

Chemical and mechanical changes in poly(ethylene-*co*-1,9-decadiene) following crosslinking induced by peroxides

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Abstract

The response of poly(ethylene-*co*-1,9-decadiene) to peroxide treatment was examined and compared with a reference. The polymers were produced in a low-pressure process using a chromium-based catalyst giving a relatively high level of inherent unsaturations through thermal termination of the polymerisation. The copolymerisation with 1,9-decadiene gave an additional 63% vinyl end groups in the polymer. A great improvement in the response to dicumyl peroxide was observed for the decadiene polymers leading to a considerably smaller need for peroxide in order to obtain a certain gel content. The reason for the improved response was previously found to be the overall higher amount of vinyl groups as well as the placement of these groups along the molecular weight distribution. The remaining amount of vinyls after crosslinking was found to be exponentially dependent on the amount of peroxide added. At high peroxide levels almost all vinyl groups were consumed. The peroxide-induced consumption of vinyls was found to increase linearly with the original amount of vinyl unsaturations. At high peroxide levels, approximately the same gel content was obtained in all samples, leading to a considerably higher consumption of vinyls in the decadiene samples as compared to the reference. Mechanical measurements indicate a higher crosslinking density for the materials containing decadiene as compared to the reference. However, at lower gel contents, e.g. 40% and below, the situation is the opposite. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Crosslinking; Peroxide

1. Introduction

This is the second paper reporting results on the crosslinking of poly(ethylene-*co*-1,9-decadiene) and a reference polyethylene (PE), polymerised on a chromium-based catalyst of Phillips type. The first paper [1] concerned electron radiation crosslinking, and in addition a thorough analysis of the examined materials was given. This paper however reports on peroxide crosslinking of the same polymers.

As many applications need improved properties of PE, crosslinking is often used as a means to reach these desired properties. Today three methods to bring about crosslinking is commonly used; radical crosslinking by peroxide or irradiation [2] and silane crosslinking [3] where water is used as the crosslinking agent.

Radical crosslinking using peroxide is used for a range of products such as high-performance hot and cold water pipes,

gas pipes and cable insulation materials, shrink products and a range of other special products needing improved properties. A common desire of manufacturers is, of course, to increase production rate and/or to improve product properties. Regarding increased production rate obtained through better peroxide response, three fundamental and inherent polymer properties are of importance; molecular weight (MW), molecular weight distribution (MWD) and the amount and type of unsaturations [4]. Additives and treatment conditions, such as temperature level and availability of oxygen, may be of importance as well.

In the papers referred to above, normal PEs of Phillips or Ziegler–Natta type were investigated, i.e. polymers where unsaturations are formed mostly during the termination step of polymerisation resulting in a vinyl group at the end of the molecular chain. In this work, however, a substantial part of the unsaturations was introduced in the polymer via copolymerisation of 1,9-decadiene. In addition, unsaturation formed during termination was still present. This combination resulted in a considerable increase in double bonds. In this paper, work on ethylene-1,9-decadiene copolymer is presented focusing on its response to peroxide

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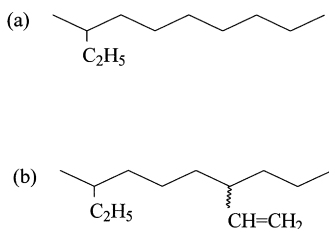


Fig. 1. Structural formulas of examined materials: (a) ethylene with butene as comonomer; (b) ethylene copolymerised with butene and 1,9-decadiene.

and the resulting crosslinking of the material. The changes in the material due to peroxide treatment were followed by means of gel measurements, IR spectroscopy and measurements of different mechanical properties.

2. Experimental

2.1. Materials

Three different ethylene copolymers were used in this study; a reference material (a) with butene as comonomer and two materials (b) containing 1,9-decadiene as well as butene as comonomer (Fig. 1). Butene was used in order to control the density and keep it on the same level for all three materials.

The reference material containing 0.70 vinyl end-groups/1000C is designated V070 and analogously the decadiene containing samples are designated V105 and V114 for the materials having 1.05 and 1.14 vinyl end-groups/1000C, respectively. All three materials were produced by polymerising in a low-pressure process using a chromium-based catalyst [5], giving a relatively narrow MWD. The materials have a density of 944 kg/m³ and a MFR21 of approximately 10 g/10 min with the only difference being the content of vinyl groups introduced via copolymerisation of 1,9-decadiene. A more detailed characterisation of the samples is given in an earlier paper [1] reporting on the response to electron beam irradiation treatment.

2.2. Sample preparation

The powder material was mixed with 0.10% phenolic antioxidant (Irganox 1076 from Ciba Geigy) and pelletised in a Collin twin screw extruder. Around 300 g of pelletised sample was put in a glass jar and was then heated up to a homogenous temperature of 80°C in an oven before dicumyl peroxide, melted at 80°C, was added. The glass jar was then shaken for 20 min to obtain a homogenous distribution of peroxide, on the outside surface of the pellets, before the material was finally placed in an oven at 80°C for 6–20 h enabling the peroxide to be soaked into the material properly. Afterwards the jar was shaken for another 5 min for further homogenisation [6].

The soaked pellets were subsequently crosslinked through compression moulding to ca. 2 mm thick sheets,

first for 3 s at 160°C and 20 bar followed by 27 min at 190°C and 200 bar. For the Hot Set test, dumbbells of a total length of 75 mm, made according to DIN 53504-S2, were cut from the sheets described above.

For the elastograph measurements soaked pellets were pressed to samples of 5 mm thickness and 37 mm in diameter during 10 min. The temperature was kept at moderate 150°C in order to avoid precurving.

2.3. Analyses

2.3.1. Gel content

The gel content was determined with decaline extraction [7]. After milling and sieving (particles larger than 100 mesh), the sample was put into a metal net cushion which was kept in boiling decaline for 7 h. The solvent was replaced after 6 h. After drying the crosslinked material was determined gravimetrically.

2.3.2. Hot set

As performed above the crystalline melting point, the hot set test should better reflect the network structure of a cross-linked PE polymer than a normal tensile test. The test specimens in the form of dumbbells were subjected to a nominal stress of 0.2 MPa at 200°C. The length of an originally 20-mm long mid-section of the specimen was measured after 15 min and the elongation was calculated according to the following equation:

$$E = ((L_1 - 20)/20)100 \quad (1)$$

where E is the sample mid-section elongation (%), L_1 the sample mid-section length after 15 min (mm).

By using the classical theory of rubber elasticity [8] the number-average MW for a chain between adjacent crosslinking points (M_c) was obtained according to Eq. (2) [9]. It is assumed that the terminal chain segments do not contribute to the elastic force [8]:

$$M_c = \frac{1}{2/M_n + \sigma_n/\rho RT(\lambda - 1/\lambda^2)} \quad (2)$$

where

$$\lambda = L_1/L_0 \quad (3)$$

Here L_1 is the mid-section length after 15 min (mm), L_0 the original sample mid-section length (20 mm), R the gas constant, T the temperature in Kelvin, M_n the original number-average MW, ρ the density in the melt (753.6 kg/m³) and σ_n the nominal stress.

2.3.3. Tensile testing

A tensile testing machine of type ALWETRON TCT 25 (Lorentzon & Wettre, Sweden) was used at ambient temperature (23°C) to determine the mechanical properties. Digital extensometer equipment was used and the speed of testing was 100 mm/min except for the determination of the E -modulus where 1 mm/min was used instead.

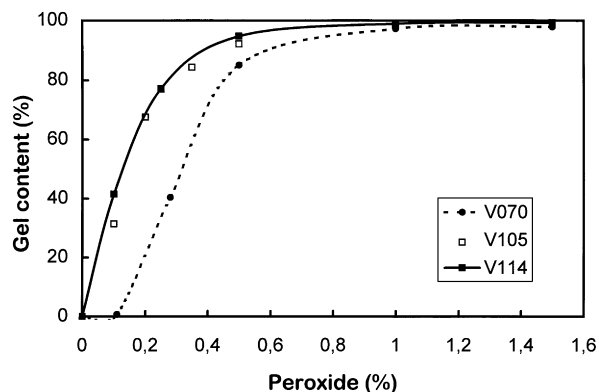


Fig. 2. Gel formed as a function of added peroxide for the three examined materials: (●) V070; (□) V105 and (■) V114.

2.3.4. IR spectroscopy

Infrared spectroscopy measurements were performed using a Perkin–Elmer 783 dispersive device. Films of even thickness (0.5–1 mm) were pressed and carefully analysed. The amount of unsaturations/1000C was then calculated according to Ref. [1].

2.3.5. Differential scanning calorimetry

Thermal measurements were undertaken using a Mettler TC 10A DSC device recording the melting of samples originally crystallised at a cooling rate of 5°C/min from a melt of 180°C. The melting was performed at a heating rate of 5°C/min. For calculation of crystallinity 290 kJ/g has been used as melting enthalpy for a 100% crystalline sample [10].

2.3.6. Elastograph measurements

Elastograph measurements were carried out on a Göttfert 67.85 equipment [11] at 180°C, 50 oscillations/min and angle of torsion of 0.5°. Test time was 10 min.

3. Results and discussion

Each of the three examined sample types were treated with six to eight different peroxide concentrations. The resulting gel is shown in Fig. 2. The shape of the curves is typical for dicumyl peroxide [12].

It is obvious that the response towards peroxide is significantly different for the three samples. Two of the samples, containing decadiene and consequently a higher amount of unsaturation, show an immediate response towards dicumyl peroxide, i.e. only a very small amount of peroxide (0.1% or less) is needed in order to detect gel formation. On the other hand, the reference sample, only containing 0.70 vinyl/1000C, did not give any crosslinking at all when 0.10% of peroxide was added, whereas V114 gave over 40% crosslinking for the same peroxide concentration. However, the difference between V105 and V114 is very small, especially compared to what was found at irradiation of the same

materials, where a clear difference is obtained between the two [1]. The crosslinking by electron beam takes place in the solid state, and crosslinking reactions occur primarily in the amorphous parts of the polymer [13,14] where the concentration of double bonds is considerably higher than the average determined value as side branches tend to be forced out in the amorphous regions on crystallisation. With a crystallinity of about 65%, this would lead to approximately three times the average concentration, i.e. ca. 0.3 mol% double bonds in the amorphous regions in V114 originating from decadiene. This is probably responsible for the relatively significant difference between V114 and V105 in response to electron beam crosslinking as compared to the corresponding case at peroxide crosslinking. In the latter case, the crosslinking takes place in the molten state and before crystallisation the double bonds are distributed in the whole material with smaller differences in concentration.

For further comparisons, it may be of interest to look at gel contents usually used in industrial applications, e.g. 80%. To reach this level 0.45–0.50% peroxide is needed for V070 whereas only around 0.25% is sufficient for V105 and V114, i.e. a reduction of up to 50% would be possible. This reduction seems to be surprisingly large. In earlier studies [15] where EPDM compounds with MW = 6000 g/mol were added to high-density PE of Phillips type (V070), no significant changes in peroxide response was obtained even when 5 wt% was added. On a molar basis this means that approximately the same amount of unsaturations was available as in the decadiene material reported in this paper. On the other hand, other authors report significantly positive results in peroxide response on adding low molar mass polybutadiene [9]. In this case, however, LDPE with an extremely low level of inherent unsaturations was used. These two referred examples indicate that externally added compounds containing unsaturations may be effective if the base material itself contains only small amounts of inherent double bonds, whereas the relative effect of adding these products to a base resin with a large number of inherent double bonds is limited or null. The solubility of low molar mass EPDM and polybutadiene in HDPE and LDPE, respectively, may be part of the explanation to the observed differences. In addition it should also be mentioned that addition of polymers of low molar mass, of course, lowers the overall M_n -value of the composition, normally leading to a reduced crosslinking response.

In the case of ethylene–decadiene copolymers, however, where the double bonds are incorporated into the polymer backbone in the polymerisation step, significant effects on the crosslinking response is experienced, in spite of the fact that these resins are of a Phillips type and hence have a large inherent amount of unsaturations. This behaviour could probably be explained by several factors. First, the unsaturations, originating from decadiene, give the material a larger total amount of unsaturations and through this an improved response to peroxide. The reactivity of the double bonds originating from decadiene is, however, expected to be the

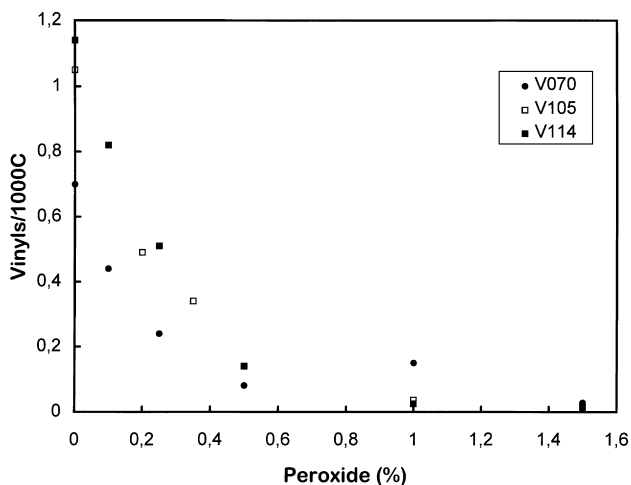


Fig. 3. Number of remaining vinyl groups/1000C after treatment of different amounts of peroxide: (●) V070; (□) V105 and (■) V114.

same as the normal vinyl end groups [16,17]. Secondly, neither solubility effects nor a reduced M_n , through addition of unsaturated low molar mass compounds, reduce the peroxide response.

As discussed in an earlier paper [1] the estimated decadiene content in V114 corresponds to about one decadiene unit per 1000 ethylene units (0.1 mol%), i.e. less than one decadiene per M_n -molecule. The difference in total amount of vinyl groups between the three different samples is hence not so dramatic and may therefore not account directly for the whole difference in the response to peroxide. Other reasons are also likely to contribute. In an earlier work [1] it was found that the distribution of decadiene comonomer along the MWD may be important as well. The results obtained show that the longer molecules contain a larger number of decadienes/1000C compared to smaller chains. Hence the longer chains contain proportionally to length more decadienes than the smaller ones. Furthermore, larger

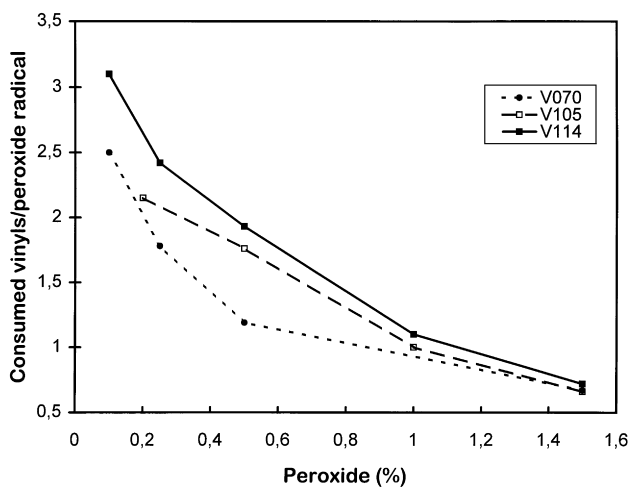


Fig. 4. Consumed vinyls per theoretical peroxide radical as a function of added amount of peroxide: (●) V070; (□) V105 and (■) V114.

chains incorporate more readily into the network as compared to smaller chains, provided other parameters are the same. Thus an increased number of double bonds on the larger molecules will dramatically enhance the peroxide response.

In the following section results on the changes in unsaturations, following on the peroxide treatment and crosslinking, are presented. In Fig. 3, the content of vinyl groups remaining after crosslinking, measured by IR at 910 cm^{-1} , is given versus peroxide added. The amount of vinyl groups decreases strongly with the amount of peroxide. At high peroxide levels practically all vinyl groups are consumed. No significant difference in the shape of the curves can be noticed and in mathematical form an expression like $-dV/dP = k[V]$ could be expected, leading to an exponential decrease in vinyl content according to $[V] = V_0 e^{-kP}$ and in logarithmic form we hence obtain:

$$\ln[V] = \ln V_0 - k[P] \quad (4)$$

where V is vinyls/1000C, P the concentration of peroxide and k , V_0 are constants.

Using linear regression analysis the constants V_0 and k can be determined and the results are given below. Hence the remaining vinyl content can be calculated for a certain amount of peroxide added, after a given crosslinking time and at a given temperature, by using the following equations:

$$[V]_{070} = 0.6 e^{-3.5P} \quad \text{Correlation coeff.} - 0.994$$

$$[V]_{105} = 1.0 e^{-3.4P} \quad \text{Correlation coeff.} - 0.993$$

$$[V]_{114} = 1.2 e^{-3.9P} \quad \text{Correlation coeff.} - 0.997$$

Note that the vinyl content value corresponding to $P = 1.5\%$ has been left out in these calculations. These values do not fit into an exponential model. A possible explanation to this might be that competing reactions, such as normal hydrogen abstraction from secondary carbons, dominate when such large amounts of peroxide as 1.5% are added to the polymer. In this case, the concentration of vinyl double bonds will be relatively low compared to the peroxide radicals and direct termination between radical chains, resulting from hydrogen abstraction, will become more important whereas the double bonds play a less important role. It is also worth noting that high peroxide levels result in a low vinyl content and a small absolute difference in the amount of vinyl double bonds between the samples (Fig. 3). Direct termination between radical chains at high peroxide levels, making double bonds less important, would also explain the observations made in Fig. 2, i.e. there is no longer any difference in gel content between the samples when large amount of peroxide is used.

The relatively small differences between the exponents of the samples may also be an indication to the relative similarity in reactivity between inherent double bonds and

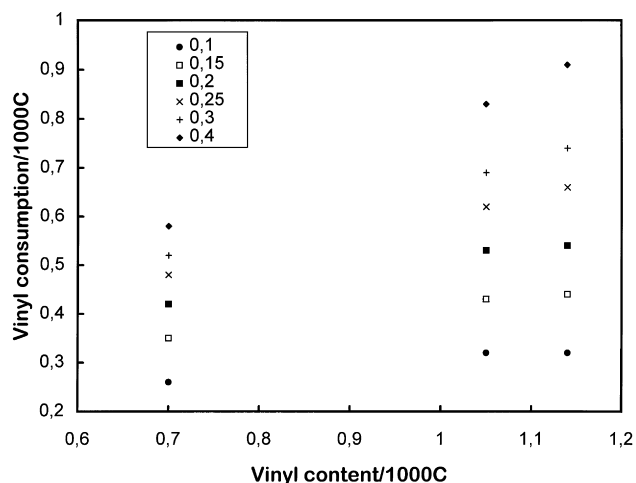


Fig. 5. Amount of consumed vinyls/1000C as a function of the original vinyl concentration of the sample given at different peroxide levels: (●) 0.1%; (□) 0.15%; (■) 0.2%; (×) 0.25%; (+) 0.3%; (◆) 0.4%.

double bonds incorporated via the polymerisation of decadiene comonomers. If there was a significant difference between these two types of unsaturations, in terms of reactivity, it would probably have influenced the exponent.

The calculations for the peroxide efficiency give very interesting results. The number of vinyl end groups that has been consumed per theoretical peroxide radical shows drastic changes. Such data are represented by Fig. 4. A common feature is a higher consumption of vinyls per peroxide radical for samples containing larger amounts of vinyl end groups. Drastic differences in efficiency are also observed with respect to the amount of peroxide added to the sample. For addition of peroxide at higher concentrations, the consumption of vinyls per peroxide radical is nearly the same for all three samples. At lower additions, e.g. at 0.10% peroxide, 3.1 vinyls per peroxide radical is

consumed for V114 whereas only 0.72 vinyls are consumed per radical if 1.5% is used, i.e. more than a four-fold increase in efficiency. For the V070 sample the efficiency increases almost six times. These observations are also in agreement with data obtained from LDPE material [19]. The increased peroxide efficiency can probably be explained in the following way; at a small amount of peroxide, the concentration of the formed peroxide radicals will be low. In this case they preferably attack allylic hydrogens with a low abstraction energy or they attack double bonds directly. Therefore a relatively large proportion of the radicals will be used for vinyl consumption and subsequent crosslinking. If, instead, a large amount of peroxide is added to the material, the concentration of peroxide radicals will be high and there will be a deficit of available allylic hydrogens and double bonds leading to the abstraction of normal secondary hydrogens as well. This of course gives a relatively lower consumption of vinyls per radical as well as a relatively small difference between the materials. Another possible explanation for the lower peroxide efficiency at higher peroxide concentrations might be the increased termination reaction rate as the rate of termination is proportional to the initiator concentration [17]. Thus a strong competing reaction would be active leading to lower effectiveness of the peroxide. As mentioned above, Fig. 4 also shows that the peroxide efficiency is better for the samples containing decadiene. It can easily be explained by the higher total content of double bonds present in the melt in these cases.

In Fig. 5, the vinyl consumption is instead shown against the original vinyl content of the samples for six different peroxide concentration levels. It is obvious that a linear relation exists. It is interesting to note that this finding is also in accordance with what has been found for LDPE [18]. Thus, at addition of a certain amount of peroxide, a linear increase in consumption of vinyl groups with initial concentrations of vinyl groups is obtained.

In Fig. 6, the number of *trans*-vinylene groups vs. peroxide is shown. An increase in *trans*-vinylene is obvious as more peroxide is added. A notable aspect is that the change in absolute values is considerably lower in the case of peroxide curing than in the case of irradiation treatment by a factor of 4 [1]. One possible explanation could be that peroxides act more selectively than the electron beam, leading to the situation, with two neighbouring carbons losing one hydrogen each, and hence *trans*, less likely in the case of peroxide curing. Owing to the so-called “cage effect” [18], formation of crosslinks is instead favoured. *trans*-Vinylene formation should, in the case of peroxide crosslinking, be dependent on this “cage effect”. In another work [18] regarding LDPE, also with double bonds introduced by copolymerisation of decadiene, a total independence on vinyl content in the forming of *trans*-vinylene groups has been observed. In addition, a linear relationship was found between added peroxide and the amount of *trans*-vinylene formed. In Fig. 6 a different behaviour is shown. Instead of a linear relationship this curve levels off as the amount of

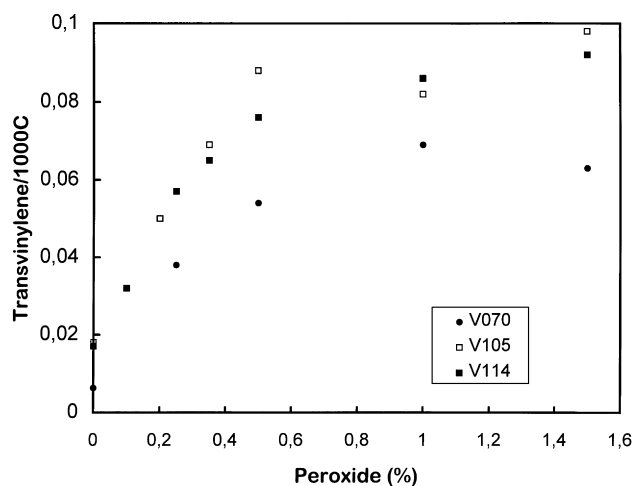


Fig. 6. Number of *trans*-vinylenes/1000C present in the material after treatment with different amounts of peroxide: (●) V070; (□) V105 and (■) V114.

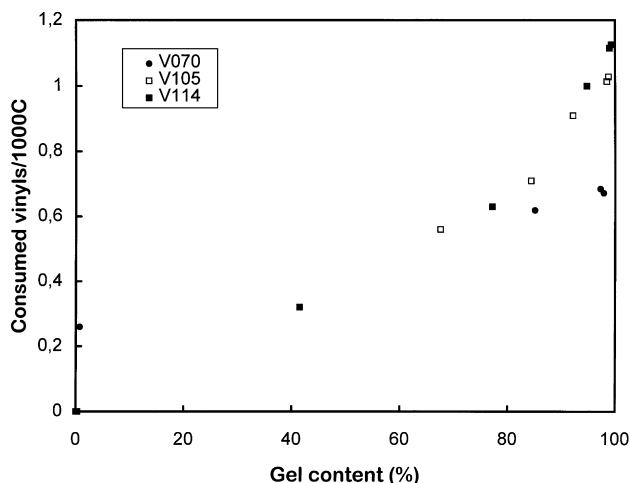


Fig. 7. Consumption of vinyls/1000C as a function of gel formed: (●) V070; (□) V105 and (■) V114.

peroxide is increased. A possible explanation could be that a consumption of *trans*-vinylenes could, due to addition of radicals to the double bond, take place at 190°C (crosslinking temperature for HDPE in this work compared to 160°C for LDPE) and this reaction increases with increased radical concentration. Hence a balance of formation and consumption could result in a levelling off at higher concentration of radicals (peroxide). However, it must be remembered that the changes in *trans*-vinylene are very small and can be attributed to measurement errors. Finally the vinylidene double bonds were examined. The values are all on a relatively low absolute level (<0.04/1000C) and are not considered to be of any significant importance in this context.

Fig. 3 shows that the consumption of vinyls is larger for the polymers containing decadiene as compared with the reference sample for a certain amount of peroxide added. Even at small additions such as 0.10% the difference in consumed vinyls can be detected. These differences are

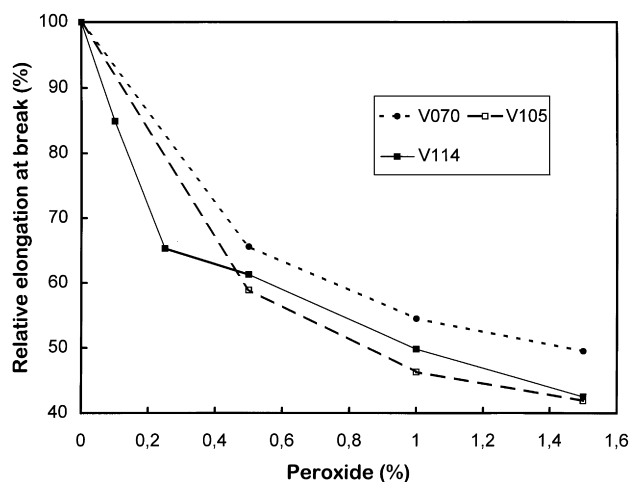


Fig. 8. Relative elongation at break vs. peroxide added: (●) V070; (□) V105 and (■) V114.

enhanced at larger additions of peroxide. At the 1.5% level about 0.45 vinyls/1000C more is consumed in the decadiene material (V114) as compared to the reference. This observation could of course easily be attributed to the fact that V114 originally contains 0.45 vinyls/1000C more than V070 and that all of these double bonds can be consumed in the crosslinking process without that any hydrogen abstraction at secondary carbons taking place in V114. In V070 hydrogen abstraction at secondary carbons probably starts at a lower peroxide level.

Fig. 7 shows the number of consumed vinyls vs. gel content. It is obvious that all the available double bonds are consumed, but the crosslinking still continues in the reference sample above ca. 80% gel. The decadiene samples, on the other hand, continue to crosslink using double bonds all the way up to 100% gel content. This might lead to differences in the network structure at higher gel contents, and, as a consequence, also to differences in mechanical properties between the materials.

In Fig. 8, the relative elongation of samples exposed to the same amount of radicals can be compared. A difference of maximum 8% units in relative elongation at break was obtained between the samples from 1.0% peroxide and above.

A combination of Figs. 8 and 2 reveals the relative elongation at break at room temperature versus gel content, the region above 80% gel being of most interest. However, within this interval there are no significant differences between the samples; the deviations from an imagined average curve are only within a few percent units. This is in strong contrast to what was obtained after irradiation curing that showed a 30% unit difference in relative elongation at break between V114 and V070 at 70% gel.

In order to determine the crosslinking density M_c of the samples, the so-called hot set test was performed; a nominal load of 0.2 MPa at 200°C was applied and the sample elongation E was measured according to Eq. (1). The resulting M_c data are given in Fig. 9 vs. peroxide added. The relative order between the three samples is as expected, i.e. the reference sample has a higher M_c than the decadiene samples. Exception is the last point for V114 at 1.5% peroxide which probably could be regarded as measuring error.

For the reference sample a constantly higher M_c value was obtained because of the lower amount of gel formed for a certain peroxide level. Above about 0.8% of peroxide added, the content of gel for all three samples is practically the same. However, the M_c values are slightly different. For example, at 1% peroxide the reference has an M_c of about 5800 whereas V105 has 4700 and V114 ca. 3500 g/mol. At the highest peroxide level of 1.5% the reference has about 4050, V105 at 3400 and V114 at 4050 g/mol. Thus the samples containing decadiene have a slightly higher crosslinking density as compared to the reference, just as indicated in Fig. 8. If the value obtained for V114 at 1.5% peroxide is considered as a measuring error as mentioned before, the materials containing decadiene still have a

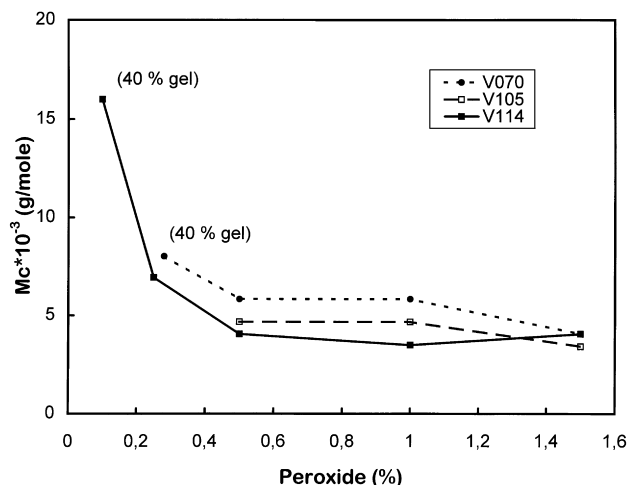


Fig. 9. Number-average molecular weight for a chain between adjacent crosslinking points (M_c) as obtained from hot set measurements vs. added peroxide: (●) V070; (□) V105 and (■) V114.

somewhat lower M_c as compared to the reference. It follows from Figs. 2 and 9 that at high gel levels the M_c values are approximately the same for all three samples. However at 40% gel the results are reversed to what could be expected. This can be explained by Figs. 2 and 9; to reach 40% gel V114 needs only 0.10% peroxide which leads to a M_c of ca. 16 000 whereas V070 needs 0.30% leading to 8000 g/mol instead. The greater amount of peroxide gives more crosslinks through radical coupling whereas roughly the same amount of double bonds are used. The combined effect in crosslinking density, measured as M_c , however, is that V070 contains more crosslinks than V114. It is further worth noting that the reference sample in the hot set test failed at 0.11% of peroxide added whereas V114 was resistant to the heat treatment under load even at such a small level of peroxide. This can be assigned to differences in the double bond structure. In V070 the double bonds consist of

end-group unsaturations and MW enlargement occurs in the first place through low MW material which does not lead to crosslinking. In V114 double bonds are available as side groups and crosslinking of large molecules is favoured, i.e. a loose but extensive network is rapidly built up.

Fig. 8 shows the relative elongation at break vs. peroxide added. It decreases also for peroxide levels above 0.5%. This is in contrast to the behaviour of M_c which shows an almost constant value above 0.5% peroxide concentration. It should, however, be remembered that the elongation test is performed at room temperature, i.e. much below the crystalline melting temperature, whereas the hot set test is made at 200°C. Above 0.5% peroxide, it is mainly the low molar mass part of the distribution that is connected to the network, most probably only at one position. In the melt they will thus not contribute but in the solid state they might be effective if the loose ends are included in the crystalline areas.

E-modulus measurements were made to obtain another parameter in order to evaluate differences in the network structure. The results are presented in Fig. 10. A continuous decrease in *E*-modulus with increasing peroxide amount was observed for all three samples as well as a small difference in modulus between the materials at high peroxide levels. A reduced crystallinity, as shown in Fig. 11, is the obvious explanation to this decline in modulus.

In addition to the tensile tests described above, performed uniaxially above as well as below the crystalline melting point, some experiments were performed using an oscillating rheometer, a so-called elastograph. In Fig. 12, data from the elastograph measurements are given. The obtained moment values refer to final values for fully crosslinked samples. The parameter indicates a difference between the samples for all peroxide levels including the 1.5% level, i.e. the level at which almost exactly the same gel contents were measured for all three samples. The sample is subjected to

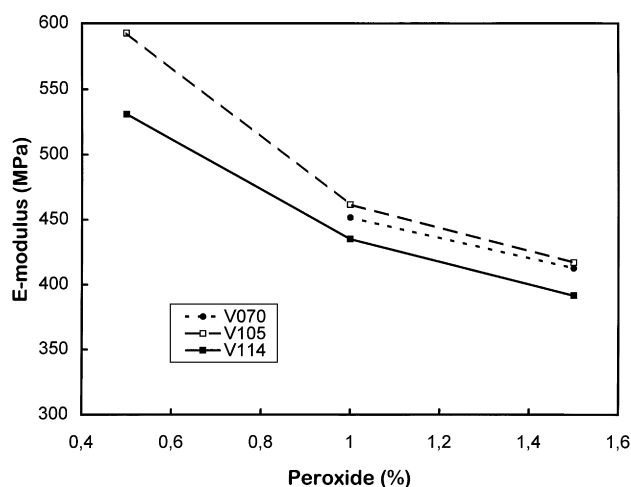


Fig. 10. *E*-modulus as a function of added peroxide: (●) V070; (□) V105 and (■) V114.

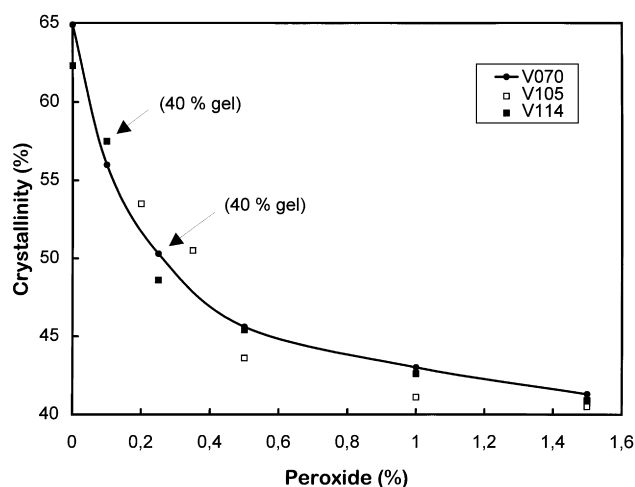


Fig. 11. Crystallinity measured from the second melting cycle as a function of added peroxide: (●) V070; (□) V105 and (■) V114.

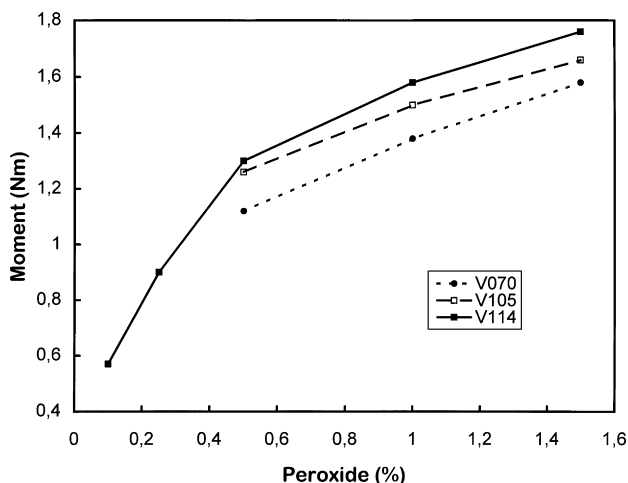


Fig. 12. Elastograph data showing the final moment after curing vs. added peroxide: (●) V070; (□) V105 and (■) V114.

much smaller deformations in the oscillating equipment than in the hot set test, and it is likely that the elastograph measures additional network junctions, e.g. entanglements, as compared to hot set testing. The results obtained indicate a higher crosslinking density for the material containing decadiene, as expected. It can also be noted that the crosslinking density seems to increase above 0.5% peroxide in contrast to what was observed in the hot set test.

A comparison of the results from the oscillating measurements with the M_c values presented in Fig. 9, suggests that the unexpected deviation for V114 at 1.5% peroxide is less reliable and probably a measuring error.

In conclusion, it is likely that the materials containing decadiene have a higher crosslinking density (above 0.3% peroxide) as compared to the reference. This is also the case when all three samples have approximately the same gel content. At lower gel contents, e.g. 40% and below, the situation is the opposite, i.e. the decadiene material has a lower crosslinking density than the reference because of the considerably lower amount of peroxide needed in order to reach that certain gel level. In addition the crosslinking density for a certain sample seems to increase somewhat with peroxide level.

In order to study possible effects of the incorporated decadiene comonomer further, a comparative DSC study was performed on the three sample types. In the following some results on the peak melt temperature (T_{max}), heat of fusion and crystallinity are given. Comparing an untreated material to a material containing 98–99% gel, a decrease of about 13–16°C is observed for all three samples regarding T_{max} . The heat of fusion drops about 62–68 J/g and the crystallinity ca. 22% units (Fig. 11), for all three samples, i.e. no significant effect of the decadiene comonomer can be observed regarding completely crosslinked material. The decline in crystallinity depends on introduced disturbances. The most dominating disturbances are the crosslinks that are formed through radical couplings. As the reference material

needs more peroxide to reach a certain gel content, more crosslinks are introduced through couplings, which leads to the observed reduction in crystallinity. Looking more in detail, however, some significant differences between the studied materials can be revealed. At very high gel levels, i.e. high peroxide content, the maximum crystallinity for the three materials seem to be rather close to each other. At a little bit lower gel contents, however, there is a clear difference between the reference and the decadiene containing samples. The reference has a lower crystallinity compared to V105/V114 for a certain gel content. This must be explained by the more frequent disturbances induced in the reference material V070 as a result of the larger amount of peroxide used in order to reach a certain gel level, e.g. 40% (Fig. 11). Hence it is the crosslinking site created by the peroxide that creates disturbances in the crystal lattice and not the gel content, which is only a consequence of the peroxide treatment. The crystallinity for the three materials instead depends on the amount of peroxide used. A certain amount of peroxide will, however, lead to different gel content in the different materials depending on the structure. An interesting conclusion of the discussion above is that a higher crystallinity, or density, for decadiene material, compared to the reference, will be obtained at a certain gel level. This is something that might be of interest in practical applications.

4. Conclusions

By copolymerising ethylene with 1,9-decadiene using a chromium-based catalyst it is possible to increase the number of vinyl end-groups by more than 60%. As a result, the crosslinking response to dicumyl peroxide is improved significantly. A considerably smaller amount of peroxide is needed in order to obtain a certain gel content. The reason for the improved response to peroxide is, in general, related to the overall higher content of double bonds, but more specifically to the distribution of double bonds along the MWD.

The remaining amount of vinyls after crosslinking was found to be exponentially dependant on the amount of peroxide added. The consumption of vinyls, as a result of crosslinking, increases linearly with the original amount of vinyl unsaturations.

At high levels of peroxide added, almost all vinyl groups are consumed and approximately the same gel content is reached in the reference sample and in the samples containing decadiene. This means a considerably higher consumption of vinyls in the decadiene samples as compared to the reference for a certain gel content. Mechanical measurements indicate a higher crosslinking density for the decadiene materials. At lower gel contents, e.g. 40% and below, the situation is the opposite.

For a certain gel content, a higher crystallinity was

obtained for the decadiene materials as compared to the reference.

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