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Effect of molecular structure and topology on network formation in peroxide crosslinked polyethylene

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Abstract

The present study compared the crosslinking performance of single site linear low density polyethylenes (LLDPE) with high pressure, free radical polymerised, low density polyethylenes (LDPE). The difference in crosslinking performance is not fully explained by different structural parameters such as molar mass distribution (MMD), M_n, MFR_2 value and vinyl groups but is related more to the phenomenon of a long chain branched LDPE macromolecule being smaller in size in the molten state than a macromolecule of a linear LLDPE sample of the same molar mass. The result of the difference in size is that the LDPE will contain a larger number of intramolecular crosslinking points than the LLDPE, which, on the other hand, will contain a larger fraction of intermolecular crosslinking points. The crosslinking points mentioned are of either a physical or chemical nature. From the perspective of the network build-up, the intermolecular crosslinking points are the most efficient. To compensate for the larger fraction of intramolecular crosslinking points in LDPE, more peroxide can be added or vinyl groups can be introduced.

Keywords: Polyethylene; Peroxide crosslinking; Molecular size

1. Introduction

Our earlier studies have treated the crosslinking properties and network formation of an unsaturated low density polyethylene [1]. The unsaturations, vinyl groups, are introduced by copolymerising ethylene with a diene, 1,9-decadiene, in a high pressure reactor. During polymerisation, the 1,9-decadiene copolymerises with one of its vinyl groups while the other vinyl group remains unreacted. These groups were found to be used efficiently in the crosslinking reaction, and a high gel content was reached faster in the diene copolymer than in the reference low density polythylene (LDPE) material, which has a low content of vinyl groups. Lower molar masses between crosslinks, M_c, than expected were observed in an investigation of the network structure. This was explained by the presence of trapped entanglements [2,3].

One of the most important areas of application of crosslinked polyethylene (XLPE) is as insulation material in power cables. Crosslinked LDPE has been the preferred material for about 30 years. However, new types of linear low density polyethylene (LLDPE) materials polymerised with a metallocene or single site catalyst are now discussed extensively in the literature. Metallocene catalysts have actually been known since the 1950s [4,5], but it was not until Kaminsky et al. discovered the strong effect of methylalumoxane (MAO) on the activity of metallocene catalysts [6,7] that the present enormous activity in this field began. These catalysts are assumed to have only one active site, and it is thus possible to produce polyethylene materials with high M_n values as well as polyethylenes with a narrow molar mass distribution (MMD). The narrow MMD results in poor processability, i.e. these materials are less shear sensitive, exhibit melt fracture at lower shear rates and give rise to higher pressures in the extruders at a specific output as compared with an LDPE.

Despite the processability problems, it is expected that these materials may be alternatives for use in crosslinked applications in the future. We thus considered it valuable to investigate the effect of different structural parameters on

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the crosslinking properties and on properties of the crosslinked polyethylene. Low density polyethylenes with different MFR_2, MMD and vinyl group contents, were selected and compared with the single site polymerised linear low density polyethylenes.

2. Experimental

2.1. Samples

The present study included a reference LDPE material with $MFR_2 = 2$ manufactured by BOREALIS A/S. One LDPE with a narrower MMD and one with quite a broad MMD, both with the same MFR_2 as the reference, were then chosen. One LDPE with a higher MFR_2 value, 4, and one with a lower value, 0.9, than the reference material were also selected. One sample with an extremely broad MMD and a new low density poly(ethylene-co-1,9-decadiene) polymer with $MFR_2 = 2$ were included as well. All the samples mentioned are low density polyethylenes produced via a free radical mechanism under high pressure. These LDPE samples are compared with three single site LLDPE materials, all known to have a narrow MMD but having different densities and MFR_2 values. All three single site resins were commercially available grades from the Exxon Chemical Company: Exact 4003, Exact 4015 and Exact 2009. The MFR_2, density and number of vinyl groups are summarised in Table 1 below.

2.2. Characterisation

All the materials were characterised by Size Exclusion Chromatography (SEC), FT-IR and mechanical testing.

2.2.1. SEC

SEC was used for the determination of the molar masses and the molar mass distribution before and after crosslinking. The samples, in a concentration of 2 g/l, were dissolved in 1,2,4-trichlorobensene (TCB) at 135 °C overnight. The SEC runs were made at 135 °C on a Waters 150 CV equipped with a refractive index (RI) and a Wyatt Dawn F Multi Angle Light Scattering (MALLS) detector. The results were evaluated with the Waters Expert Ease programme, and the molar masses were calculated according to the principal of universal calibration. The M_n-RI, M_w-RI and M_w-LS molar masses are reported for all samples.

2.2.2. FT-IR

The type and content of different unsaturated groups, vinyl, vinylidene and *trans*-vinylene, in polyethylene can be measured with FT-IR. In this study, the FT-IR spectra were recorded on a Perkin–Elmer FT-IR 2000X collecting 25 scans and using a resolution of 4 cm^{-1}. Only the value of the vinyl groups absorbing at 909 cm^{-1} is presented. The quantitative determination was made using the extinction coefficient reported by Haslam et al. [8].

2.3. Crosslinking

We decided to add dicumylperoxide to the respective materials in amounts sufficient to reach 100% elongation in the hot set test with a load of 20 N/cm^2. Thus the same concentration of peroxide was not added to the different polyethylene samples. All the tests on the respective materials in the crosslinked form were carried out with the specific peroxide concentration yielding 100% elongation. The crosslinking properties were evaluated by FT-IR, gel content, swelling, torque and uniaxial tension measurements (hot set test), as well as by mechanical testing. The tests were made on samples prepared in three different ways: peroxide impregnated pellets pressed into a plaque, peroxide impregnated pellets pressed into a thin film and peroxide impregnated powder pressed into a thin film. Pellets impregnated with dicumylperoxide were pressed into a 1.8-mm thick plaque and then crosslinked at 165 °C for 25 min at 200 bar. Dumbbell shaped specimens were punched out from the plaque for the uniaxial tension and mechanical tests. The peroxide impregnated pellets were

Table 1
Description of the samples investigated

Sample	Sample code	MFR_2 (g/10 min)	Density (g/cm^3)	Initial number of vinyl groups/1000 C
LDPE samples				
Reference LDPE	Reference	2	0.923	0.13
LDPE narrow MMD	PE1	2		0.44
LDPE broad MMD	PE2	2		0.45
LDPE higher MFR	PE3	4	0.92	0.13
LDPE lower MFR	PE4	0.9	0.92	0.12
LDPE very broad MMD	PE5	15	0.915	0.17
Poly(ethylene-co-1,9-decadiene)	UnLDPE	2	0.923	0.68
Single site samples				
Single site LLDPE	S-S1	2.8	0.923	0.29
Single site LLDPE	S-S2	9.4	0.895	0.15
Single site LLDPE	S-S3	1.3	0.899	0.16

also used for the torque measurements. For the FT-IR, gel content and swelling measurement pellets were ground into powder in a Retch rotary cutter. The powder from the respective materials was impregnated with a methanol solution containing the dicumylperoxide [1] concentration yielding 100% elongation. From the powder containing peroxide, thin films of 0.1–0.15 mm were pressed at 125 °C for 30 s without pressure and 2 min at 30 bar. The film was immediately transferred into another press at 180 °C, and the sample was allowed to crosslink for 10 min at 30 bar and was then cooled to room temperature. The crosslinked film was washed in methanol at 45 °C for 2–3 h to remove the peroxide decomposition products. After the washing, the film was dried at room temperature under vacuum for 3 h. The films must be washed before FT-IR measurements because the peroxide decomposition products have absorptions in the same region as the vinyl groups.

2.3.1. Gel content

Gel content was determined on thin crosslinked films from which the decomposition products were removed. The gel content was determined on thin films pressed from both the peroxide impregnated pellets and the peroxide impregnated powder according to the pressing procedure described in Section 2.3 for the powder sample preparation. Both peroxide impregnated pellets and peroxide impregnated powder were used in order to ensure that there was no difference in the properties obtained by the two methods of adding peroxide.

0.3 g of the crosslinked film was placed in a pre-weighed stainless steel basket. Twelve baskets were placed in 1.1 l of decahydronaphtalene containing a hindered phenol antioxidant, and the crosslinked films were extracted at 190 °C. After 6 h, the solvent was replaced with 0.9 l of fresh decahydronapthalene, and the extraction continued for another hour. The samples were dried at 80 °C under vacuum for 5 h and the remaining gel was then weighed and the gel content calculated.

2.3.2. Swelling measurements

The gel, still in the stainless steel basket used for the gel content determination, was allowed to swell in *p*-xylene at 120 °C for at least 2 h. The amount of solvent taken up by the gel was measured, and the Flory–Rehner equation (1) [9] was used for the calculation of the molar mass between crosslinks, $M_{\mathrm{c,swell}}$.

$$-\ln(1 - V_{\mathrm{r}}) - V_{\mathrm{r}} - \chi V_{\mathrm{r}}^2 = \rho_{\mathrm{p}} V_0 M_{\mathrm{c}}^{*-1}\left(V_{\mathrm{r}}^{1/3} - \frac{V_{\mathrm{r}}}{2}\right) \tag{1}$$

To correct for loose chain ends present in the material, M_{c}^{*-1} is replaced with the following expression:

$$M_{\mathrm{c}}^{*-1} = M_{\mathrm{c,swell}}^{-1}\left(1 - 2M_{\mathrm{c,swell}}\overline{M_n^{-1}}\right) \tag{2}$$

V_{r} is the volume fraction of polymer in the swollen gel

$$V_{\mathrm{r}} = \frac{1}{\left(\frac{M_{\mathrm{s}}\rho_{\mathrm{p}}}{M_{\mathrm{p}}\rho_{\mathrm{s}}}\right) + 1} \tag{3}$$

where

M_{p} is weight of the dry gel
M_{s} is weight of the solvent taken up by the gel
$\rho_{\mathrm{p}} = 0.806\ \mathrm{g/cm^3}$, density of the polymer [10]
$\rho_{\mathrm{s}} = 0.761\ \mathrm{g/cm^3}$, density of the solvent [10]
$\chi = 0.31$, the solvent interaction parameter for polyethylene swelled in *p*-xylene [10]
$V_0 = 139.3\ \mathrm{cm^3}$, the molar volume for *p*-xylene [10]
—
M_{n} is the number average molar mass of the polymer prior to crosslinking

The values for ρ_{p}, ρ_{s}, χ and V_0 were taken from Ref. [10] even if the authors had used boiling *p*-xylene for their measurements.

2.3.3. Torque

From the peroxide impregnated pellets, a circular specimen 37 mm in diameter and 5 mm thick was pressed according to the following procedure: melting for 2 min at 120 °C without pressure, 2 min at 120 °C at 5 ktons and cooling to room temperature. These specimens were used for the torque measurements made in a Göttfert Elastograph operating at 180 °C. The evolution of the torque was measured as a function of time over a period of 10 min. The maximal torque value as well as and the rate of crosslinking can be determined from the elastograph curve. We have only reported the final torque value in this study.

2.3.4. Uniaxial tension measurements, hot set test

A dumbbell shaped specimen was loaded with 20 N/cm^2 and marked with a reference length, L_0, of 20 mm. The loaded sample was placed in an oven at 200 °C and the length between the reference marks, L_1, was measured after 15 min. The value presented for each material is the average of three individual measurements. Using the ratio $\lambda = L_1/L_0$ and the rubber elasticity theory, the $M_{\mathrm{c,hot\ set}}$ value can be calculated from Eq. (4):

$$M_{\mathrm{c,hot\ set}} = \frac{1}{\left(\frac{2}{\overline{M}_n} + \frac{\sigma}{\rho_{200}RT\left(\lambda - \frac{1}{\lambda^2}\right)}\right)} \tag{4}$$

where

σ is the nominal stress
$\rho_{200} = 753.6\ \mathrm{kg/m^3}$, the density of the polymer at 200 °C [11]

$R = 8.3144$ J/(mole K)
T is the absolute temperature (K)

The $M_{\mathrm{c,hot\ set}}$ value was not corrected for the energy elastic contribution to the retractive force [12].

2.3.5. Mechanical properties

The mechanical properties before and after crosslinking were measured on an Alwetron TCT10. Dumbbell shaped specimens were punched out from a conditioned crosslinked plaque. The tensile testing was done in a room with a constant temperature of 23 °C and relative humidity of 50%. The tensile strength at break, σ_b, and the elongation at break, ϵ_b, were determined at a strain speed of 250 mm/min.

3. Results and discussion

The aim of this study was to evaluate the influence of different characteristics, such as different MFR_2 values, MMD and the presence of vinyl groups, on crosslinking properties.

3.1. Characterisation

The results of molar mass characterisation of the materials are first presented in Table 2, as these data will be used for the interpretation of the results generated in the crosslinking tests.

The difference between M_w-RI and M_w-LS in the LDPE samples is a result of the long chain branches (LCB) that are present. The S-S1 and S-S3 have a clearly higher M_n value than the other materials included in this study. All the single site materials also have a very narrow MMD, between 2.7 and 3.7.

3.2. Crosslinking properties

The hot set test is extensively used for XLPE to monitor the degree of crosslinking. It was thus decided to crosslink the materials included in this study with an amount of DCP that would make it possible to obtain 100% elongation in the hot set test. 100% elongation was selected because this criterion is a frequently used requirement for crosslinked polyethylene used as cable insulation material. Fig. 1(a)–(c) shows the hot set value at different peroxide concentrations for each material. All the materials investigated show more or less the same behaviour, i.e. the materials are not especially sensitive to a small change in the DCP concentration at low hot set values. At a certain DCP concentration, however, the slope of the curve drastically

Table 2
SEC data for the samples before crosslinking

Sample	M_n-RI (g/mole)	M_w-RI (g/mole)	M_w-LS (g/mole)	M_w-LS/M_n-RI
Reference	17,000	67,000	187,000	11
PE1	19,900	66,000	143,000	7.2
PE2	16,800	93,000	276,000	16.4
PE3	16,400	71,000	160,000	9.8
PE4	17,700	79,000	145,000	8.2
PE5	18,200	120,000	383,000	21
UnLDPE	16,100	69,000	221,000	13.7
S-S1	27,400	75,000	75,000	2.7
S-S2	18,700	56,000	53,000	2.8
S-S3	27,000	85,000	99,000	3.7

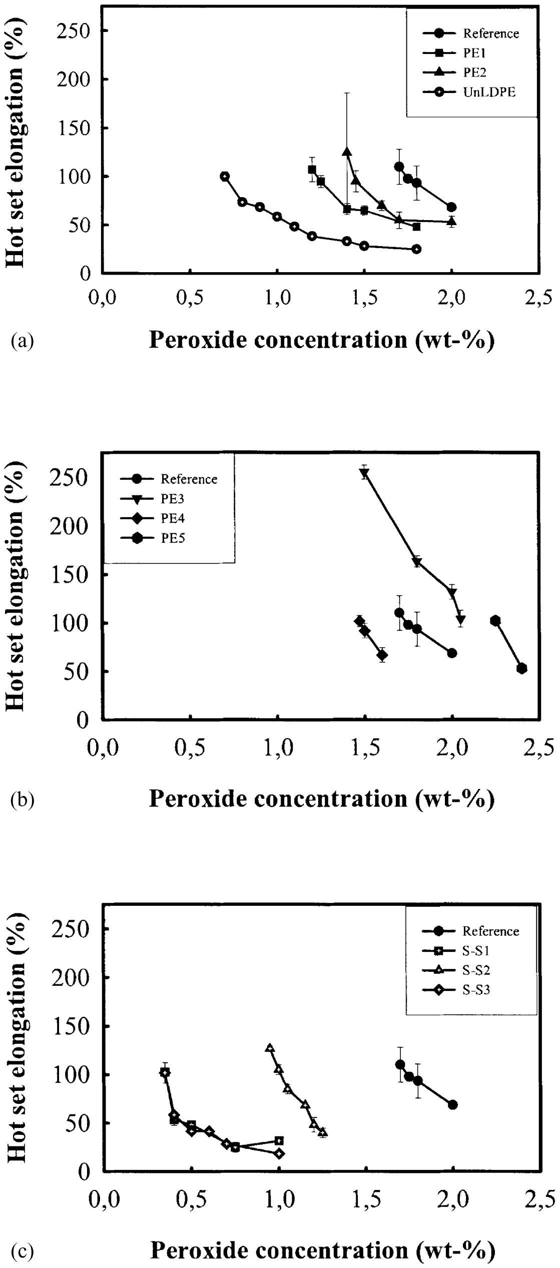

Fig. 1. (a) Hot set elongation vs. peroxide concentration for PE1, PE2, UnLDPE and the reference material. (b) Hot set elongation vs. peroxide concentration for PE3, PE4, PE5 and the reference material. (c) Hot set elongation vs. peroxide concentration for S-S1, S-S2, S-S3 and the reference material.

increases. There was some difficulty in finding the peroxide concentration that resulted in exactly 100% elongation as the slope is very steep in that region.

Table 3 gives the peroxide concentrations required, the gel contents obtained and the number of reacted vinyl groups. There seems to be two groups of materials, one in which a DCP content >1 wt% is required and one in which a DCP concentration ≤ 1 wt% is required in order to reach 100% elongation. The conventional LDPE samples all require more than 1 wt% DCP, while the linear single site materials and the UnLDPE material all require 1 wt% DCP or less.

The deviation in gel content between pellet and powder samples is most pronounced for the single site materials, especially when a low peroxide concentration was used. It is very difficult to add peroxide in such small amounts, which probably explains the deviation. In examining the gel content achieved at 100% elongation in the hot set test, two groups of materials were observed, one in which all the LDPE materials were found to yield 70–80% gel and one in which the single site materials were found to yield 0–67% gel. In each material group, LDPE and single site, a material with a higher MFR_2 value generally requires more DCP to yield 100% elongation.

The vinyl groups present in the materials contribute additional chemical crosslinks. The number of reacted vinyl groups correlates to the initial concentration of vinyl groups and the DCP concentration used [1]. The highest number of reacted vinyl groups is found in the UnLDPE sample but vinyl groups were also consumed in PE1, PE2, PE5 and S-S1. Common to these samples is that they contain a somewhat higher or a clearly higher initial number of vinyl groups than the other materials.

The UnLDPE sample is outstanding among the LDPE materials. This sample has the same MFR_2 value and molar mass characteristics similar to those of the reference material. The only difference between the two materials is the number of vinyl groups that are present, which explains the difference in DCP concentration required for these two samples, 0.7 wt% DCP in the UnLDPE sample and 1.75 wt% DCP in the reference sample. This stresses the strong influence that the vinyl groups have on the crosslinking reaction. As reacted vinyl groups result in chemical crosslinking points the contribution of the chemical crosslinking points from the peroxide, i.e. the combination of alkyl macroradicals, can be reduced.

Among the other LDPE materials with $MFR_2 = 2$, it can be observed that PE1 and PE2 both require less peroxide, 1.25 and 1.45 wt%, respectively, than the reference, which is most probably due to the low concentration of vinyl groups in the reference. The difference in crosslinking behaviour between PE1 and PE2, both of which have almost the same number of initial vinyl groups, may be explained by the higher M_n-RI value of PE1. While PE2 has a higher M_w-LS value than PE1, it has previously been shown that the high molar mass tail assists in the initial crosslinking reaction only [2] and that it has almost no effect on the final degree of crosslinking.

When the reference material is compared with PE3, PE4 and PE5, all with almost the same initial number of vinyl groups, a clear correlation can be observed between the MFR_2 value and the amount of DCP required. PE5 would probably have required more than 2.25 wt% DCP to reach 100% elongation because of its very high MFR_2 value but, as this sample contains somewhat more vinyl groups initially and has a somewhat higher M_n-RI value, 2.25 wt% is sufficient.

It is not possible to compare the MFR_2 value of an LCB branched LDPE and a non-LCB branched LLDPE, and the two groups will thus be discussed separately in this section. The same trend is observed in the single site material as is seen in the LDPE materials: the higher the MFR_2 value, the more DCP is required. S-S1 and S-S3 require very little peroxide, only 0.35 wt%, probably due to their very high M_n-RI values. The reason why they require the same amount of DCP even though S-S1 has a higher MFR_2 value than S-S3 can be explained by the contribution of the vinyl groups present in S-S1. S-S2 requires the highest DCP concentration among the LLDPE samples because of its high MFR_2 value. However, this single site material has almost the same content of vinyl groups and almost the same M_n-RI value as some of the LDPE materials and, in that comparison, 1 wt% DCP is quite low.

The molar masses of the sol fractions are summarised in

Table 3
DCP concentration required, gel contents and the number of reacted vinyl groups

Sample	MFR_2 (g/10 min)	DCP conc. (wt%)	Gel content pellets (%)	Gel content powder (%)	Reacted vinyl groups/1000 C
Reference	2	1.75	78	64	0.05
PE1	2	1.25	77	74	0.09
PE2	2	1.45	80	80	0.13
PE3	4	2.05	71	63	0.08
PE4	0.9	1.45	75	74	0.06
PE5	15	2.25	81	87	0.11
UnLDPE	2	0.70	77	72	0.22
S-S1	2.8	0.35	0	15	0.13
S-S2	9.4	1.00	67	56	0.07
S-S3	1.3	0.35	0	0	0.03

Table 4. Although not all materials were tested, clear trends can be observed.

In the LDPE samples, M_n-RI and M_w-RI are both lower after crosslinking because of the greater probability that the high molar mass chains will locate to the gel. A higher M_w-RI value is measured after crosslinking in S-S3, almost the double the initial value, which is expected as no gel was measured in this sample. One interesting observation is that the M_n-RI values in the single site materials are the same as before crosslinking. This may be taken as a strong indication that no chain scission has occurred during the crosslinking reaction at the temperature used in this study. However, the M_w-RI values presented were not corrected for any LCB that could have been created during the peroxide crosslinking step.

3.3. Network properties

3.3.1. $M_{c,\ swell}$ and $M_{c,\ hot\ set}$

The M_c values calculated using Eqs. (1) and (4), respectively, are given in Fig. 2 as a function of the M_n-RI value. The $M_{c,hot\ set}$ results in a linear correlation, which is expected as all values in the expressions except for the M_n-RI value are assumed to be constant. As mentioned in the Section 2, the values presented were not corrected for the energy elastic component to the retractive force. The energy elastic component is said to be -42% of the retractive force for polyethylene [12]. To give examples showing the effect of this correction, the $M_{c,hot\ set}$ value for the reference material would be 6402 g/mole without correction and 5800 g/mole with correction, and the $M_{c,hot\ set}$ for S-S3 would be 8878 g/mole without and 7762 g/mole with correction.

As seen in Fig. 2, all values of the $M_{c,swell}$ data are lower than the corresponding $M_{c,hot\ set}$ data with one exception. The reason for the lower $M_{c,swell}$ value is that 100% of the material in the the $M_{c,hot\ set}$ data is considered, both gel and sol, while only the gel is taken into consideration in the $M_{c,swell}$ value. One exception is S-S2, which yields a higher $M_{c,swell}$ than $M_{c,hot\ set}$. If the $M_{c,swell}$ value were corrected, as it represents only 56% of the sample, the value would be even higher. The S-S1 and S-S3 samples do not contain enough chemical crosslinking points to withstand the gel content determination test procedure, as no gel was observed in these samples. It was thus not possible to determine $M_{c,swell}$ in these samples.

The linear single site materials do indeed contain a number of effective crosslinking points, however, as the 100% elongation in the hot set test is achieved. It seems that the gel content extraction test is a ‘tougher’ test for the material than the hot set test. The gel content test requires that the crosslinking points are truly permanent, i.e. that they are chemical crosslinking points and ‘fully’ trapped entanglements. In order to be ‘fully’ trapped all four strands in the entanglement must be connected to the network [13, 14]. If all strands are not connected to the network for a physical crosslink, it will be only partially trapped, i.e. it will be a temporary entanglement [14]. Besides chemical crosslinking points and ‘fully’ trapped entanglements, partially trapped, temporary, entanglements are probably also detected in the hot set test. Since $M_{c,swell}$ indicates a looser network than $M_{c,hot\ set}$, all single site materials contain a large fraction of temporary entanglements and a small fraction of permanent crosslinking points, fully trapped entanglements and chemical crosslinking points.

3.4. Torque measurements

The results of the torque measurements are shown in Table 5.

Although the samples are crosslinked to the same hot set elongation, the torque value varies widely. M_n is the property that appears to have the greatest impact on the torque value, which is shown in Fig. 3. Since the phase angle is not measured in the torque measurement, it is not possible to calculate the modulus and thus not the $M_{c,torque}$ value. However, if it is assumed that the torque is proportional to the modulus, the $M_{c,torque}$ would be lower in S-S1 and S-S3 than in the LDPE samples.

Among the LDPE samples, the UnLDPE material is still different, as this material has a relatively low M_n-RI and at the same time requires only a low amount of DCP. Still, this material shows a torque value comparable with the other

Table 4
Molar mass of the sol fraction after crosslinking

Sample	M_n-RI	M_w-RI
Reference	11,000	35,900
PE1	14,200	47,000
PE2	11,500	48,400
PE3	Not measured	Not measured
PE4	12,000	30,800
PE5	Not measured	Not measured
UnLDPE	11,400	37,500
S-S1	Not measured	Not measured
S-S2	19,700	73,700
S-S3	27,800	149,000

Table 5
Measured maximum torque values in the samples investigated

Sample	Torque value (Nm)
Reference	0.57
PE1	0.65
PE2	0.56
PE3	0.51
PE4	0.53
PE5	0.67
UnLDPE	0.57
S-S1	0.93
S-S2	0.78
S-S3	0.87

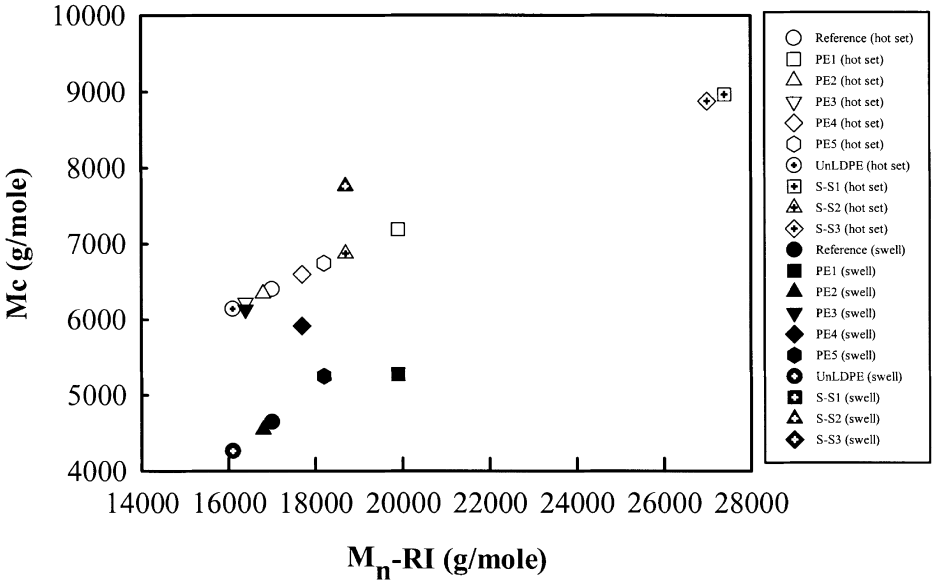

Fig. 2. $M_{c,swell}$ and $M_{c,hot\ set}$ vs. M_n-RI.

LDPE materials, most probably because of the effect of the reacted vinyl groups.

The single site materials behave differently from the LDPE materials in the torque test as well. This is most obvious for S-S2, which, despite an M_n-RI value in the same range as in the LDPE, and in combination with a relatively low DCP concentration, still shows a high torque value. As a result of the small deformation to which the material is exposed in this test, the chemical and physical crosslinks, ranging from temporary to 'fully' trapped entanglements, all contribute effectively to the torque.

The three techniques, swelling, hot set and torque measurements, detect different types of crosslinking points, from temporary to permanent. Swelling measures 'fully' trapped entanglements and chemical crosslinking points, hot set measures 'fully' trapped entanglements, chemical crosslinking points and some temporary entanglements and torque measures 'fully' trapped entanglements, chemical crosslinking points and quite a large fraction of the temporary entanglements.

3.5. Mechanical testing

The mechanical properties at room temperature before and after crosslinking have also been measured. The results are summarised in Table 6.

The general trend is that σ_b increases and ϵ_b decreases after crosslinking. The single site materials give substantially

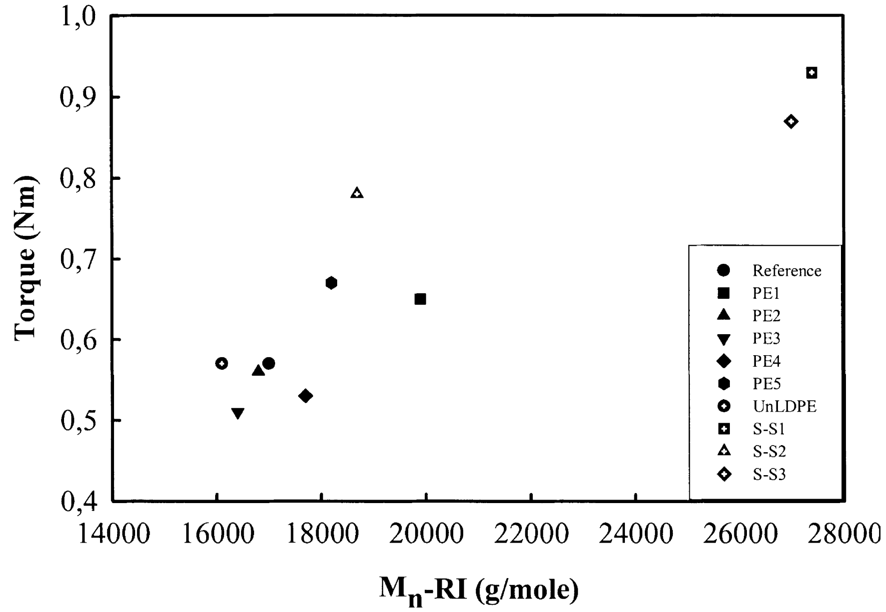

Fig. 3. Torque value as a function of M_n-RI.

Table 6
Mechanical properties before and after crosslinking

Sample	$\sigma_{b,before}$	$\sigma_{b,after}$	$\epsilon_{b,before}$	$\epsilon_{b,after}$
Reference	16	25	680	555
PE1	17	29	681	605
PE2		22		543
PE3		22		567
PE4		24		597
PE5		23		518
UnLDPE		24		545
S-S1		37		654
S-S2		34		700
S-S3	25	35	815	720

higher σ_b and ϵ_b values than the LDPE materials, both before and after crosslinking. A possible explanation of this behaviour would be the high M_n-RI values on the sol fraction, see Table 4. This fraction contains fewer chain ends. It is thus easier for one chain to be a part of several crystallites, which reduces the stress concentration in the amorphous phase and thereby increases the σ_b and ϵ_b values. PE1 yields slightly higher σ_b and ϵ_b values than the other LDPE materials. This is also a result of the slightly higher M_n-RI value in the sol fraction, according to the explanation given above for the single site materials. A thorough interpretation of the mechanical properties is difficult, however, as the measurements were made at room temperature and thus both the crystallinity and crystal structure have an impact on the results.

3.6. Discussion of the effect of different structural parameters

From the point of view of gel formation, in combination with the results shown in Table 5, M_n is one of the most important parameters since:

- a high M_n value reduces the number of chain ends
- when the M_n value is high, there is a greater probability of locking in physical crosslinking points so that they are in the range of 'fully' trapped to temporary entanglements
- a high M_n value also indicates that the fraction of very low molar mass material is reduced. Relatively speaking, the low molar mass material requires more peroxide before it is incorporated into the gel

The single site materials utilise to a greater extent the physical network when 100% hot set elongation is reached. An earlier study [2,3] showed that trapped entanglements constitute the major part of the elastically effective crosslinking points found in LDPE. The molar mass required for the formation of an entanglement, $M_{c,entanglement}$, is ~4000 g/mole in the case of polyethylene. The importance of effective use of physical crosslinking points, 'fully' trapped entanglements or temporary entanglements, is explained in Fig. 4.

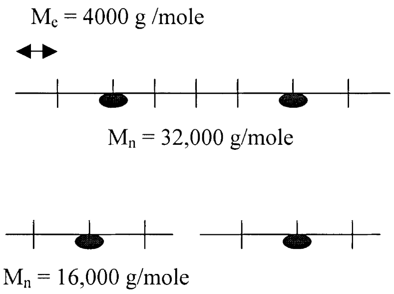

Fig. 4. Impact of the M_n value on the utilisation of the physical crosslinking points.

The M_c value achieved with 2 wt% DCP, considering only the peroxide and under the assumption that the peroxide is 100% efficient, is about 16,000 g/mole. The chemical crosslinking points are marked with ● in Fig. 4. For the polyethylene chain with an M_n equal to 32,000 g/mole, the result is two crosslinking points and three potential physical crosslinking points. For the polyethylene represented by two chains and having a M_n value equal to 16,000 g/mole, this results in only two chemical crosslinking points and no opportunity for the formation of any physical crosslinking points.

It seems that there are two options for achieving a certain degree of crosslinking:

- increasing the M_n value
- increasing the number of chemical crosslinking points. This may be accomplished by the introduction of vinyl groups or by crosslinking points originating from the peroxide via combination of created alkyl macroradicals.

In addition to the M_n value, the number of vinyl groups also has a considerable influence on the crosslinking performance, as was shown in the UnLDPE. The reason for this strong effect is that one single radical can give rise to several chemical crosslinking points when the vinyl groups react via polymerisation. This means that the radical reactivity is preserved at the same time as chemical crosslinks are created. The radical may reach the vinyl groups via radical migration, see Ref. [1] for a more thorough discussion on the proposed mechanism. A larger number of chemical crosslinking points also results in more extensive utilisation of trapped physical crosslinking points. This kind of crosslinking behaviour makes the UnLDPE resin unique in that it combines good crosslinking performance with the excellent processing characteristics of an LDPE.

In this study, the network was tested by different techniques, i.e. hot set, gel content and torque measurements. We chose to keep the hot set value equal to 100% elongation. The relative network performance as measured by the three techniques as a function of M_n is illustrated in Fig. 5.

The effective crosslinking points in materials with high M_n values consist to a large extent of physical crosslinking points. At small deformations, as in the torque test, all these

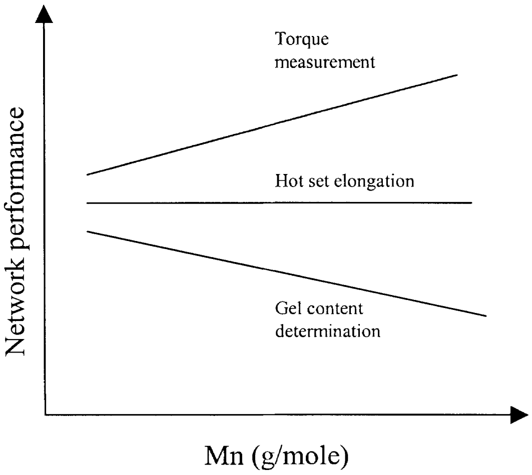

Fig. 5. Network performance determined by different techniques for materials with varying M_n values.

crosslinking points contribute, thus explaining the unexpectedly high torque values that were reached. However, in a test that truly stresses the crosslinking points, as in the gel content and swelling tests, physical crosslinking points 'disentangle' unless they are 'fully' trapped. The gel content test requires the network to contain chemical crosslinking points that hold it together under the force of great stresses to which it is exposed in these conditions.

The LDPE materials are among the low M_n-RI values in Fig. 5. Since a certain number of chemical crosslinking points are necessary in order to reach the 100% hot set elongation, these types of materials are not very sensitive to different test procedures. A correlation between the hot set, gel content and torque value can be distinguished, even if some deviation exist.

The fact that two of the single site materials pass the 100% hot set elongation without the formation of any gel makes it tempting to believe that there is a fundamental difference in the crosslinking structure between this group of material and conventional LDPE materials, a difference that cannot be explained soley by the M_n effect. This hypothesis is supported by the behaviour of the S-S2 material, which, although it has the same M_n-RI value as the LDPE samples studied, requires less peroxide and shows a lower gel content at 100% hot set elongation than the LDPE samples. A reasonable explanation would be that the network formed in the linear polyethylene consists to a greater extent of intermolecular entanglements than in the LDPE. One possible reason may be the different topologies of linear and LCB branched polyethylene. It is well known that a long chain branched polyethylene molecule has a smaller hydrodynamic volume, size, than a linear polyethylene molecule of the same molar mass [15]. It can thus be expected that a long chain branched polyethylene molecule has a higher density of its own segments. The total segment density in the melt, C_{tot}, is of course constant:

$$C_{\text{tot}} \propto \frac{\rho N_A}{M_{\text{repeating unit}}} \tag{5}$$

The size of the coiled linear polymer molecule, V_c, can be obtained from the radius of gyration, assuming that the mean-field picture is valid:

$$V_c = \tfrac{4}{3}\pi s^3 \tag{6}$$

where s is the radius of gyration.

Within that volume, the molecule has n_c segments:

$$n_c = \frac{M_{\text{polymer molecule}}}{M_{\text{repeating unit}}} \tag{7}$$

The concentration of segments of one single molecule is thus:

$$C_c = \frac{n_c}{V_c} = \frac{\dfrac{M_{\text{polymer molecule}}}{M_{\text{repeating unit}}}}{\tfrac{4}{3}\pi s^3} \tag{8}$$

Under θ conditions, s^2 is proportional to the molar mass of the polymer, and C_c can thus be expressed as:

$$C_c \propto \frac{1}{\sqrt{M_{\text{polymer molecule}}}} \tag{9}$$

The fraction of segments from one single molecule is thus:

$$X_{\text{intra}} = \frac{C_c}{C_{\text{tot}}} \propto \frac{\dfrac{1}{\sqrt{M_{\text{polymer molecule}}}}}{\dfrac{\rho N_A}{M_{\text{repeating unit}}}} \tag{10}$$

or

$$X_{\text{intra}} \propto \frac{1}{\sqrt{M_{\text{polymer molecule}}}} \tag{11}$$

This expression indicates that the probability of any intramolecular interactions, whether it is a chemical crosslink or an entanglement, decreases when the molar mass increases.

In the case of a long chain branched molecule, the relation between the radius of gyration and the molar mass is more complex and Eq. (6) is not valid. Instead, the branched molecule is compared with a linear molecule of the same molar mass. The following relation is valid:

$$g = \frac{\langle s_\theta^2\rangle_{\text{br}}}{\langle s_\theta^2\rangle_{\text{lin}}} \tag{12}$$

where $g < 1$.

The relation between the size, V_{br} and V_{lin}, can then be written as:

$$\frac{V_{\text{br}}}{V_{\text{lin}}} = \frac{\tfrac{4}{3}\pi s_{\text{br}}^3}{\tfrac{4}{3}\pi s_{\text{lin}}^3} = \frac{s_{\text{br}}^2 s_{\text{br}}}{s_{\text{lin}}^2 s_{\text{lin}}} = g^{1.5} \tag{13}$$

In practice, θ conditions are not used to determine g. The corresponding expression with intrinsic viscosities, $[\eta]$, is more frequently used instead:

$$g' = \frac{[\eta]_{\mathrm{br}}}{[\eta]_{\mathrm{lin}}} \tag{14}$$

$$g' = g^B \tag{15}$$

For polyethylene dissolved in a good solvent, B is considered to be in the range of 0.8–1 [16,17]. To illustrate the effect of long chain branching on the concentration of own segments, we used data on g' for the reference material generated in Ref. [18]. The average value for the whole sample is $g' = 0.33$. Assuming that $B = 0.85$, g will then be equal to 0.28. Inserting this value into Eq. (13) gives the relation between the branched and the linear molecule of

$$V_{\mathrm{br}} = 0.15V_{\mathrm{lin}} \tag{16}$$

This means that the volume of the LDPE polymer molecule will be only around 15% of the volume of a linear polyethylene molecule with the same molar mass. The concentration of intramolecular segments in the branched polyethylene is thus six times higher than in the linear polyethylene. Ultimately this means that LDPE requires more peroxide than a linear polyethylene in order to be crosslinked to a certain degree. First of all, a larger part of the peroxide added to an LDPE will be 'inefficient' since it will be used to form intramolecular chemical crosslinks. Furthermore, the LDPE molecule contains fewer intermolecular entanglements than are needed for the formation of an efficient network. The effect of four linear polyethylene macromolecules and four long chain branched macromolecules in a certain equal volume segment and at the same density can be described schematically as it is in Fig. 6. With the long chain branched macromolecules, the overlap between the coils is smaller than it is for the linear macromolecules, thereby creating fewer intermolecular interactions. To compensate for the lower number of intermolecular chemical and physical crosslinking points, the overall number of chemical crosslinking points in an LDPE must be increased. This can be achieved either by increasing the peroxide concentration or by using a base resin modified with additional vinyl groups.

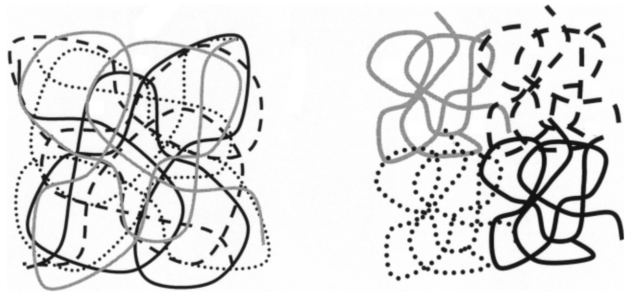

Fig. 6. Schematic comparison between a network based on linear polyethylene chains (left) and a network based on polyethylene chains containing LCB (right).

The figures given above should of course only be valid for the polymer used to obtain the data in Ref. [18]. The relation between V_{br} and V_{lin} will be strongly dependent on the amount of LCB. This helps a more detailed understanding of the difference between the LDPE samples. It was noted above that the amount of peroxide needed to obtain 100% elongation in the hot set test increased with the MFR_2 value—compare samples: PE4, reference, PE3 and PE5. A general trend is that the increase in MFR_2 value is accompanied by an increase in the M_{w}-LS value, see Table 2. This should have led in the case of linear polyethylenes to an increase in the melt viscosity. In the four samples under discussion here, the increase in M_{w}-LS is compensated for by an increase in the number of LCB. The drastic effect of LCB on the size will thus give the observed increase in the MFR_2 value. For these polymers, the MFR_2 value is in fact an indication of the molecular size. The observed relation between the required peroxide level and the MFR_2 value can therefore be explained by the increased fraction of intramolecular interactions with decreased size. Considering the MFR_2 value, PE5 should have the smallest molecular size and, as a result require the highest amount of peroxide [3]. The difference with PE3 is, however, not very great, 2.25 wt% compared to 2.05 wt% DCP. The effect of size in PE5 is compensated for to a certain extent by a somewhat higher number of reacted vinyl groups.

4. Conclusions

This investigation shows that there are three major structural parameters that influence the crosslinkability and the network quality achieved for polyethylene:

- M_{n}
- number of vinyl groups
- number of long chain branches

The direct effect of M_{n} is that less peroxide is required in order to obtain a certain heat deformation strength in the sample when M_{n} is increased. Indirectly, the network quality is affected owing to the physical crosslinking points naturally present, as more or less trapped entanglements are utilised to a greater extent. Two of the single site resins investigated in this study have a high M_{n} value. This partly explains the low DCP concentration needed to reach 100% elongation, as only a few chemical crosslinking points are needed to 'fix' the entanglement network naturally present in the polymer.

The direct effect of the vinyl groups is that an increased number of chemical crosslinking points are formed at a given amount of decomposed peroxide. This indirectly leads to the naturally physical crosslinking points present being 'fixed' and thus utilised to a greater extent [2,3].

The most striking observation in this investigation is the drastic effect of the molecular size on crosslinkability and network quality. In addition to being controlled by the molar mass, the size of a polymer molecule is also governed to a great extent by the number of long chain branches present. For a given molar mass, an increasing number of long chain branches leads to a decrease in the size of the polymer molecule. This in turn leads to an increased fraction of intramolecular interactions at the expense of the desired intermolecular interactions. The effect of size means that the probability of forming an entanglement within the same molecule is greater in LDPE than in a linear polyethylene. This thinking can also be extended to be valid for the crosslinking reaction, as the most efficient crosslinking points are those linking together two different chains, intermolecular crosslinking points.

However, the smaller size can be compensated for by a larger amount of peroxide or by introducing vinyl groups. As an example, the poly(ethylene-co-1,9-decadiene) polymer, UnLDPE, offers a dramatically enhanced crosslinkability and network quality while maintaining the excellent processability of an LDPE, as compared with a linear polyethylene.

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