Stange et al. [30] have advocated to make a plot of the zero shear viscosity η_0 of the melt versus the intrinsic viscosity $[\eta]$. A positive deviation from the η_0 versus $[\eta]$ relationship for linear polymers is an even stronger indicator for the presence of long chain branching, whereas short chain branched polymers would not deviate.

All branched polymers show in Fig. 5 a strong positive deviation from the linear polymers indicating that indeed long chain branches are present in these materials. Because of the random nature of the polyamide-6 polymers it is difficult to further detail the molecular topology of the chains with any experimental technique.

Using the statistical mechanics models of Macosko and Miller [31] predictions for the molecular weight distribution and its moments can be obtained. However, in practice for polyamide-6 this is complicated by the incomplete conversion of caprolactam during the melt synthesis. Typically, about 10% of unreacted caprolactam remains after the polymerisation and is removed during the washing step. This is the main reason for the reported weight loss and affects the recipes. Moreover, after the melt polymerisation step the materials have been post-condensated to further increase the conversion. However, because of the limited mobility of the polymeric chains during this solid-state post-condensation step, typically non-equilibrium molecular weight distributions will be obtained. Both effects limit the utility of these models significantly and predictions at full conversion of the monomers are overestimating the actual molecular weight distribution. However, because of the use of the benzoic acid as chain stopper, some indicative trends can be obtained from the recipes for comparison with the experimental results.

4.2. *Detailed analysis of the recipes*

The samples linear 1 and branched 1 have been synthesized using the same (high) amount of benzoic acid (BA) and consequently are designed to have similar number average molecular weight (experimentally: 10 vs. 12 kg/mol, respectively). In branched 1 the molar amount of branching agent (TCAM/HMDI) amounts to half the molar amount of the chain stopper (BA). Consequently, branched 1 contains theoretically – on average – one branch point per two polymeric chains, i.e. the material is a mixture of linear and branched (mainly star polymers, but also multiple branched) chains. The number average molecular weight of the arms in the branched polymer is expected to be less than half the mass of the linear polymer and therefore not much larger than the entanglement molecular weight of polyamide-6 (2500–3000 g/mol). Despite this, the presence of these arms still has a strong influence on the rheological properties. Consequently, the branched polymer has a zero shear viscosity which is about equal to the zero shear viscosity of the medium molar mass linear polymer.

Table 8
The ‘onset of failure’ stress (σ) and strain (ϵ) parallel and perpendicular to the flow direction in injection moulding, respectively.

Material	M_w ± 5% [kg/mol]	$\sigma_{f//}$ ± 3 [MPa]	$\sigma_{f\perp}$ ± 3 [MPa]	$\varepsilon_{f//}$ ± 5 [%]	$\varepsilon_{f\perp}$ ± 5 [%]
Linear 1	25	68	65	28	33
Linear 2	36	66	65	32	32
Linear 3	54	61	63	25	22
Branched 1	40	67	66	25	26
Branched 2	52	73	70	23	21
Branched 3	56	77	71	27	20
Branched 4	56	74	76	22	16

Table 9
The IZOD impact strength parallel and perpendicular to the flow direction in injection moulding and the K_{IC} fracture toughness of the polyamide-6 materials, respectively.

Material	M_w ± 5% [kg/mol]	$IZOD_{//}$ ± 0.9 [kJ/m^2]	$IZOD_{\perp}$ ± 0.9 [kJ/m^2]	K_{IC} ± 0.5 [MPa $\sqrt{m}$]
Linear 1	25	6.0	5.5	3.8
Linear 2	36	5.4	5.6	5.0
Linear 3	54	5.9	5.1	6.0
Branched 1	40	6.1	5.7	4.2
Branched 2	52	7.0	5.7	5.7
Branched 3	56	6.4	4.5	5.6
Branched 4	56	6.9	4.2	6.1

In order to increase the molar mass of the branch segments at equal branching density, the branched 2 recipe also has half the molar amount of branch points in comparison with the chain stopper, but contains only 40% of the amount of chain stopper and branching agent in comparison with the branched 1 recipe. Therefore, the molecular weight of this polymer will be higher. Because slightly less chain stopper is used in branched 2 in comparison with linear 2, its number average molecular weight is expected to be higher (experimentally: 16 vs. 13 kg/mol, respectively). The rheological properties show that this increase in molecular weight has indeed a major effect. The zero shear viscosity of the sample branched 2 is even higher than that of the linear material with the highest molecular weight (linear 3), and strong shear thinning effects are observed.

To explore the effect of the number of branch points per chain in more detail the relative molar amount of the branching agent (versus BA) in branched polymer 3 has been raised and amounts to 75% of the molar amount of the chain stopper. However, in order not to reduce the molecular weight of the branches/segments again, it was decided to increase the number average molecular weight of the chains by lowering the amount of benzoic acid by one third, while keeping the original amount of branching agent. Consequently, the sample branched 3 contains theoretically on average three branch points per four polymeric chains, i.e. the material is a mixture of linear and a larger amount of branched (star and multiple branched) chains. The rheological properties of branched 3 are similar to branched 2, which contains fewer branch points per chain, but has longer chain segments. Both the flow curve (viscosity vs. rate) and the viscoelastic behaviour (phase angle) are very similar, showing that the two can be interchanged to some extend.

Finally, the recipe of branched 4 is also based on this higher amount of branch points per chain (on average 0.75 per chain), but with even less chain stopper, thus longer chain segments. In this case, the molar amount of the chain stopper is the same as in the medium molar mass linear sample 2. Because of the combination of more branch points and the higher molar mass of the chain segments, branched 4 has the highest zero shear viscosity of all materials and shows the strongest viscoelastic behaviour.

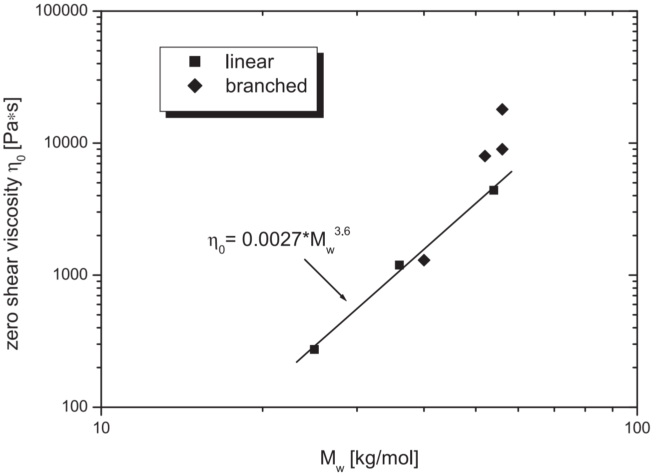

Fig. 4. The zero shear melt viscosity of the linear and branched polyamide samples at 230 °C as a function of the weight average molar mass.

The observed effects are in qualitative agreement with the model predictions by Janzen and Colby [6], who have shown that up to 1–2 branch points per chain the zero shear viscosity increases with increasing branch density. This is attributed to the presence of long chain branches. They also reported that, like for linear polymers, the zero shear viscosity of branched polymers continuously increases with increasing molecular weight.

In practice of polyamide-6 polycondensation full conversion is not obtained, nor during the melt synthesis nor after solid-state post condensation. Consequently, the effects will be smaller than described above since more linear and less multiple branched chains will be present. Using the work of Macosko and Miller [31] we have estimated the actual (number) average number of branch points per chain from the experimental weight average molecular weights of the branched polymers, as determined with GPC. The estimated actual number of branch points per chain has been added in the last column of Table 1, and amount to about 40–70% of the theoretical values.

4.3. Solid-state mechanical properties

With respect to the solid-state behaviour it is found that branching affects the mechanical properties of the materials much less than the rheological properties. A small increase in modulus and yield stress with branching is found. Thermal analysis did not reveal any significant differences in crystallinity amongst the samples (except for the effect of molecular weight), which could explain the differences between linear and branched samples. However, a change in crystalline morphology might have occurred. Flow induced orientation, for which the branched materials are probably more susceptible because of the longer relaxation times in the melt, seems to occur causing a slight anisotropy in properties of the branched materials. Possibly, the modulus and strength in the *z*-direction (perpendicular to the surface of the plate from which the samples were taken) are lower. This, however, could not be investigated.

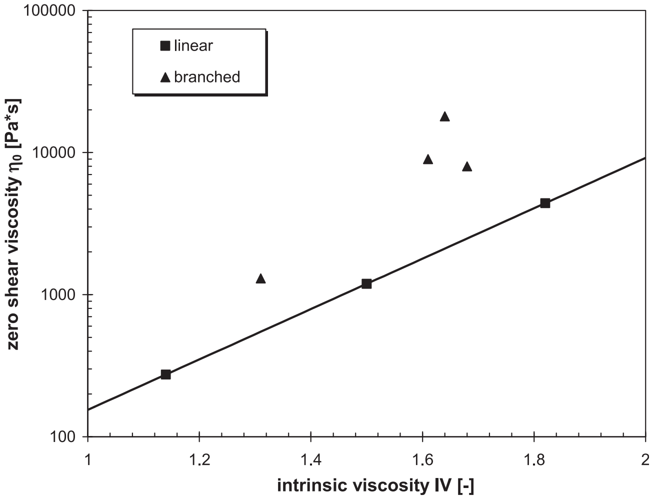

Fig. 5. The zero shear melt viscosity of the linear and branched polyamide samples at 230 °C versus the intrinsic viscosity as extracted from the SEC/DV measurements.

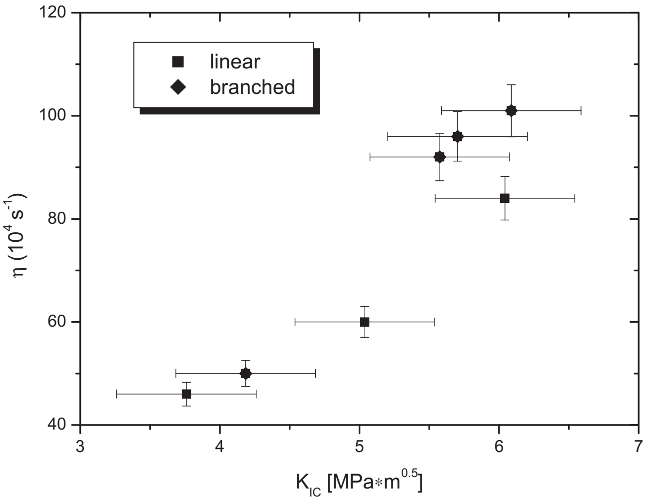

Fig. 6. The high shear rate (10^4 s^{-1}) viscosity of the linear and branched polyamide-6 samples at 230 °C versus the fracture toughness K_{IC}.

The IZOD impact strength of the materials shows no clear effect of branching and becomes slightly directional. The fracture toughness K_{IC} is also found to be independent of branching, but significantly increases with increasing weight average molar mass of the materials.

Finally, Fig. 6 shows the balance between the viscosity at high shear rates and the fracture toughness K_{IC}. Within the accuracy of the toughness measurements it is not possible to draw conclusions about a change of the property balance. No significant trend is found for the materials investigated. However, using the branched recipes, it was synthetically much easier to obtain the high weight average molecular weights (and the resulting properties) than via the linear recipes.

It is concluded that random branching can be used to enhance the zero shear viscosity and the melt strength of polyamide-6 without increasing the viscosity at high shear rates. This is especially useful for processing methods where stability during elongational flow and against sagging is required and is for instance advantageous for film applications to prevent localisation of the melt during drawing and/or failure. Some positive effects are observed for the solid-state mechanical properties too (modulus, yield strength…) but these variations are much smaller.

5. Conclusions

It is found that the rheological properties of polyamide-6 can be sensitively influenced by the incorporation of random branching. The flow can be changed such that at equal zero shear viscosity a lower viscosity at high shear rates is obtained, or alternatively, that at equal high shear rate viscosity a higher zero shear viscosity is obtained. This is of use for many processing operations. Moreover, the melt strength (elongational flow) can be significantly enhanced by the incorporation of branches of adequate length.

By contrast the deformation behaviour of the (semi-crystalline) solid state is hardly affected by the incorporation of branching at equal weight average molar mass. Both the modulus and the yield stress are slightly increased and indicate some effects of flow induced orientation. With thermal analysis it has been shown that the incorporation of branching in the samples studied did not affect their crystallinity. The failure properties, IZOD impact and K_{IC} fracture toughness, are found to be independent of branching. However, as expected, the weight average molar mass determines the fracture toughness, which can be obtained more easily with the branched recipes.

Considering the possibilities to change the rheological properties of the materials by branching while the solid-state mechanical properties are hardly affected, it is concluded that – *depending on processing method* – polyamide-6 materials with an improved balance between processability and mechanical properties can be obtained. Moreover, the increase in modulus and yield stress observed, though small and dependent on the direction, might be exploited in designing construction parts and shapes.

Further optimisation of the synthesis recipes for a certain application is necessary.

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