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Crosslinking of bimodal polyethylene

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Abstract

Two bimodal polyethylenes, differing only in polymerisation order, were investigated with respect to crosslinking behaviour and network properties. The crosslinked materials were examined using size exclusion chromatography (SEC), gel-content measurements, and calculations of the network density. Dynamic mechanical analyses in the melt were performed to monitor the crosslinking and to provide another measure of the network density. The experiments were performed to investigate any potential influence of the polymerisation order on the crosslinking as well as to study the network formation in the crosslinked polymers. The bimodal polyethylenes were also compared to two monomodal polyethylenes representing the short chain branched, high molecular weight fraction, and the linear, low molecular weight fraction, respectively. The SEC measurements clearly showed how the crosslinking starts with the consumption of the high molecular weight fraction. The gel-content measurement showed the importance of a high molecular weight material for the gel formation. The network density calculations demonstrated how long chains can give rise to apparent networks which are mainly due to chain entanglements. The experiments showed that the polymerisation order for the bimodal polyethylenes has no effect on the crosslinking.

Keywords: Bimodal PE; Peroxide crosslinking; Network

1. Introduction

Crosslinked polyethylene, XLPE, is a widely used material with cable insulation and hot-water pipes as the most important fields of application [1]. The crosslinked polyethylene forms a network, which gives the material several desirable properties, such as toughness and resistance against heat and chemicals [2,3]. The crosslinking reaction needed to create the network can be initiated with peroxides, by irradiation or by addition of silanes [4]. The first two methods have a similar course of action as they create radicals, which then form crosslinks between the polyethylene chains. In the third method, silane forms bridges between the polymer chains. In this work, we have used peroxide as the crosslinking agent.

Polyethylene (PE) comes in several grades. A common way of grouping the different grades is based on material density, from low density polyethylene (LDPE) with a density of approximately 0.915–0.930 g/cm^3 to high density polyethylene (HDPE) with densities around 0.940–0.958 g/cm^3 [5]. LDPE is produced in a high-pressure process, giving a polymer with both long- and short chain branches (SCB) and hence low crystallinity and low density. HDPE is produced using Phillips or Ziegler–Natta catalysts, resulting in a polymer with a low amount of branches. A third type of PE is linear low-density polyethylene, LLDPE, which is a co-polymer of ethylene and one or several α-olefins such as 1-butene, 1-hexene, or 1-octene. LLDPE is normally polymerised with a Ziegler–Natta catalyst, which gives a linear polymer, but the incorporation of SCB from the co-monomer results in densities in the same range as in LDPE.

In recent years, there has been an interesting development towards new polyethylene grades since the demand is increasing for polyethylenes with specific properties for certain product applications. This tailor-making has not been possible through the radical polymerisation process used for the making of LDPE. Instead, we see an increased use of polyethylenes polymerised in the presence of catalysts, especially LLDPE [6,7]. However, it is difficult to make a unimodal polymer with a desired set of properties. A shift in the molecular weight (MW) or molecular weight distribution (MWD) may improve one property, but may

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also compromise another. One solution to these problems has been a PE with a bimodal MWD. In such a material, the two 'humps' can be independently adjusted, making it possible to combine a high molecular weight with a good processability. A branched, high molecular weight fraction adds strength to the material, and a linear, lower molecular weight fraction facilitates the processing. Theoretically, this could be achieved by simply melt-blending two polyethylenes with the desired MWDs. However, the miscibility upon cooling is not satisfactory and it is difficult to obtain well-dispersed morphologies [8,9]. To retain miscibility at a molecular level, it is necessary to polymerise the different polyethylene qualities at the same catalyst particle. This can be achieved in two ways, by a specially designed process or by a specially designed catalyst, and yields a homogenous blend with a broad or bimodal distribution upon processing. The specially designed catalyst is a combination of two catalysts with different catalytic activities, each polymerising polyethylenes with different properties. The commercial way to create bimodality is, however, through a two-stage process [10,11].

In this project, bimodal PE is produced according to the Borstar technology [12]. The Borstar process consists of two consecutive reactors, a slurry loop reactor followed by a gas-phase reactor. Ethylene and the catalyst are fed into the loop reactor where unbranched, low molecular weight PE is polymerised. The product, together with the catalyst, is transferred to the gas-phase reactor where more ethylene and a co-monomer are added. This results in a high molecular weight, short chain branched PE, which polymerises on the same catalyst particle. The difference in branching will ensure that the two fractions crystallise simultaneously. It is reasonable to believe that these bimodal polymers will be the most commonly used polyethylenes in the future as they are comparably easy to make for specific purposes. Furthermore, Bimodal PE shows better overall properties than unimodal PE, which leads to a lower material consumption [10]. However, their crosslinking properties have not been thoroughly examined yet. Since bimodal polyethylene grades most likely will be dominating the market in the future, this will certainly be an interesting task to pursue.

Crosslinking of polyethylene has for a relatively long time been a research field at this department, with a main focus on peroxide crosslinking of LDPE. In these studies, we found that the crosslinking properties of PE can be affected by adding reactive vinyl groups to the polymer chain to improve the effectiveness of the added peroxide [13]. The formation and structure of the network have also been investigated. The observed network density was considerably higher than expected from the amount of peroxide added [14]. The network was found to be a combination of chemical crosslinks and entanglements, where the entanglements are entrapped by the chemical crosslinks. To obtain such effects of entanglements on the network density, the number average molecular weight, $\overline{M}_n$, must be reasonably high. In fact, the molecular weight has to be above 4000 for entanglements to form at all, i.e. the critical molecular weight for entanglements ($M_{e,\,PE}$) is ~4000 for polyethylene [15]. Therefore, only a few chemical crosslinks will be sufficient to obtain a network consisting of mostly entanglements as long as the polymer chains are long enough. These results are of great interest to the manufacturers of PE as the amount of peroxide added can be kept low. However, long chains render melt processing more difficult, something which can be overcome with a bimodal distribution.

In this work, we have examined and compared two bimodal polyethylenes. The first one is produced by standard polymerisation, with the low molecular weight PE polymerised in the first reactor and the high molecular weight part added in the second reactor. This polymer is compared to another bimodal polyethylene, which is similar to the first one, except for a reversed polymerisation order. The two different fractions that these bimodal polyethylenes are theoretically composed of were also examined separately. The aim of the study was threefold: (i) to investigate the possibility to crosslink bimodal polyethylene in a satisfactory way, (ii) to study the resulting properties of the crosslinked material, and (iii) to investigate if the polymerisation order has any influence on the crosslinking and the crosslinking properties of the material. To monitor the crosslinking, the changes in molecular weight, gel-content, and crosslinking density were examined.

2. Experimental

2.1. Materials

Two bimodal polyethylenes were analysed, both containing approximately equal amounts of high molecular weight and low molecular weight material. They were both HDPE materials of experimental quality from a pilot plant and differed only in terms of polymerisation order. The material properties are given in Table 1. MFR (Melt flow rate) is a method used to determine the melt viscosity of a sample and is thereby a rough estimation of the molecular weight. The suffix "21" implies that a weight of 21.6 kg is used to force the PR-melt through the dye. FRR (Flow Rate Ratio) is defined as the ratio of two MFR values obtained with two different weights. It thereby gives an indication of the molecular weight distribution of the sample. The comonomer in the high molecular weight fraction is 1-butene.

Table 1
General characteristics for the bimodal PEs as provided by the supplier

	Polymerisation mode	MFR_{21} (g/10 min)	FRR 21/5	Density (g/cm^3)
bimPE	Normal	5.8	26	0.945
bim-revPE	Reversed	6	18	0.949

The two bimodal PEs are referred to as bimPE (normal polymerisation order) and bim-revPE (reversed polymerisation order). These two polyethylenes are compared to two monomodal polyethylenes, one representing the high molecular weight fraction and the other representing the low molecular weight fraction. They are referred to as hmwPE and lmwPE. These two fractions were both taken from the same pilot plant as the two bimodal materials. The bimodal polyethylenes were delivered as both untreated powders and pellets while the two separate fractions were only obtained as untreated powders.

2.2. DSC

Melting points and crystallinities were determined using differential scanning calorimetry on a Perkin Elmer DSC 7. The heating and cooling rates were 10 °C/min, respectively, and T_m was defined as the peak temperature of the melting in the second heating run. The crystallinity was determined by comparing the measured heats of fusion ($\Delta H_{\mathrm{fusion}}$) with $\Delta H_{\mathrm{fusion}}$ for a 100% crystalline polyethylene. According to Wunderlich et al. [16], a value for $\Delta H_{\mathrm{fusion}}$ of 293.6 J/g was used.

2.3. Crosslinking

The peroxide crosslinking was performed using dicumylperoxide (DCP), Dicup R from Hercules, as a crosslinking agent at concentrations ranging from 0.1 to 8 wt% depending on the material. Due to melting and homogenisation difficulties with the untreated bimodal PE powder, only bimodal PE pellets were used. The polyethylene pellets were cooled in liquid nitrogen and ground to a powder, to facilitate the penetration of DCP. The monomodal hmwPE and lmwPE, which were supplied as untreated powders, were used as obtained. The peroxide was dissolved in methanol and added to the powder; 1 ml peroxide solution/1 g PE. The polymers were impregnated for 1 h with agitation every 15 min and dried under vacuum for 3 h at RT, to ensure complete evaporation of the methanol. The soaked powder was first allowed to melt between Teflon sheets in a press at 145 °C for 1 min, with no pressure applied, and thereafter transferred to another press where the crosslinking was performed at 180 °C for 10 min with an applied pressure of approx. 25 bar. The polyethylenes were then regarded as completely cured [13].

2.4. SEC

The molecular weights and molecular weight distributions were determined using size exclusion chromatography (SEC) on a Waters 150 CV equipped with a refractive index detector using 1,2,4-trichlorobenzene (TCB) as solvent. The samples (~3 mg) were dissolved over-night in TCB at 135 °C to a concentration of 1 g/dm^3, filtered on a 0.5 μm Waters original metal net filter to remove undissolved particles and separated on a column system packed with a polystyrene-divinylbenzene gel at 135 °C. Santonox R from Monsanto was added during the dissolution to avoid degradation. The flow rate was 1 ml/min and calibration was performed with narrow molecular weight polystyrene standards. The molecular weights were calculated using the universal calibration method.

2.5. Gel-content determination

The gel-content of the crosslinked samples was determined gravimetrically using a solvent extraction technique. The samples (~30 mg) were placed in pre-weighed 100 mesh stainless steel baskets, and extracted in 1.1 dm^3 refluxing 1,1,1-decahydronaphthalene for 6 h. An antioxidant, 10 g Irganox 1076 from Ciba-Geigy, was added to prevent degradation. After 6 h, the solvent was exchanged for 0.9 dm^3 new 1,1,1-decahydronaphthalene (pre-heated) and the extraction continued for another hour. The samples were left to evaporate in a hood over night and dried under vacuum for 5 h at 80 °C, until a constant weight was reached. The non-soluble fraction left in the baskets was weighed, and the gel-content of the polymers was calculated.

The gel-content for the polyethylenes was also calculated based on the SEC-measurements by comparing the areas of the chromatograms from the cured samples with the area of a completely soluble reference polyethylene sample. The difference in area gave an approximate value of the gel-content. Note, however, that this method is not as reliable as the extraction technique, especially not at low gel-contents.

2.6. Swelling measurements

The density of the network was determined by measuring the swelling of the crosslinked sample [17]. The crosslinked, extracted samples from the gel-content determination, devoid of all uncrosslinked chains and still in their stainless steel baskets, were placed in refluxing p-xylene (b.p. = 138 °C) for a minimum of 2 h. At this point, equilibrium swelling is presumably achieved. The uptake of p-xylene was measured by weighing the swelled samples immediately after the boiling in p-xylene. The crosslinking density was then calculated according to the Flory–Rehner equation: [18]

$$-\ln(1 - V_r) - V_r - \mu V_r^2 = \rho_p V_0 M_c^{*-1}(V_r^{1/3} - V_r/2),$$

where V_r = volume fraction of gel in the swelled sample, μ = interaction parameter of solvent-PE, in this case 0.32 [19], ρ_p = density of the polymer at 138 °C, in this case 0.806 g/cm^3 [17], V_0 = molar volume of the solvent, in this case 139.3 cm^3 [17], M_c^* = molecular weight between the crosslinks. V_r is calculated according to

$V_r = 1/((M_s\rho_p/M_p\rho_s) + 1)$, where M_s = amount of solvent absorbed, M_p = weight of the dry gel, ρ_s = density of the solvent at 138 °C, in this case 0.761 g/cm^3 [17].

In order to correct for loose chain ends, M_c^{*-1} is replaced with $M_c^{-1}(1 - 2M_c\overline{M}_n^{-1})$. Here, $\overline{M}_n$ is the number average molecular weight prior to crosslinking [20].

2.7. DMA

Dynamic mechanical analyses were performed to complement the swelling measurements with information regarding the density of the network. The torque was measured as a function of curing time at a constant frequency of 2.3 rad/s in a Rheometrics RDA II, using two parallel plates. Since it was difficult to ensure that the torque was measured in the bulk material, a constant pressure of 4 N was applied on the material and ridged plates were used. Planar plates were not used due to irreproducible results. The DMA-samples were prepared by melting the soaked polyethylene powder in a press at 145 °C with no pressure applied for 1.5 min, and thereafter applying a pressure of ~40 bar for 30 s. This gave circular samples with a diameter of 20 mm and a thickness of 1.5 mm. A total melting time of 2 min was needed to get a homogeneous sample but the sample can still be considered as being uncured. The sample was then placed between the two parallel plates in the rheometer and the torque was measured for 10 min at 180 °C. DMA measurements could not be performed on all samples. The viscosity of lmwPE is too low at 180 °C to allow accurate measurements with a low peroxide content. Measurements with 5% DCP succeeded, however. HmwPE was difficult to analyse in a satisfactory way since it became too stiff to be reasonably penetrated by the rifled plates.

3. Results and discussion

3.1. DSC

The melting points and crystallinities of the samples are shown in Table 2. The melting temperatures of the bimodal PEs are both approx. 130 °C, which lies within the range of a HDPE material. The crystallinities are approximately 65% lower than for HDPE, due to the short-chain branched, high molecular weight fraction, which does not crystallize to the same extent. The result for hmwPE confirms this, exhibiting a crystallinity of 40%. The crystallinities of hmwPE and lmwPE agree well with the notion that these materials represent the two fractions in the bimodal distribution.

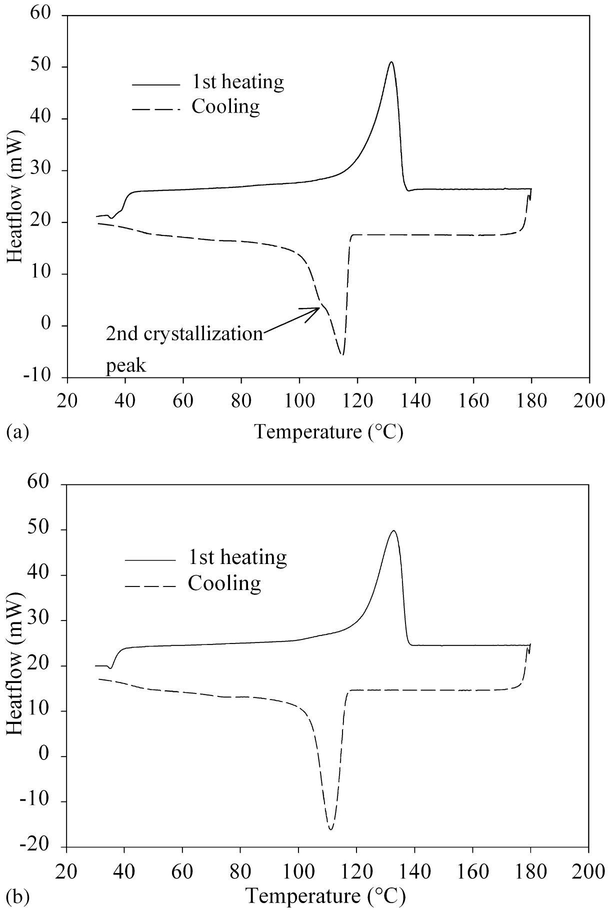

Fig. 1. (a) DSC run of sample bimPE showing the first heating run and the subsequent cooling. The cooling shows a second crystallisation peak. (b) Corresponding DSC run of sample bim-revPE, showing no second crystallisation.

Fig. 1(a) shows the first heating run and the cooling of sample bimPE (bimodal PE, normal polymerisation mode) as an untreated powder. The cooling curve shows an indication of two crystallization peaks, indicating a non-simultaneous crystallisation of the two fractions. This behaviour disappears upon pelletising and is not seen at all for sample bim-revPE (reversed mode), Fig. 1(b).

3.2. Molecular weight and gel-content measurements

Table 3 shows the molecular weights and gel-contents of all samples, both non-crosslinked and crosslinked at different peroxide contents. The SEC-chromatograms from

Table 2
Melting points and crystallinities of the samples

	bimPE, pellets	bimPE, powder	bim-revPE, pellets	bim-revPE, powder	hmwPE	lmwPE
T_m (°C)	129.5	130.5	131.0	131.5	123.0	133.0
Crystallinity (%)	62	55	65	65	40	81

Table 3
Molecular weights and gel-contents

	M_n (10 − ^{3})	M_w (10 − ^{3})	Gel-content SEC (%)	Gel-content gravimetric (%)
bimPE n.c.[a]	22	210	–	–
bimPE 0.5%	20	170	13	47
bimPE 1%	17	130	30	55
bimPE 2%	12	45	60	70
bimPE 5%	9	17	93	91
lmwPE n.c	8	30	–	–
lmwPE 2%	9	90	11	6
lmwPE 5%	9	21	60	62
lmwPE 8%	6	10	90	83
hmwPE n.c.	41	176	–	–
hmwPE 0.1%	47	289	15	40
hmwPE 0.5%	30	155	70	82
hmwPE 1%	23	70	80	91
bim-revPE n.c.	29	215	–	–
bim-revPE 0.5%	26	150	29	47
bim-revPE 1%	18	86	49	59
bim-revPE 2%	16	58	72	71
bim-revPE 5%	10	22	95	89

[a] n.c. = non-crosslinked.

the two bimodal samples, the hmwPE sample, and the lmwPE sample, are presented in Fig. 2(a)–(d), respectively. From the SEC-chromatograms of the two bimodal samples it is clear that the high molecular weight fraction is consumed first upon crosslinking. The normalised SEC-chromatograms of sample bimPE (Fig. 2(a)) most clearly illustrate the consumption of the high molecular weight part. The high molecular weight fraction of sample bimPE is completely consumed at 1–2% of added peroxide. For sample bim-revPE, the corresponding amount of peroxide is somewhat smaller. A higher amount of crosslinking agent shifts the distribution towards lower molecular weights, because a larger fraction of the long chains are tied up in the network. Fig. 2(c) shows the molecular weight distributions for the lmwPE sample. The area under the dashed curve (2% peroxide) is only somewhat smaller than for the non-crosslinked sample, indicating non-extensive gel formation. Furthermore, a high molecular weight tail has developed with a simultaneous increase in $\overline{M}_w$ from 30,000 to 90,000, whereas neither $\overline{M}_n$ nor M_{peak} is affected. This shows that when lmwPE crosslinks in the presence of 2% DCP, gel formation is limited and molecular enlargement of the soluble portion is the dominating process taking place. At 5%, the high molecular weight tail has diminished and does

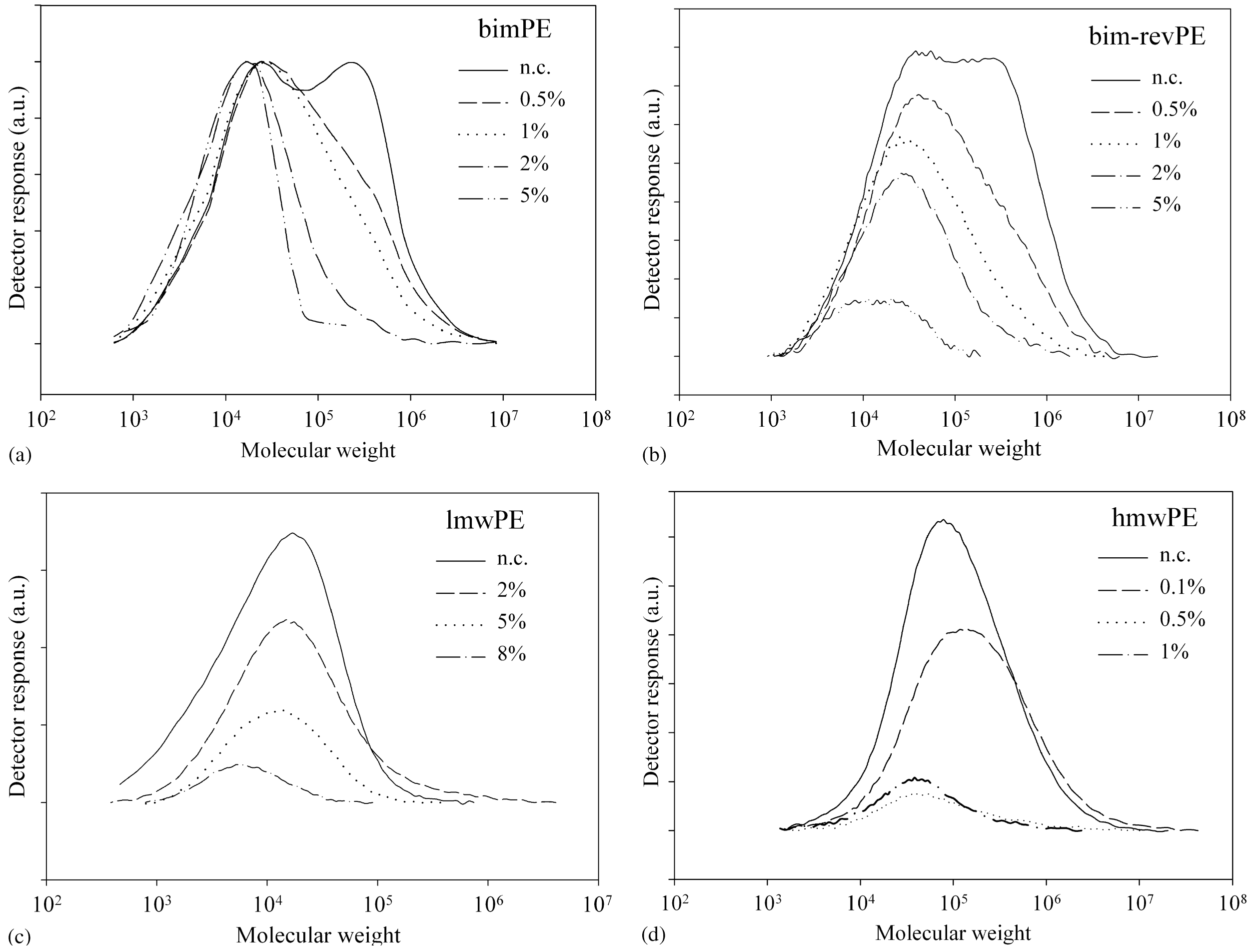

Fig. 2. SEC chromatograms of sample (a) bimPE, (b) bim-revPE, (c) lmwPE, (d) hmwPE.

now participate in the network. At 8% DCP the high molecular weight tail has completely disappeared and the curve has clearly shifted to lower molecular weights, indicating that a large amount of the chains now participate in the network. Fig. 2(d) shows the SEC chromatograms of hmwPE. HmwPE starts to crosslink already at a very low DCP content, 0.1%. Molecular enlargement is also apparent at this low DCP concentration as the curve shifts to the right and M_{peak} increases. However, only a small tail develops at the high molecular weight end and the MWD broadening is smaller than for lmwPE. Both $\overline{M}_{\mathrm{w}}$ and $\overline{M}_{\mathrm{n}}$ increase for the resulting soluble material as compared to the non-crosslinked sample. When 0.5% DCP is added to hmwPE, there is a clear shift of the distribution to lower molecular weights with a decrease in both $\overline{M}_{\mathrm{n}}$ and $\overline{M}_{\mathrm{w}}$. The diminishing area under the curve indicates that extensive crosslinking has taken place.

Neither the molecular weights nor the gel-contents differ when comparing the two bimodal samples (Table 3). For both materials, the gel-content increases from around 50% for 0.5% DCP to around 90% for 5% DCP. For lmwPE, hardly any gel develops at a peroxide content of 2%, but mostly molecular enlargement, as mentioned above. At higher peroxide concentrations, however, the gel-content is higher, and as much as 80% of the material forms a gel at 8% DCP. HmwPE develops a gel at very low peroxide concentrations and reaches a gel-content of 80% already at 0.5% DCP.

The gel-contents, molecular weights, and molecular weight distributions are interconnected. HmwPE has a high $\overline{M}_{\mathrm{n}}$ and $\overline{M}_{\mathrm{w}}$ prior to crosslinking and a high gel-content is expected already for small amounts of added peroxide. Consequently, lmwPE needs more peroxide (>2%) to develop a gel. However, since the gel-content for the bimodal samples is around 70% at 2% DCP, and the high molecular weight part constitutes only 50% of the material, it is clear that a part of the lmw fraction in the bimodal PE is indeed incorporated into the network. This cannot be attributed to physical entanglements, since the gel-content is due only to chemical crosslinks. The explanation is that the lmw fraction in the bimodal PE cannot be considered as a separate fraction. In the bimodal PE, i.e. in the presence of 50% high molecular weight material, the probability for lmw molecules to be connected to a network with longer chains originating from the hmw fraction is relatively high.

At 5% of added peroxide, the gel-content for bimPE and bim-revPE has increased to ~95%, which indicates that quite a substantial amount of low molecular weight material must participate in the network. At the same peroxide content, the gel-content for lmwPE has reached ~60%, and the extrapolated gel-content for hmwPE is as high as 95%. Theoretically, this would generate an overall gel-content in the bimodal polyethylenes of 75–80%, not the observed 90%. The observed high gel-content of the bimodal material supports the idea of a higher probability for the lmw fraction to participate in the gel as grafted, pendant chains, in the presence of longer polymer chains.

From the gel-contents of hmwPE, it is clear that due to the high $\overline{M}_{\mathrm{n}}$ value (40,000), only low amounts of peroxide are needed to tie the polymer chains together in a network and create a reasonable high percentage of gel. The low $\overline{M}_{\mathrm{n}}$ value (8000) of lmwPE reflects shorter polymer chains, and this material consequently requires a higher amount of peroxide to create a network and develop a gel. Obviously, the probability of creating a second crosslinking point on one chain is lower on a short chain than on a long chain. More peroxide is therefore required to incorporate several short chains into a network to obtain a certain gel-content. A 'normal' peroxide addition of 1.5–2% therefore only generates a negligible amount of gel in lmwPE. Fig. 3 summarises the gel-content as a function of peroxide concentration. The gel-content increases rapidly for hmwPE and the two bimodal polyethylenes are virtually indistinguishable.

3.3. Swelling measurements

The swelling measurements, performed on the obtained gel, give information about the crosslinking density of the samples. Calculations based on the uptake of *p*-xylene give average values of the molecular weight between the crosslinks, M_{c}, for each sample. Table 4 gives the M_{c} values for the PEs used in this study. The two bimodal samples show similar results, as the crosslinking densities obtained are approximately the same for both samples bimPE and bim-revPE. Upon crosslinking with 2% peroxide, lmwPE contained only a small amount of gel (5–10%) as mentioned above. A M_{c} value of 3900 shows that the obtained network is quite dense within the part of the polymer that has crosslinked. However, considering the fact that $\overline{M}_{\mathrm{n}}$ is as low as 8000, a M_{c} of 4000 is approximately what may be expected, assuming 2 crosslinks/chain. This is in accordance with the discussion above, regarding the $\overline{M}_{\mathrm{n}}$ values. The probability of gel formation is quite low at 2%

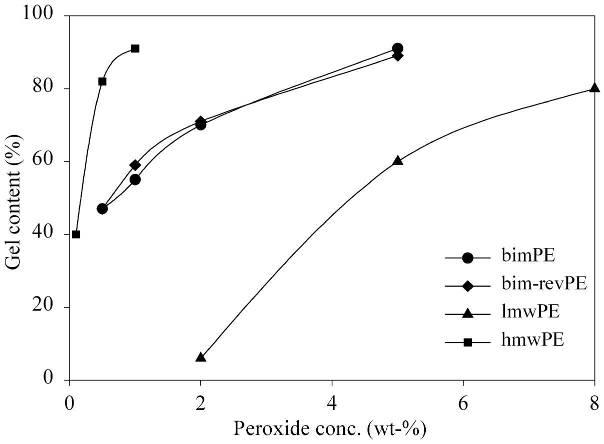

Fig. 3. The gel-content as a function of peroxide concentration for all samples.

Table 4
Molecular weight between the crosslinks, M_{c}

	M_{n} (10 − ^{3})	M_{c} (10 − ^{3})
bimPE n.c.	22	
bimPE 0.5%	20	8200
bimPE 1%	17	7700
bimPE 2%	12	6000
bimPE 5%	9	1800
lmwPE n.c.	8	
lmwPE 2%	9	3900
lmwPE 5%	9	3300
lmwPE 8%	6	2600
hmwPE n.c.	41	
hmwPE 0.1%	47	12,300
hmwPE 0.5%	30	6300
hmwPE 1%	23	4000
bim-revPE n.c.	29	
bim-revPE 0.5%	26	8900
bim-revPE 1%	18	7100
bim-revPE 2%	16	5400
bim-revPE 5%	10	3500

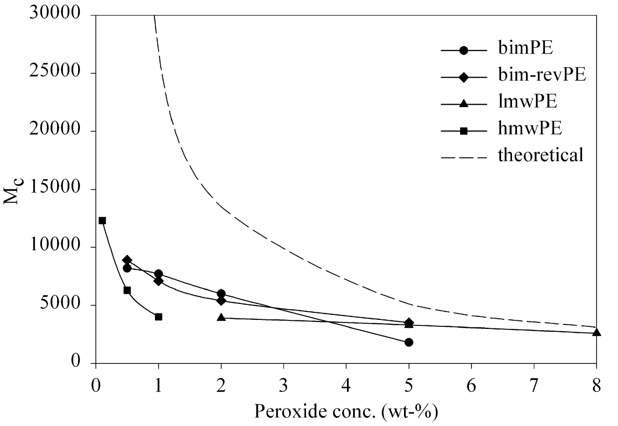

Fig. 4. The molecular weight between the crosslinks (network density) as a function of peroxide concentration for all samples. The experimental results are compared to a theoretically calculated curve, based on the assumption of 1 crosslink/peroxide molecule.

DCP, due to the low $\overline{M}_{\text{n}}$ of lmwPE. The short chains reduce the probability of creating an extensive network as well as the possibilities of forming entanglements, as $M_{\text{e,PE}} = \sim 4000$. This means that the network created within lmwPE consists mostly of chemical crosslinks. When the possibility of the chains to entangle is small, the added peroxide affects mostly the gel-content and not the density of the network, as more and more chains are tied up in the network. Therefore, even though the gel-content increases from 6 to 80%, the M_{c} value only decreases from 3900 to 2600.

Fig. 4 shows the peroxide concentration plotted versus M_{c} for the tested polyethylenes. The dashed line represents the theoretical M_{c} values obtained when taking only the peroxide-induced crosslinks into account and assuming that each DCP molecule causes one crosslink. For all PE samples, the measured crosslinking densities are much higher, i.e. M_{c} is lower, than suggested by the theoretical curve. LmwPE cannot follow the theoretical curve because of its low $\overline{M}_{\text{n}}$, as discussed above. For the two bimodal samples and hmwPE, the explanation of the low M_{c} values is entanglements. Trapped entanglements generate the major part of the crosslinking points at low peroxide concentrations, especially in hmwPE. At high $\overline{M}_{\text{n}}$ values (40,000 for hmwPE), dense networks are easily created with only small amounts of chemical crosslinks, as the probability of entanglement formation is very high. This means that the network formed for hmwPE at low concentrations of DCP to a large extent consists of entanglements. At higher peroxide concentrations, the entanglements do not contribute to the crosslinking to the same extent, and at $>5\%$ it is mainly the chemical crosslinks that contribute to the network formation. At 5%, the M_{c} values of all the tested polyethylenes approach the theoretical values.

When comparing the two bimodal polyethylenes in Fig. 4, it is clear that their crosslinking results are very similar. Since their molecular weights and gel-contents are also essentially the same, our results show that the polymerisation order does not affect the crosslinking properties. Note, however, that we used ground pellets when preparing the crosslinked samples, and that the analyses might have given other results if it had been possible to use the original powder without any additional processing. According to the DSC runs, the two untreated bimodal samples exhibited different crystallisation behaviour, which could indicate some difference between the samples. This difference either disappears during the processing step or does not affect the crosslinking properties of the materials.

3.4. Dynamic mechanical analyses (DMA)

Measuring the torsion resistance of a sample in the melt is another way of obtaining information about the density of the network in a crosslinked sample. Since the torsion resistance increases with increasing crosslinking, the DMA analyses are also a way to monitor how the crosslinking proceeds. Due to experimental difficulties, it was not possible to include all the materials in the tests but the analysed samples can nevertheless be considered as being representative. Several difficulties occurred which initially made it difficult to obtain reproducible results (see Section 2). Because of these difficulties, we decided not to calculate any M_{c} values based on these experiments but to instead use the results as basis for a more qualitative discussion.

The results from the DMA tests are presented in Fig. 5. The measurements did not indicate any difference between the samples bimPE and bim-revPE. Therefore, the two bimodal samples are represented as averages in Fig. 5. As expected, lmwPE gives the lowest torsion resistance and hmwPE the highest. For the bimodal PE, the results are also plausible as the torsion resistance increases with increasing amount of peroxide. Before discussing the DMA results in

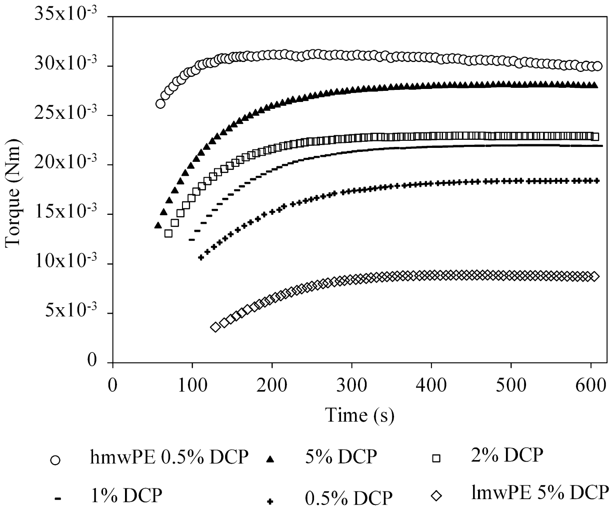

Fig. 5. DMA measurements of all samples. The bimodal polyethylenes are represented together as average values.

more detail, it should be noted that there is a pronounced difference between the swelling tests and the DMA tests in how the network quality is obtained. In the swelling test, the network density is tested on the pure gel only, while the DMA samples contain also non-crosslinked material. The overall network density from the DMA runs, if calculated, would therefore be expected to be lower than for the corresponding swelling test. However, even if the amount of gel is taken into consideration, we still find that the results are markedly different compared to those from the swelling measurements. For example, the gel-contents for bimodal PE 2%, hmwPE 0.5%, and lmwPE 5% are approximately the same and they contain accordingly the same amount of non-crosslinked material during the DMA tests. The M_c values obtained by the swelling measurements of bimodal PE at 2% peroxide are similar to the M_c values of hmwPE at 0.5% peroxide, and the networks can thus be assumed to have similar strength and density. The network density for lmwPE 5% obtained from the swelling measurement is 55–60% higher compared to the other two samples mentioned above. However, the DMA runs show that hmwPE has a pronounced higher torsion resistance than both the bimodal PE and the lmwPE. In fact, lmwPE 5% has the lowest torsion resistance of all the analysed samples, despite of its high network density of the gel. The explanation lays in differences in $\overline{M}_n$ and the difference in how much the two methods affect the entanglements. Dynamic mechanical testing is a relatively mild method that causes only small deformations in the material, i.e. entanglements that are not trapped by chemical crosslinks remain intact. Swelling, on the other hand, has a stronger effect on the material. Entanglements that are not locked in chemically may disentangle, resulting in a less dense network. Therefore, a high value of $\overline{M}_n$ strongly affects the network density obtained from dynamic mechanical testing, since the effect of entanglements is more pronounced in this method. The $\overline{M}_n$ values for the three discussed samples differ substantially and $\overline{M}_n$ for the hmwPE material is approximately 5 times higher than for the lmwPE material and almost twice as high as for the bimodal samples, resulting in extensive entanglement formation. An extreme scenario is a material with a very high $\overline{M}_n$ where the entanglement formation is expected to be abundant. A dynamic mechanical test would then indicate a high network density while a swelling measurement would indicate no network for such a material.

4. Conclusion

The starting point of this study was to investigate the crosslinking properties of bimodal polyethylene. The order of polymerisation, i.e. the low molecular weight fraction first or vice versa, was a particular issue of interest. All data show, however, that the two bimodal samples behave very similarly regardless of the polymerisation order. However, both samples were first pelletised and thereafter ground to a powder prior to crosslinking, which means that potential differences were possibly removed during processing.

Notably, the gel-content at 2 wt% DCP is 70%. This peroxide concentration is typical for commercial crosslinking of PE, e.g. for cable insulation, and normally renders a gel-content of approximately 80–85%. A probable explanation to the somewhat lower gel-content for the bimodal polyethylenes is the higher amount of low molecular weight chains in the polymer, compared to “normal” polyethylene, something which affects the crosslinking negatively. The bimodal polyethylenes used in this investigation were obtained with a Ziegler–Natta catalyst, which gives low concentration of vinyl end groups in the polymer. If a higher gel-content is of importance, a possible way is to incorporate vinyl groups through a co-polymerisation, as described by Palmlof *et al.* [21] and Smedberg *et al.* [13].

When the low molecular weight fraction is crosslinked separately in lmwPE, high concentrations of peroxide is needed to obtain reasonable gel-contents. This is expected but it must be pointed out that the lmw fraction contributes markedly to the gel-content when it is crosslinked in the presence of the hmw fraction. At 2 wt% DCP, the total gel-content is 70% and the contribution from the high molecular weight fraction is presumably 95%, therefore almost 50% of the lmw fraction contributes to the gel-content. However, only the gel content is increased by the lmw fraction, the density of the network is not affected. A large amount of the chains from the lmw fraction are relatively short and can be considered as grafted onto the network as pending chains. Thereby, they affect only the gel-content and not the network density.

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