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Peroxydicarbonate modification of polypropylene and extensional flow properties

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Abstract

Long chain branches (LCB) were added to initially linear polypropylene (PP) using reactive extrusion in the presence of selected organic peroxydicarbonates (PODIC). The LCB structure was confirmed by high temperature size exclusion chromatography combined with on-line intrinsic viscosity measurements. Compared to the initial linear PP, the branched samples showed distinct strain hardening of the elongational viscosity, slightly lower Melt Flow Index, increased extrudate swelling and improvement of the melt strength by up to a factor of two. All elastic properties increased with the degree of branching. The efficiency of PODIC with varying structure for the LCB modification of PP was evaluated. PODIC with non-linear or large linear alkyl groups resulted in modified PP with the highest degree of branching and the fastest strain hardening. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polypropylene; Elongational properties; Melt strength

1. Introduction

Polypropylene (PP) is the fastest growing commodity resin in the polymer world market. It has many desirable properties when compared to other thermoplastics, such as high melting point, low density, high tensile modulus and low cost. Commercial PP is produced with Ziegler–Natta or metallocene catalysts resulting in highly linear chains and a relatively narrow molecular weight distribution. Conventional linear PP, however, has poor melt strength and cannot easily be used in processes where elongational flows are dominant, such as foaming, thermoforming, extrusion coating or blow molding. This is due to the extensional viscosity of the PP melt. Linear chains do not show strain hardening in extensional flow. Polymers with strain hardening elongational viscosity are known to exhibit high spinning viscosity and melt strength [1].

The influence of the molecular structure on the melt strength of polymers has been studied extensively. For several commercial polyethylenes (PE), Ghijssels et al. [2–4] found that the melt strength increases with decreasing Melt Flow Index (MFI) and decreases with increasing temperature in the same way as its viscosity. The melt strength of LDPE was a factor 2 higher than that of LLDPE and HDPE with the same MFI. This is probably caused by the presence of long chain branches (LCB) in the former polymer, which induce strain hardening in the elongational viscosity of the melt. The effect was stronger with the 'tree-type' than with the 'comb-type' long chain branching, while no effect could be seen by using different co-monomers (1-butene, 1-hexene and 1-octene) as short branches in LLDPE. In the case of PP, the samples that were used had linear chains. The melt strength of PP also increased strongly with decreasing MFI. A wider molecular mass distribution (MMD) led to higher melt strength.

The differences between several linear and branched PP and PE polymers were studied by Demaio and Dong [5]. The branched PP was obtained by electron beam (EB) irradiation. The melt strength of the branched PP was found to be ten times higher than the one of a linear PP with the same MFI. The melt strength of the LDPE was five times higher than HDPE. In that report, the melt strength was related to the loss tangent (tan δ). The melt tension rose as the loss modulus decreased, indicating that higher elasticity is coupled with higher melt strength.

Gotsis and Ke [6], among others, showed that both the spinning viscosity, as it is measured in a fiber spinning

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experiment (Rheotens®), and the uniaxial elongational viscosity depend strongly on the molecular structure of the melt. Three PE melts with equal MFI at 190°C were examined: A long chain branched polymer (LDPE), another with short branches (LLDPE) and a third without branches (HDPE). While their shear viscosities were the same in a large range of shear rates, the melts showed quite different elongational properties. The LDPE showed distinct strain hardening of the elongational viscosity and the highest melt strength of the three. On the other hand, the LLDPE showed very little strain hardening and low melt strength, even lower than that of HDPE. It seems that the broader MMD of the HDPE had a stronger contribution to strain hardening and melt strength than the shorter branches of LLDPE, at least at the strain rates, that were used. Münstedt et al. [7] have reported strain hardening for LLDPE, but only at low strain rates. This was probably due to a small fraction of very high molecular mass and its immiscibility with the rest of the material. It is doubtful, therefore, whether short branches can contribute effectively to higher entanglement density and thus to higher extensional properties. Long chain branching, on the other hand is the factor that contributes the most to the enhancement of the melt strength.

1.1. High melt strength polypropylene (HMS-PP)

It is expected that the improvement of the melt strength behavior of PP will substantially contribute to the growth of this polymer in the plastics market. For this reason, many plastic manufacturers are developing HMS-PP grades. The melt strength of PP can be improved by increasing the molecular mass, broadening the distribution (e.g. creating a bimodal MMD) or by introducing branches. The latter seems to be the most efficient way and it may be achieved by radical reactions. Radicals can be introduced in the polymer chain by irradiation or by chemical free radical initiators, such as organic peroxides.

Patents exist for the manufacturing of HMS-PP by EB irradiation [8,9]. The EB irradiation causes scission of the PP chains followed by crosslinking, leading to long chain branching. Patents for the modification of PP by chemical initiation also exist. The reactive extrusion of PP with peroxydicarbonates (PODIC) has been patented by Basell (formerly HIMONT) [10] and by Akzo-Nobel, [11,12]. Other publications describe the modification of PP with peroxides in combination with multifunctional monomers [13] or in particular with butadiene gas in a post-reactor process [14], with the aim to introduce LCB on initially linear chains.

Similar to PE, the most successful way to improve the melt strength of PP seems to be the addition of long chain branching. In the present study, this was achieved by modification of (initially) linear PP in a reactive extrusion process in the presence of PODIC. Our aim is to evaluate the effectiveness of the several types of PODIC for this modification, study their effect on the melt strength, detect the presence of strain hardening in elongational flows and explain the mechanism which causes the improved melt strength.

2. Experimental

The PP used in the present study was a reactor grade powder from Borealis with a MFI of 3.2 g/10 min at 2.16 kg and at 230°C. The weight average molecular mass, M_w, was 450,000 (though this was reduced after extrusion to 410,000), $M_w/M_n = 6.4$ and $M_z/M_w = 5.3$. This polymer was stabilized with 0.1% antioxidant, Irganox 1010 (Ciba). The peroxides that were used are listed in Table 1. They are PODIC except the PND, which is a perester, are produced by Akzo Nobel and are commercially available, except for the EP, NPP and IPP. The PODIC and the perester are of equal reactivity and their dissociation can be described by an Arrhenius equation; the activation energy (E_A) and the pre-exponential factor (A) are also listed in Table 1, together with the temperature, $T_{1/2}$, for a half-life time of 360 s.

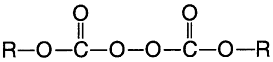
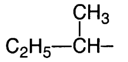
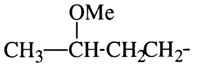
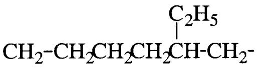
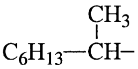
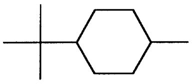
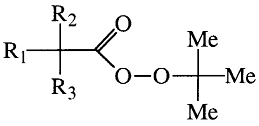
The modification of the linear PP took place in a Haake Rheomix TW100 twin-screw extruder. The extruder had a pair of co-rotating conical intensive mixing screws and a die with a diameter of 3 mm. The temperature ranged from 180°C at the feeding zone, to 210°C at the die. The extruder operated at 50 rpm. Amounts of 0–3 mmol PODIC/100 g PP were used. A solution of the PODIC (in hexane) was added to the PP powder in a vessel under a blanket of argon gas and the closed vessel was tumble-mixed by hand for 120 s. This premix was then placed in the feeder of the extruder, which was purged with nitrogen. After extrusion, the strand was cooled in a water bath under nitrogen to prevent oxygen-induced degradation of the extrudate. After cooling, the strand was pelletized.

Addition of PODIC solution directly into the extruder without premixing with PP gave similar results. Further, the results were independent of the solvent used (hexane, isododecane, toluene, dichloromethane and water) and the concentration of PODIC in the solvent, as long as more than 10% PODIC, was used in the solution [15].

The MMD and the branching structure of the modified samples were measured in a High Temperature Size Exclusion Chromatograph (HTSEC) equipped with a triple detection system: differential refractive index, light scattering and on-line viscosity measurements of the effluent (model: Polymer Labs HTSEC-220). For these measurements, the samples were dissolved in 1,2,4-trichlorobenzene with 1.25 w/v‰ butylated hydroxytoluene (BHT) as antioxidant and the measurements took place at 150°C. The error margins of the SEC measurements were less than 3%.

The MFI and the extrudate swell were measured using the standard capillary of the Melt Flow Indexer (at 230°C). The gel content of the samples was also measured for possible occurrence of crosslinking during modification. All samples

Table 1
PODIC used for the modifications, their chemical formula, molecular mass, activation energy and pre-exponential factor for their decomposition rate, and the temperature at which their half life time is 360 s (data supplied by Akzo Nobel)

General formula of PODIC:  $R-O-C(=O)-O-O-C(=O)-O-R$	Abbr.	Chemical name (PODIC)	MW (kg mol)	A (s^{-1})	E_A (kJ/mol)	$T_{1/2}$ (°C)
R: CH_3CH_2-	EP	Ethyl	178.1	–	–	82[a]
R: $CH_3(CH_2)_2-$	NPP	Propyl	206.2	–	–	82[a]
R: $(CH_2)_2CH-$	IPP	Iso-propyl	206.2	–	–	81[a]
R: $CH_3(CH_2)_3-$	NBP	*n*-Butyl	234.2	7.0×10^{15}	126.7	83
R :  $C_2H_5-CH(CH_3)-$	SBP	Sec-butyl	234.2	3.2×10^{15}	123.9	82
R :  $CH_3-CH(OMe)-CH_2CH_2-$	MBP	Methoxy-butyl	294.3	1.2×10^{14}	112.5	85
R :  $CH_2-CH_2CH_2CH_2CH(C_2H_5)-CH_2-$	EHP	Ethyl-hexyl	346.5	1.8×10^{15}	122.5	83
R :  $C_6H_{13}-CH(CH_3)-$	SOP	Sec-octyl	346.5	2.4×10^{16}	128.1	85
R : 	TBCP	Tert-butylcyclohexyl	398.5	7.4×10^{15}	126.4	82
R: $CH_3(CH_2)_{13}-$	MP	Myristyl	514.8	2.8×10^{15}	124.1	84
R: $CH_3(CH_2)_{15}-$	CP	Cetyl	570.9	3.0×10^{15}	124.3	84
 $R_1 + R_2 + R_3 = C_8H_{19}$	PND	Tert-butyl-peroxy neodecanoate (Perester)	244.4	1.5×10^{15}	115.5	84

[a] Determined from DSC scans in dilute (0.1 M) solution of monochlorobenzene.

of modified material were found to contain less than 0.5% (the minimum detectable amount) of gel.

The melt strength was measured using a Göttfert Rheotens® fiber spinning device in combination with a Göttfert Rheograph 2001 High Pressure Capillary Rheometer. Table 2 lists the settings that were used for determining the melt strength of PP (based on Ref. [3]). The filament was wound during the test on one wheel of the instrument, while the other wheel had been removed. The force and the filament velocity were registered at the time the strand broke. The amount of polymer that was thus wound around the wheel was weighed and the weight added to the measured force at break, to obtain the true melt strength. Draw resonance occurred sometimes towards the end of the experiment. This is a flow instability, which results in a periodic variation of the diameter of the filament and an oscillating force. This can lead to premature break of the thin sections of the strand. When this occurred, the melt strength was determined as the maximum force before resonance started.

The viscosity growth during uniaxial elongational flow at constant extension rate was measured using a Rheometrics® RME (extensional rheometer). Details on the design and the operation of this instrument can be found in Ref. [16]. The rheometer uses caterpillar bands to clamp and deform the molten sample at a constant rate. The flow of N_2 gas is used to support the weight of the sample and the force is monitored that is needed to extend a constant length of the sample. The elongational viscosity was calculated from the initial dimensions of the sample, the strain rate and this force. Limitations of the clamping system and the large differences found in elastic polymer melts between their shear and elongational viscosities may lead to a difference between the set rate of deformation in the instrument and the true rate. For this reason, the actual deformation of the sample was monitored by optical means as a function of time during the measurement, and the strain rate and the stress data were corrected accordingly afterwards. This is the reason why the strain rate is referred in the figures in Section 3.3 as 'around 0.1 s^{-1}', which was the nominal ('set') value. The true values for the measurement of all the samples were within 10% of 0.1 s^{-1}. The maximum

Table 2
Geometry and operating parameters for the fiber spinning experiment (Rheotens®) used to measure the melt strength and the extrudate swell

Capillary rheometer parameters			Rheotens® parameters
Die geometry:	Length = 30 mm	Diameter = 1 mm	Strand length = 70 mm
Piston:	Speed = 0.213 mm/s	Diameter = 12 mm	Acceleration = 1.2 mm/s^2
Shear rate: 245 s^{-1}	Temper. = 190°C	Melt. time = 600 s	

(Hencky) strain that the instrument can generate is 7. Most PP samples in this work, however, broke at strains between 4 and 5.

3. Results and discussion

During most of the modifications, the torque on the motor of the extruder was higher than during the extrusion of pure PP and the polymer strand surface was rougher in appearance. Since the half time of the PODIC is relatively short at the processing temperatures used, the peroxides must have completely decomposed and reacted during the residence time of the polymer in the extruder.

3.1. Molecular mass distribution (MMD) and long-chain branching (LCB)

The average molecular mass of the samples, together with the weight average values for the number of branches per molecule, B_n, are given in Table 3. The molecular mass of the effluent was measured directly by the light scattering detector of the HTSEC as the effluent exited the column. The amount of branches was calculated using the on-line viscosity measurements in the same instrument. An example of this determination is shown here for a set of samples that resulted from the modification of the original PP by using increasing amounts of di-(ethylhexyl) peroxydicarbonate (EHP) (Sample set 1 in Table 3). Fig. 1 shows the MMD curves for these samples.

Table 3
Molecular mass average, polydispersity and weight average branching number of the control PP and the samples modified with increasing amounts of EHP peroxydicarbonate (set 1) or 2 mmol of different PODIC or one perester (PND) per 100 g PP (set 2)

	$M_n \times 1000$	$M_w \times 1000$	M_w/M_n	B_n
Sample set 1 modified with EHP (mmol/100 g PP)				
PP control	74	410	5.5	–
0.5	69	400	5.7	0.03
1.0	62	410	6.6	0.15
2.0	68	460	6.8	0.23
3.0	71	485	6.8	0.36
Sample set 2 modified with (2 mmol/100 g)				
EP	72	425	6.0	0.15
NPP	66	435	6.5	0.13
IPP	69	460	6.7	0.28
NBP	66	435	6.5	0.24
SBP	73	475	6.5	0.29
MBP	68	410	6.1	0.13
EHP-1[a]	72	455	6.3	0.32
SOP	64	455	7.1	0.32
TBCP	72	440	6.1	0.23
MP	74	465	6.3	0.31
CP	74	465	6.3	0.35
PND	72	355	4.9	–

[a] This EHP came from a new batch (fresher sample) different from the one used for the modifications in Sample set 1.

The shoulder that is seen at the higher molecular mass region of these curves and which gets wider with the amount of the peroxide used for the modification could be interpreted as a broadening of the distribution because of the reaction in the extruder. In the present case, this widening is most likely due to the existence of long chain branched molecules. That long branches are generated can be deduced from Fig. 2, where the logarithm of the intrinsic viscosity of the effluent is shown as a function of the logarithm of its molecular mass. A clear deviation from the curve of the linear PP sample can be seen here for the curves of the modified samples, indicating that the Mark–Houwink exponent at high molecular mass (~0.77 for the unmodified PP) is not the same in these samples but it is reduced as the degree of the modification increases (down to 0.71 for PP modified using 3 mmol/100 g EHP PODIC).

The model of Zimm and Stockmeyer [17,18] was used here together with the methodology of Lecachaux et al. [19]. The ratio of the mean square radii of gyration, g, of the branched and the linear samples can be found from the ratio of their intrinsic viscosities: $g = ([\eta]_b/[\eta]_l)^{1/\epsilon}$. For random branching, a value of 0.75 is often used for the exponent ϵ and the average number of branches per polymer

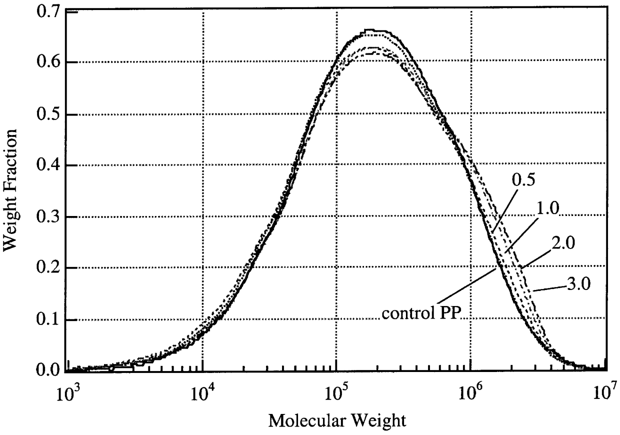


Fig. 1. MMD of PP modified by increasing amount of EHP (mmol/100 g PP).

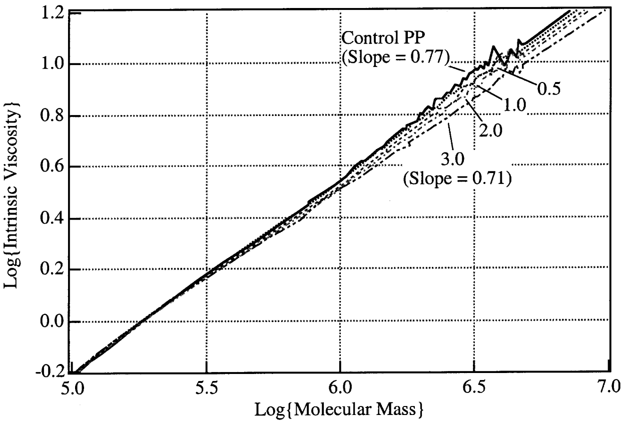


Fig. 2. Intrinsic viscosity as a function of the molecular mass of PP modified by increasing amount of EHP (mmol/100 g PP).

chain, B_n, is calculated from this ratio, by solving the following equation: $g = [\sqrt{1 + B_n/7} + 4B_n/9\pi]^{-1/2}$. The number of branches per 1000 monomers (branching frequency), λ, is defined as: $\lambda = 1000mB_n/M$, where m is the molar mass of the monomer and M the molar mass of the polymer chain.

The deviations of the molecular structure of the modified samples from that of the control PP are beyond doubt, since they correspond to measured differences that are higher than the accuracy limits of this SEC. The calculated values of B_n were based on the assumption of linear chains of the control PP. Since the same control PP was used for all samples, at least the relative differences in branching in Table 3 are real. From this table, we see that the results of the SEC measurements verify the formation of a few long-branched molecules during the modification of PP using these PODIC. However, on an average, in all samples there is less than one long chain branch point for every two molecules.

While Sample set 1 in Table 3 includes the results of the modification of the precursor PP using increasing amounts of the same (EHP) PODIC, Sample set 2 involved modification of PP using 2 mmol of different PODIC per 100 g PP. A different batch of EHP (EHP-1 in Table 3) was used in this set, which resulted in slightly different results from the previous set. As it can be seen in Table 2, all these peroxides succeeded in the addition of some long branches on the chains of PP. The differences between the effects of the several peroxides were not very pronounced, PODIC with longer linear side groups giving in general higher branching numbers than the peroxides with shorter side groups. In addition, PODIC with bulkier side groups resulted in modified samples with more LCB than PODIC with linear side groups with the same number of carbons. As we will see below, these differences in long chain branching also reflected on differences of the melt strength and the elongational flow behavior of the samples. In contrast, the perester, PND, with the same reactivity as the PODIC, induced some chain scission resulting in lower average molecular mass and no branching.

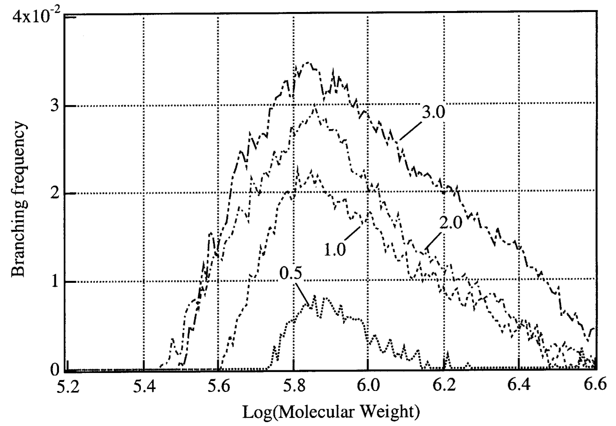


Fig. 3. Distribution of LCB as a function of the molecular mass for PP samples modified by increasing amounts of EHP (mmol/100 g PP).

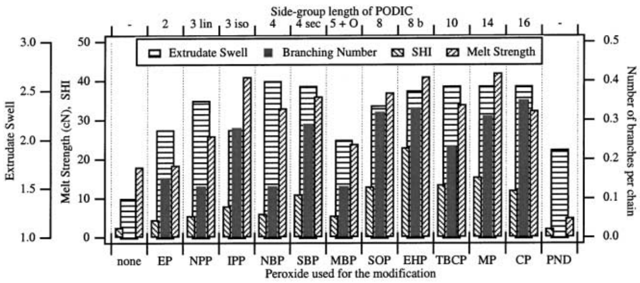


Fig. 4. Melt strength, SHI, extrudate Swell and number of branches per molecule for samples modified with 2 mmol of different PODIC/100 g PP. The samples are shown at increasing length of the side group of the PODIC.

The model of Zimm and Stockmeyer [17], together with the online measurement of the intrinsic viscosity allows one to evaluate the degree of branching (or equivalently the branching frequency, λ) as a function of the molecular mass of the effluent, as shown in Fig. 3. It is clear from this figure that the frequency of long chain branching is the highest among chains with high molecular mass. This also indicates that the shoulder in the MMD in Fig. 1 is indeed caused by the long-branched chains.

3.2. Melt strength of modified PP

The results from the melt strength measurements for the samples modified with the peroxides in Sample set 2 are shown in Fig. 4. The columns in this graph are ordered from the smallest PODIC used for the modification (EP with C_2 side groups) to the largest (CP with C_{16} side groups). The IPP, EHP and MP give the highest melt strength of around 41 cN for the present experimental conditions. This is more than twice the melt strength of the original PP sample. In addition, the use of SBP, SOP, TBCP and CP gives considerable melt strength improvement. The values for the NPP and MBP are higher than the one of the original PP (26, 23 and 18 cN, respectively) but the

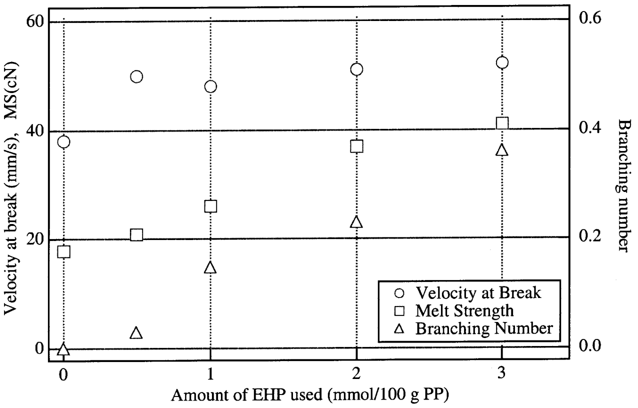


Fig. 5. Velocity at break, branching number and melt strength of PP modified by increasing amount of EHP.

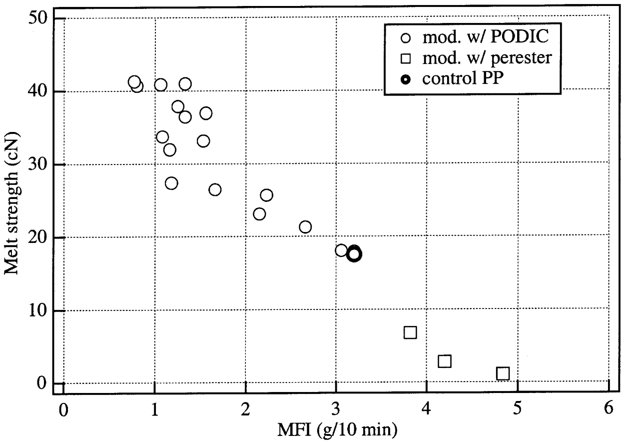


Fig. 6. Melt strength vs. MFI for PP samples modified using different peroxides or different amounts of EHP or PND.

effect is much smaller than for the other PODIC, while the EP gives no noticeable melt strength improvement.

Fig. 4 also shows the number of branches per chain (B_n) measured for the modified samples in the HTSEC. This number shows the same trend as the melt strength. Modifications that result in more branches per chain also result in higher melt strength. There is a trend of higher melt strength in samples modified using PODIC with longer side groups. If one looks at the shortest (EP) and the longest (CP) PODIC, the differences are obvious. However, in the case of the modification with MP (C_{14}) and IPP (C_3), the length of the side group seems to have no effect. MP, which is two carbon atoms shorter than CP results in a higher melt strength than CP and equal to the one of the much shorter IPP (C_3) PODIC. The MBP PODIC gives hardly any melt strength improvement. It seems that the reaction that this peroxide induces is different from the effect of the other PODIC because of the oxygen atom present in the side group of MBP. In any case, Fig. 4 shows that the side group of the PODIC affects the mechanism of the reaction by which branches are attached and which is responsible for the melt strength improvement.

Two other indicators of the elasticity of the melt are also shown in Fig. 4: the Extrudate Swell and the Strain Hardening Index (SHI). The latter will be discussed in Section 3.4 on the extensional viscosity of the melts. The amount of extrudate swell may give an indication of how much of the stress is remembered after the material passes through a capillary and of the value of the primary normal stress difference in shear flow. Both these parameters show the same trend among the PODIC-modified samples as the melt strength. Extrudate swell, melt strength and elongational viscosity are sensitive to the molecular structure, which in the present case means the number of LCB.

The effect of the amount of peroxide used for the modification of the extensional properties of the PP melt is shown in Fig. 5 for Sample set 1, corresponding to the molecular structures of Fig. 3. It can be seen that the increase in melt strength is proportional to the amount of PODIC, used for the modification. The velocity at break, on the other hand, increases when PP is modified but it remains relatively independent of the amount of PODIC used for the modification. Since the velocity of the pick-up wheels, which defines the amount of deformation on the filament and the minimum cross sectional area, is the same at the break of all modified samples of set 1, the increase in the melt strength is the result of the increase in the elongational viscosity of these samples for the same accumulated elongational strain. Since there is a similar increase in the average number of branches of these samples (Fig. 3), the above also indicates that the melt strength and the elongational viscosity increase with the increase in the number of branches per molecule.

When comparing the shear viscosity of the samples, it can be seen that it increases in general as the melt strength improves. A linear trend can be seen in Fig. 6 between melt strength and MFI (which is an inverse measure of the shear viscosity). However, this linear relation indicates that the increase in the melt strength is not the result of higher average molecular mass, since this would lead to an increase in the viscosity proportional to the 3.4 power of the M_w. Indeed, the HTSEC measurements have shown that the average molecular mass hardly increases, as it can be seen in Table 3. The melt strength improvement in the present case is the result of long chain branching, which increases the elongational viscosity at high strains much more than the shear viscosity.

3.3. Elongational viscosity of the modified samples

Measurements of the elongational viscosity of the samples were conducted and are reported in detail in the M.Sc. Thesis of Lagendijk [15]. Some of the elongational viscosity growth curves of samples modified by different PODIC, different amounts of EHP and by the perester are shown in Figs. 7 and 8 for a strain rate of around 0.1 s^{-1}.

The curves of the elongational viscosity growth versus

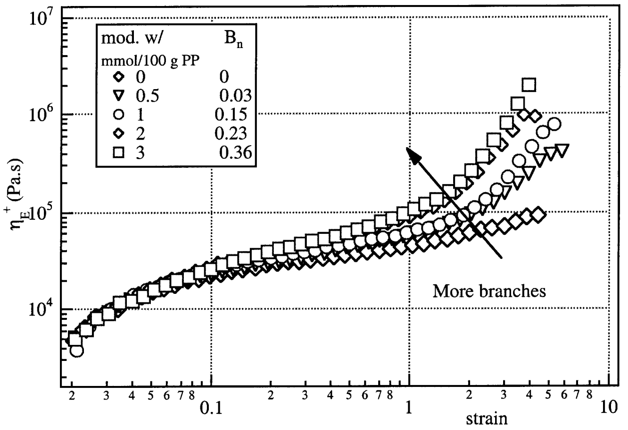


Fig. 7. Elongational viscosity growth of PP samples modified with increasing amount of EHP at a strain rate of around 0.1 s^{-1}.

elongational (Hencky) strain for the modified samples always lie above the curve of the PP (linear) precursor melt. The small differences between the elongational viscosity curves of the samples at very low strains are probably due to the slight differences in the average molecular mass of the samples. However, most important is the change in the form of these curves. Above a strain of around 0.5, the growth curves of the branched samples show an acceleration, i.e. an upward change of the slope (in the logarithmic plot), which is termed in general as 'strain hardening'. The control PP melt and the samples modified using the perester (PND) do not show any strain hardening. On the contrary, most PODIC-modified samples show some degree of strain hardening. This is more pronounced in samples that also show increased melt strength.

Similar to the melt strength, the higher the amount of peroxide used for the modification, i.e. the higher the number of LCB present, the stronger the strain hardening behavior of the molten samples is. This can be seen in Fig. 7 for Sample set 1. When the same amount of PODIC was used, it was found that longer or bulkier side groups present on the PODIC also resulted in stronger strain hardening of the PP melt. Fig. 8(a) shows the differences in the growth curves of samples that resulted using PODIC with linear groups of lengths between C_2 and C_{14}. Again, MP resulted in a melt with much stronger strain hardening than e.g. the EP. Fig. 8(b) compares PODIC with linear and non-linear groups of 3 or 8 carbon atoms. It can be seen that non-linear groups increase the efficiency of the PODIC in improving the strain hardening behavior of the PP as compared to linear groups.

3.4. Strain hardening index

In order to quantify the strain hardening behavior of branched and linear polymer chains, Wagner et al. [20] used the Molecular Stress Function, *f*, which represents the narrowing of the reptation tube of the Doi–Edwards model due to the elongational flow, and can be calculated by fitting the viscosity growth curve by a generalization of this model. For practical applications and in order to compare the effectiveness of the present modifications, it is preferable to quantify the degree of strain hardening with a simpler scalar parameter instead. The simplest such method is to compare the values of the extensional viscosity of each sample at Hencky strains before and after the onset of strain hardening. In the present samples, this onset was at around 0.5–1 strain units. Since all samples could reach strains of at least 3 before breaking, we define a SHI here as the ratio of the elongational viscosities at 0.3 (below the onset) and at 3 s.u. (above the onset of strain hardening):

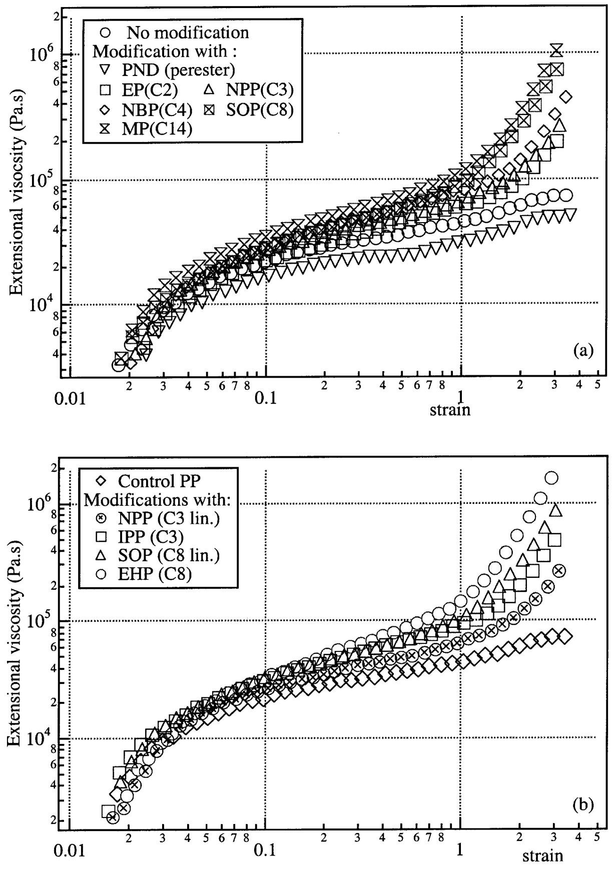


Fig. 8. Elongational viscosity growth (at a strain rate of around 0.1 s^{-1}) of PP samples modified using several PODIC (2 mmol/100 g PP) differing by (a) the length or (b) the structure of their side groups. The number of carbon atoms in the side groups is given in the legend.

$$\mathrm{SHI} = \frac{\eta_E^+(\epsilon = 3)}{\eta_E^+(\epsilon = 0.3)}$$

The SHI of the samples, modified using the several PODIC, are shown in Fig. 4, together with their melt strength. It can be seen in the figure that the trends for the melt strength and the SHI are similar: samples with higher melt strength also show higher strain hardening. Virtually, all PODIC with bulky side groups resulted in strong strain hardening. The SHI, then, seems to be an appropriate

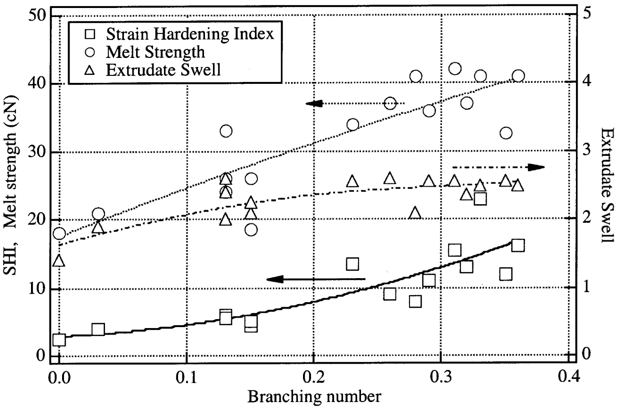


Fig. 9. SHI, Extrudate swell and melt strength as a function of the number of branches per chain for the several modified PPs. The lines are drawn only to guide the eye.

parameter for the comparison of the effectiveness of the modification.

Fig. 9 portrays the summary of the findings in the present work regarding the effect of long chain branching on the elasticity of the PP melt. The melt elasticity is manifested here in the forms of the SHI, the extrudate swell and the melt strength. These are drawn in Fig. 9 as functions of the average number of branches per polymeric chain for samples modified using the PODIC of Table 1, at different conditions. Although there is some scatter in the data, it is evident that all three properties increase with B_n. The effect of branching on the SHI seems stronger than the effect on the melt strength, while the increase in the extrudate swell may level off at higher degrees of branching. Because of this relation, this measure for strain hardening can be used as a tool for the characterization of the molecular (branching) structure. In general, Fig. 9 shows that there is a definite increase in the polymer melt elasticity, in all its manifestations, with the degree of long chain branching.

3.5. Possible reaction mechanism for the modification

The reaction of PP with the perester (PND) resulted in a decrease in the melt strength, the shear and the extensional viscosities and no strain hardening These are all indications of degradation of the PP by beta-scission induced by this perester.

The reaction of PP with the PODIC did not lead to degradation. PODIC with non-linear structure resulted in modified PP samples with more strain hardening and higher melt strength than the linear ones. They were, thus, effective for the melt strength modification of PP. Strain hardening, increased elasticity and high zero-shear viscosity are known characteristics of long chain branched polymers. A fraction of high molecular weight that could have been formed by crosslinking in the extruder, something that is also known to cause strain hardening, was not found in the SEC data of these samples. Therefore, it seems that these effects are caused in the case of PP by a long chain branched structure induced by the PODIC during the extrusion.

The special property of these PODIC is their short half-life time. This is, however, not unique, since PND had a comparable half-life time but induced degradation instead of branching. A hypothesis for the unique effect of these PODIC in inducing LCB on linear PP chains, is that they react with PP in the extruder and form alkyl-carbonate–polymer adducts, with the alkyl-carbonate group originating from the PODIC [11,12]. These or other specific reactions of the PODIC may sensitize the PP or may provide reactive sites for subsequent (radical) reactions such as recombination reactions (crosslinking), leading to the formation of LCB. The results in the present work suggest that a bulkier structure or a higher length of the alkyl-carbonate group enhances these combination reactions leading to slightly higher branching and melt strength levels.

4. Conclusions

Linear PP can be modified to obtain varied degrees of long chain branching using specific PODIC. The increase in branching number is reflected on the differences of the extensional rheology of the modified samples and their melt strength. All PODIC-modified samples show enhanced strain hardening and a higher stress at break. Further, the modifications lead to increased die swell and lower MFI. The amount of LCB can be controlled by the type and the amount of PODIC used for the modification. A perester with the same reactivity shows an opposite behavior inducing degradation through beta-scission and leading to lower extensional viscosity without strain hardening, lower melt strength, lower die swell and higher MFI.

PODIC with long linear alkyl groups are more efficient in adding branches to PP than the ones with shorter groups. Non-linear alkyl groups result in samples with more branches and strain hardening than the ones with linear groups and comparable number of carbon atoms. Higher amount of peroxide used in the extruder also leads to more branches. The best modifications, leading to most branching and the highest improvement of the processing properties of the PP melt are achieved using the di-ethyl-hexyl or the di-myristyl PODIC.

All manifestations of melt elasticity are affected by long chain branching and their measurement could be used to characterize the molecular structure of the polymer. However, even though the fiber spinning measurements can establish the differences in melt strength, they are less sensitive for the differences in the extensional rheology of the melts. On the other hand, the measured values of the stress at break and the degree of strain hardening of the extensional viscosity can show significant differences between the different branched structures.

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References

[1] Laun HM, Schuch H. J Rheol 1989;33:119–75.

[2] Ghijssels A, Ente J, Raadsen J. Int Polym Process 1990;5:284–6.

[3] Ghijssels A, De Clippeleir J. Int Polym Process 1994;9:252–7.

[4] Ghijssels A, Massardier C, Bradley RM. Int Polym Process 1997;12: 147–54.

[5] De Maio VV, Dong D. SPE ANTEC Tech Pap 1997;43:1512–6.

[6] Gotsis AD, Ke QF. SPE ANTEC Tech Pap 1999;45:1156–61.

[7] Münstedt H, Kurzbeck S, Egersdörfer L. Rheol Acta 1998;37:21–9.

[8] HIMONT Inc., Scheve BJ, Mayfield JW, DeNicola AJ. US Patent 4916198, 1980.

[9] DeNicola AJ, Galambos AF, Wolkowicz MD. ACS Polym Mater Sci Engng 1992;67:106–8.

[10] HIMONT Inc., De Nicola AJ. EP Patent 0383431B1, 1989.

[11] Hogt AH, Westmijze H. WO Patent 97/49759, 1996.

[12] Hogt AH, Fischer B, Spijkerman GK. WO Patent 99/27007, 1999.

[13] Chisso. US patent 5416169, 1994.

[14] Panzer U. Conference Proceedings of Polypropylene '98, Seventh Annual World Congress, Zürich Switzerland, 1998.

[15] Lagendijk RP. Modification of PP with peroxydicarbonates to improve its melt strength. MSc Thesis, Delft University of Technology, 1999.

[16] Meissner J, Hostettler J. Rheol Acta 1994;33:1–21.

[17] Zimm BH, Stockmayer WH. J Chem Phys 1949;17:1301.

[18] Zimm BH, Kilb RW. J Polym Sci 1959;37:4163.

[19] Lecacheux D, Lesec J, Quivoron C. J Appl Polym Sci 1982;27:4867–77.

[20] Wagner HM, Bastian H, Hanchman P, Meissner J, Kurzbeck S, Münstedt H, Langouche F. Rheol Acta 2000;39:97–109.