Crosslinking of binary blends of branched polyethylene and poly(1,2-butadiene): 1. Molecular structure and kinetics

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(Received 21 September 1992)

Blends of branched polyethylene with 2% (w/w) of dicumyl peroxide and different percentage concentrations (0–8% w/w) of a low-molar-mass poly(1,2-butadiene) prepared by melt blending were crosslinked at 180°C and then studied by gel content measurements, size exclusion chromatography of the soluble fraction, infra-red spectroscopy measuring the vinyl content, elastic modulus measurements of the crosslinked melt and differential scanning calorimetry to determine the mass crystallinity of the crosslinked polymer. The kinetics of the crosslinking reaction was recorded by differential scanning calorimetry. The addition of poly(1,2-butadiene) to branched polyethylene had a significant effect on the crosslinking reaction, indicating semi-compatibility of the two polymers. A strong increase in gel content, a pronounced decrease in the molar mass of the soluble fraction, a strong increase in exothermal heat of the crosslinking reaction and a moderate decrease in crystallinity were observed on addition of poly(1,2-butadiene). The crosslinking reactions also involved a transformation of the vinyl groups leaving only 7% of them in the crosslinked blends.

(Keywords: peroxide-crosslinked polyethylene; poly(1,2-butadiene); blends; crosslinking density; soluble fraction; molecular structure)

INTRODUCTION

There are different ways of achieving a network in crosslinked polyethylene, e.g. by the combination of radicalized polyethylene chains initiated by a decomposition of peroxides, high-energy radiation, or hydrolysis of silanes in copolymers of ethylene and vinylsilanes. An appreciable fraction of the polymer, typically of the order of 10–40%, is not implemented in the network[1]. The soluble fraction consists of the low-molar-mass tail, which for purely statistical reasons remains uncrosslinked[1]. It is known from earlier work[2] that the efficiency of the crosslinking catalyst, e.g. a peroxide, is strongly affected by the vinyl content of the polymer. In the case of a linear polyethylene with a low vinyl group concentration (0.07 per 1000 carbons) the peroxide had an efficiency of 20–40%, but in the case of a linear polyethylene with a higher vinyl content (0.5 per 1000 carbons) the efficiency was 76%[2]. With a branched polyethylene, the efficiency approached 100%[3,4].

There are several possible ways of decreasing the amount of uncrosslinked material, e.g. by decreasing the concentration of low-molar-mass material in the polymer prior to crosslinking, by increasing the reactivity of the low-molar-mass material or by blending polyethylene with a compatible compound which enhances the crosslinking efficiency. This paper reports studies on binary mixtures of branched polyethylene and low-molar-mass poly(1,2-butadiene) crosslinked with peroxide. Data are presented relating to the gel content, crosslink density, kinetics of the crosslinking reaction, molar mass of the remaining soluble fraction, vinyl content and crystallinity of the crosslinked polymer.

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EXPERIMENTAL

Binary blends of branched polyethylene (DFDS-47, Neste Polyeten AB, Sweden; $\bar{M}_n = 14\,000$ g mol^{-1}, $\bar{M}_w = 77\,900$ g mol^{-1} from size exclusion chromatography (s.e.c.); 0.3 mol% ethyl branches, 0.7 mol% butyl branches, 0.1 mol% pentyl branches, 0.3 mol% long chain branches and 0.016 mol% vinyl groups from ^{13}C n.m.r.; containing antioxidants) and poly(1,2-butadiene) (Grade B-1000, Nisso Soda Co, Japan; $\bar{M}_n = 1170$ g mol^{-1}; 89.3% of 1,2-vinyl content and 10.7% of *trans*-1,4 content) were prepared by mechanical mixing at 130°C for 12 min. Different blends with 0 to 8% (w/w) of poly(1,2-butadiene) were prepared. Prior to the melt-blending, the polyethylene pellets were impregnated with dicumyl peroxide (Merck–Schuchardt, Germany) at 70°C for 24 h. All blends contained 2 ± 0.2% dicumyl peroxide prior to vulcanization.

Thin films, 50–200 μm in thickness (the individual thicknesses were selected to suit the particular analysis performed on the samples), were prepared by compression moulding at 180 ± 3°C during which the samples were kept for 10 min (22 × half the dicumyl peroxide decomposition time) to ensure complete decomposition of the peroxide. The samples were finally cooled at a rate

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of 100°C min^{-1} to room temperature while being kept under pressure.

The crosslinked samples were treated with hot *p*-xylene (130°C) for 24 h to separate the soluble fraction from the gel fraction. The concentration of the dissolved polyethylene was always <1% (w/w). The gel content determinations involved 20–50 independent measurements of 20 mg pieces of each crosslinked blend. To the solution that was separated from the swollen gel, an excess amount of methanol was added to precipitate the dissolved polymer. The solvent/non-solvent mixture was finally removed in a rotation evaporator.

The soluble fraction samples were analysed by size exclusion chromatography (s.e.c.). The s.e.c. analyses, which were carried out by Dr S. Holding, RAPRA Technology Ltd, UK, involved the dissolution of 10 mg samples in 10 ml 1,2-dichlorobenzene with antioxidant at 160°C. After filtration, the sample solutions were injected into a P.L. column which was thermostatically maintained at approximately 140°C and equipped with an infra-red detector recording at 3.4 μm. Each solution was run in duplicate. The data were analysed using the universal calibration procedure with the Mark–Houwink parameters for low-density polyethylene (LDPE).

The crosslink density of the crosslinked samples was determined by measuring the modulus of molten samples. Dumbbell-shaped specimens with applied ink spots (original distance = L_0) were subjected to a constant load (nominal stress $\sigma_n = 0.2$ MPa) at 200°C for 10 min, at which time the longitudinal distance (L) between the ink spots was measured to determine the elongation $\lambda = L/L_0$. Using classical rubber elasticity theory and considering that the terminal chain segments do not contribute to the elastic force[5], the number-average molar mass for a chain between adjacent crosslinking points ($\bar{M}_c$) was obtained according to the equation:

$$\bar{M}_c = \frac{1}{(2/\bar{M}_n) + \sigma_n/\rho RT\left(\lambda - \frac{1}{\lambda^2}\right)} \quad (1)$$

where $\bar{M}_n$ is the number-average molar mass of the polymer before crosslinking, R is the gas constant, T is the absolute temperature, and ρ is the density of the sample (equal to 753.6 kg m^{-3} at 200°C)[6].

The vinyl content in 20 ± 5 μm films of the polymer before and after crosslinking was determined by transmission infra-red (i.r.) spectroscopy in a Perkin–Elmer FTIR-1760× spectrometer. The absorbance spectra were normalized with reference to the methylene band at 1465 cm^{-1} and the absorbance at 915 cm^{-1} (1,2-vinyl)[7,8] (A_{915}) was compared with the absorbance of the methylene band (A_{1465}).

The kinetics of the crosslinking reaction was studied by differential scanning calorimetry (d.s.c.) in a Perkin–Elmer DSC-7. Uncrosslinked polymer samples weighing 5.5 ± 0.5 mg were heated at 10 or 20°C min^{-1} from 100°C to 250°C while the reaction exotherm was recorded and the heat of reaction evolved was measured as a function of temperature. The data were analysed according to the procedure proposed by Barton[9] in order to obtain the activation energy of the reaction. The thermal history given to the uncrosslinked polymer in the extruder was simulated in the d.s.c. apparatus and possible early crosslinking was measured by comparing the total evolved heat of reaction after a simulation run with that from a 10°C min^{-1} scan between 50 and 250°C. The simulation run was as follows: initial temperature = 50°C; heating to 127°C at 58°C min^{-1}, heating to 136°C at 18°C min^{-1}, cooling to 132°C at 1°C min^{-1}, 132°C (constant temperature) for 2 min. The simulation run was followed by 10°C min^{-1} heating to 250°C during which the remaining total heat of reaction was measured.

The mass crystallinity of the crosslinked samples was obtained by d.s.c. recording of the melting of samples originally crystallized during a 10°C min^{-1} cooling from the melt (170°C). The melting endotherms were obtained in a Perkin–Elmer DSC-7 at a heating rate of 10°C min^{-1} and the recorded values of heat of fusion ΔH_f were transformed into mass crystallinity w_c using the total enthalpy method[10], using 293 kJ kg^{-1} as the heat of fusion (Δh_f^0) for 100% crystalline polymer at the equilibrium melting point (144.9°C)[11]:

$$w_c = \frac{\Delta h_f}{\Delta H_f^0 - \int_{T_1}^{144.9} (c_{pa} - c_{pc})\,dT} \quad (2)$$

where T_1 is an arbitrary temperature below the melting range, and c_{pa} and c_{pc} are the specific heats of the amorphous and 100% crystalline phases, respectively. Data for c_{pa} and c_{pc} presented by Wunderlich and Baur[12] have been used.

RESULTS AND DISCUSSION

Figure 1a shows that the gel content increased with increasing poly(1,2-butadiene) content from 74.5% for pure PE to about 86.5% for the blends with 4–6% poly(1,2-butadiene). The sample with 8% poly(1,2-butadiene) consisted of 85% gel. Pure poly(1,2-butadiene) exhibited a complete transformation to a network polymer upon heating to 200°C. The straight line shown in *Figure 1a* shows the predicted gel content for a completely immiscible mixture of the two polymers. The experimental gel content was always significantly greater than that predicted from the simple rule of mixing. *Figure 1b* shows that the difference between measured and predicted gel content first increases with increasing poly(1,2-butadiene) concentration indicating a compatibility of the polymers at a low concentration of poly(1,2-butadiene). In samples with poly(1,2-butadiene) concentrations greater than 6%, the difference between measured and predicted gel content decreased with increasing poly(1,2-butadiene) concentration.

Figure 2 presents the data from the elastic modulus measurements transformed into $\bar{M}_c$ according to equation (1). $\bar{M}_c$ decreased strongly with increasing poly(1,2-butadiene) concentration at low concentrations and reached a minimum at 4–5% (w/w) of poly(1,2-butadiene). The minimum in $\bar{M}_c$ is consistent with the maximum in gel content at approximately the same poly(1,2-butadiene) concentration, cf. *Figures 1a* and *b*. The maximum relative difference in $\bar{M}_c$ was about 20%. The total heat of crosslinking (ΔH_{tot}) increased markedly with increasing poly(1,2-butadiene) content (*Figure 3*). The total heat of crosslinking may be expressed by the equation:

$$\Delta h_{tot} - \Delta h_{perox} = \Delta h_{mix}(1 - w_{PB,segr}) + \Delta h_{PB} w_{PB,segr} \quad (3)$$

where Δh_{perox} is the heat of the decomposition of the peroxide (a value of 11 ± 2 kJ kg^{-1} (ref. 13) was used),

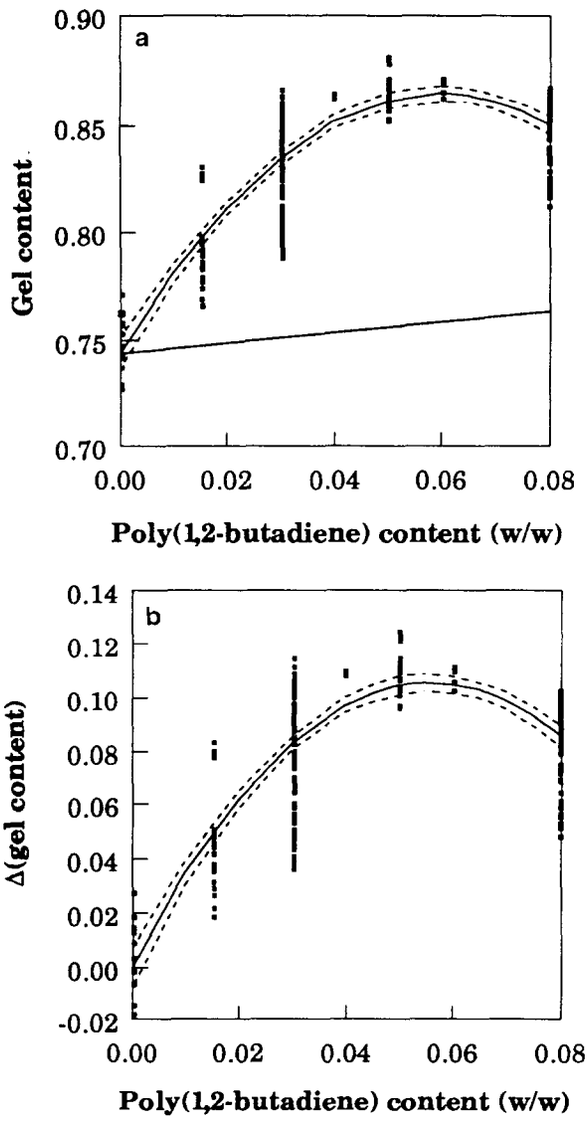

Figure 1 (a) Gel content as a function of poly(1,2-butadiene) content. The straight line indicates the gel content of incompatible mixtures assuming 100% gel of the poly(1,2-butadiene): $w_{gel} = w_{PB} + (1 - w_{PB})w_{PE,gel}$, where w_{gel} is the gel content, w_{PB} is the poly(1,2-butadiene) content (100% gel) and $w_{PE,gel}$ is the gel content of the PE component. (b) Difference between measured and predicted gel content assuming complete incompatibility of the polymers

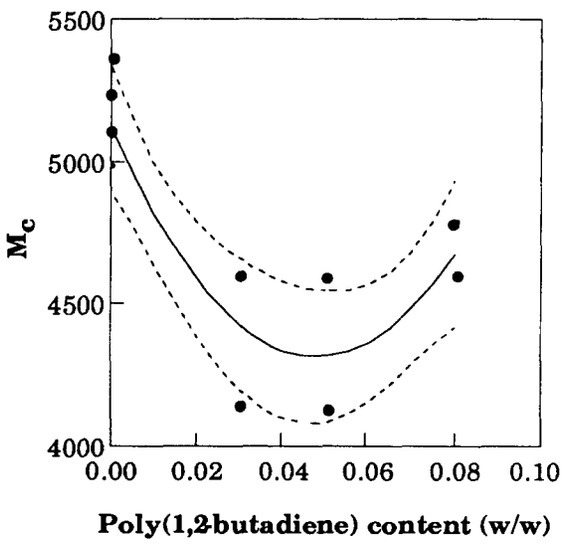

Figure 2 Crosslinking density expressed in M_c as a function of poly(1,2-butadiene) content calculated from elastic modulus data according to equation (1)

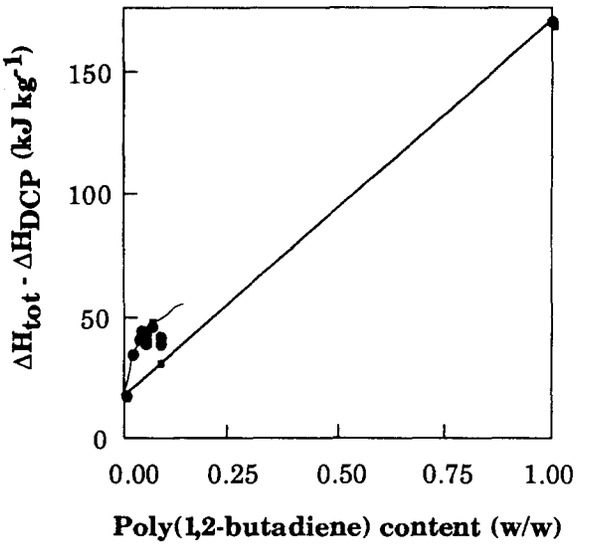

Figure 3 Total heat of crosslinking (Δh_{tot}) minus the heat of decomposition of the peroxide as a function of poly(1,2-butadiene) content. The straight line indicates additive contributions from each polymer. The solid line is the fit to equation (3)

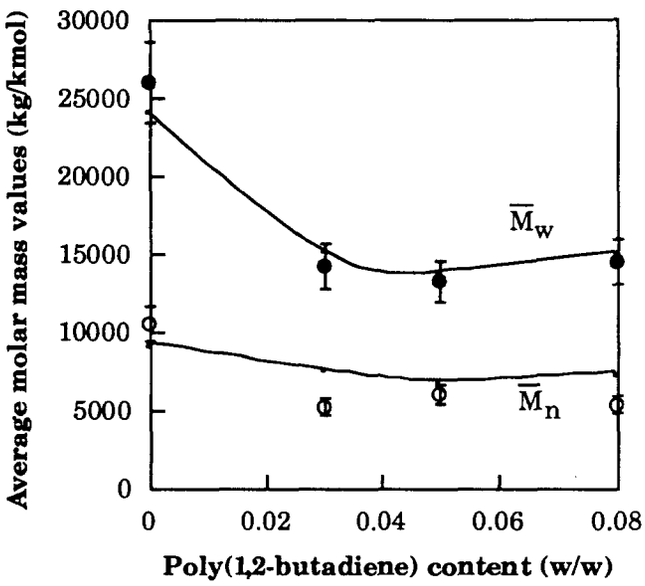

Figure 4 Number-average (○) and mass-average (●) molar mass of the soluble fraction as a function of poly(1,2-butadiene) content. The solid lines are constructed from values predicted from a theoretical model using the values of the adjustable parameters obtained by fitting the model to the gel content data

Δh_{mix} is the heat of crosslinking of the blend phase, $w_{PB,segr}$ is the content of segregated poly(1,2-butadiene) and Δh_{PB} is the heat of crosslinking of the poly(1,2-butadiene) phase. Equation (3) contains two unknown, adjustable parameters. Equation (3) was fitted to the experimental data assuming that PE and poly(1,2-butadiene) formed a single-phase system ($w_{PB,segr} = 0$) for poly(1,2-butadiene) contents $\leqslant 0.03$ (*Figure 3*).

The average molar mass values of the soluble fraction samples decreased significantly with increasing poly(1,2-butadiene) content at low poly(1,2-butadiene) contents, and reached an almost constant molar mass value in blends with poly(1,2-butadiene) contents greater than 3% (*Figure 4*). A minor increase in $\overline{M}_w$ was, however, recorded for the sample with 8% poly(1,2-butadiene).

The molar mass data was further analysed according to the model first presented in ref. 1. A similar approach

was reported by Peacock[14]. It was assumed in ref. 1 that the probability that a given main chain carbon atom becomes crosslinked (P_t) is constant and independent of the chain length. The probability $P(I, M)$ that a molecule of molar mass M is associated with other molecules via I crosslinks is given by the equation:

$$P(I, M) = \frac{(1 - P_t)^{M/14 - I} P_t^I (M/14)!}{(M/14 - I)!\, I!} \tag{4}$$

For any polymer, P_t is given by:

$$P_t = \frac{2f(x_{DCP}/M_{DCP})}{(1 - x_{DCP})/M_{CH_2}} \tag{5}$$

where f is the crosslinking efficiency, x_{DCP} is the mass fraction of added dicumyl peroxide, M_{DCP} is the molar mass of dicumyl peroxide and M_{CH_2} is the molar mass of the repeating unit of PE. The molar mass distribution $F(I, M)$ of the 'primary' molecules before crosslinking with I crosslinked carbons per molecule is given by

$$F(I, M) = F^0(M)P(I, M) \tag{6}$$

where $F^0(M)$ is the molar mass distribution of the uncrosslinked polymer. The molar mass distribution of the soluble fraction ($F_{SOL}(M)$) of the crosslinked polymer is given by:

$$\begin{aligned} F_{SOL}(M) = {} & F(0, M) + F_{11}(M) + F_{211}(M) + F_{3111}(M) \\ & + F_{41111}(M) + F_{2211}(M) \\ & + F_{22211}(M) + F_{32111}(M) \end{aligned} \tag{7}$$

where $F_{ijklm}(M)$ is the mass-based molar mass distribution of molecules consisting of primary molecules with i, j, k, l and m crosslinks. Only combinations involving five primary molecules or fewer were considered. The contribution from molecules with a greater number of primary molecules is insignificant. The mass fraction (w_{ijklm}) of each type of combined molecule was derived from the following equations:

$$\begin{aligned} w_0 &= w(0) \\ w_{11} &= w(1)x_{nr}(1) \\ w_{211} &= w(2)x_{nr}(1)^2\left(1 + \frac{2\bar{M}_w(1)}{\bar{M}_w(2)}\right) \\ w_{3111} &= w(3)x_{nr}(1)^3\left(1 + \frac{3\bar{M}_w(1)}{\bar{M}_w(3)}\right) \\ w_{41111} &= w(4)x_{nr}(1)^4\left(1 + \frac{4\bar{M}_w(1)}{\bar{M}_w(4)}\right) \\ w_{2211} &= w(2)x_{nr}(2)x_{nr}(1)^2\left(1 + \frac{\bar{M}_w(1)}{\bar{M}_w(2)}\right) \\ w_{22211} &= w(2)x_{nr}(2)^2x_{nr}(1)^2\left(1 + \frac{2\bar{M}_w(1)}{3\bar{M}_w(2)}\right) \\ w_{32111} &= w(3)x_{nr}(2)x_{nr}(1)^3\left(1 + \frac{\bar{M}_w(2)}{\bar{M}_w(3)} + \frac{3\bar{M}_w(1)}{\bar{M}_w(3)}\right) \end{aligned} \tag{8}$$

where $w(I)$ is the mass fraction of primary molecules with I crosslinks, $x_{nr}(I)$ is the fraction of crosslinks in the group of primary molecules with I crosslinking points and $\bar{M}_w(I)$ is the mass-average molar mass of the group of primary molecules of I crosslinks:

$$w(I) = \sum_M F(M, I) \Big/ \sum_M F^0(M) \tag{9}$$

$$x_{nr}(I) = In(I)/\sum_I In(I) \tag{10}$$

$$n(I) = \sum_M \frac{F(M, I)}{M} \Big/ \sum_M \frac{F^0(M)}{M} \tag{11}$$

$$\bar{M}_w(I) = \sum_M F(M, I)M \Big/ \sum_M F(M, I) \tag{12}$$

The gel content was calculated according to equation (13) assuming that the poly(1,2-butadiene) was completely crosslinked and that the decomposition products of dicumyl peroxide were partially soluble (fraction x). Particularly in blends with a high concentration of poly(1,2-butadiene), reactions between the alkoxy radicals formed from the decomposition of the peroxide and the vinyl groups give insoluble decomposition products of the peroxide.

$$\begin{aligned} w_{gel} = {} & w_{PB} + (1 - w_{PB})(1 - w_0 + w_{11} + w_{211} + w_{3111} \\ & + w_{41111} + w_{2211} + w_{22211} + w_{32111}) - w_{DCP}x \end{aligned} \tag{13}$$

The major adjustable parameter in equation (13) and the equations implicit in this equation is f, the efficiency of crosslinking. *Figure 5* presents values of f obtained from fitting equation (13) to the experimental data. The range shown in the graph corresponds to x values in the range 0–1. It is probable that x will approach very low values in samples containing larger proportions of poly(1,2-butadiene).

For the pure branched PE, the best fit of equation (13) gives the crosslinking efficiency value of 0.86 which is in fair agreement with earlier data published by Dannenberg *et al.*[3] and Simunkova *et al.*[4]. The crosslinking efficiency increased with increasing poly(1,2-butadiene) content and reached a maximum value of about 1.50 ($x = 0$) at

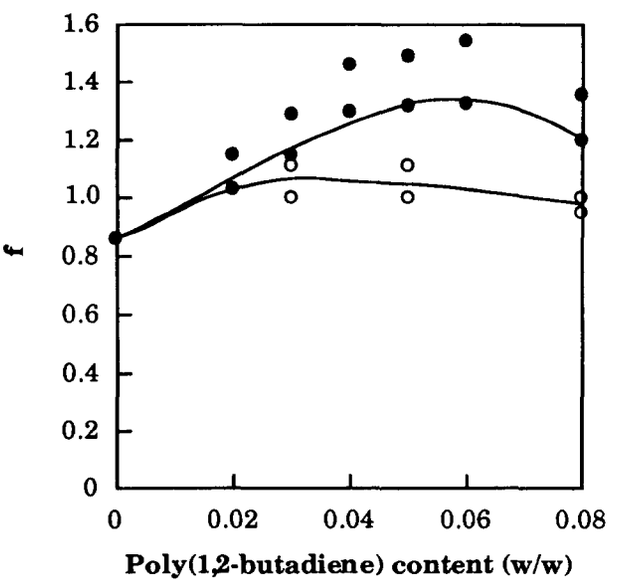

Figure 5 Crosslinking efficiency (f) as a function of poly(1,2-butadiene) content: (●) from gel content data: the lower value corresponds to $x = 0$ and the higher value to $x = 1$; the solid line is fitted to the data corresponding to $x = 0$; (○) from hot set data ($\bar{M}_c$)

4–5% of poly(1,2-butadiene). Samples with even higher poly(1,2-butadiene) contents exhibited a decrease in crosslinking efficiency with increasing poly(1,2-butadiene) content (*Figure 5*). The crosslinking density was derived from $\bar{M}_c$ data (f = constant/$\bar{M}_c$), assuming $f = 0.86$ for pure PE (*Figure 5*). The predicted f values are significantly greater than those obtained from the $\bar{M}_c$ data. We have at present no explanation for the discrepancy but it may be due to heterogeneous crosslinking. *Figure 6* presents gel content predictions for samples with different concentrations of dicumyl peroxide assuming 100% crosslinking efficiency and $x = 1$.

The molar mass distribution of the soluble fraction was obtained from:

$$\begin{aligned} F_{SOL}(M) = {} & w_0 F^*(0, M) + w_{11} F^*(1, M + \bar{M}_w(1)) \\ & + w_{211} F^*(2, M + 2\bar{M}_w(1)) \\ & + w_{3111} F^*(3, M + 3\bar{M}_w(1)) \\ & + w_{4111} F^*(4, M + 4\bar{M}_w(1)) \\ & + w_{2211} F^*(2, 2M + 2\bar{M}_w(1)) \\ & + w_{22211} F^*(3, 3M + 2\bar{M}_w(1)) \\ & + w_{32111} F^*(3, M + \bar{M}_w(2) + 3\bar{M}_w(1)) \end{aligned} \quad (14)$$

Predicted and experimental average molar mass values are compared in *Figure 4*. The predicted data were based on the fitting of equation (13) to the experimental gel content data. The values obtained for the adjustable parameters, f and x (*Figure 5*), were used and the resulting molar mass distributions of the soluble fractions were calculated. The agreement between experimental and predicted mass-average molar mass values is very good (*Figure 4*). The number-average data show a greater discrepancy. The procedure for using 'average' type of molecules for combined molecules (11, 211, etc.) leads to an underestimation of the low molar mass species which then primarily affect $\bar{M}_n$.

The i.r. spectrum of the uncrosslinked samples exhibited a distinct absorption band at 915 cm^{-1}, indicating the presence of poly(1,2-butadiene). The relative absorption of the 915 cm^{-1} band was approximately proportional to the poly(1,2-butadiene) content (*Figure 7*). The vinyl content of the polyethylene was 0.016 mol%, which is negligible compared with the contribution from poly(1,2-butadiene). The vinyl content of the crosslinked samples was much lower than that of the corresponding non-crosslinked samples (*Figure 7*). The remaining vinyl content was on average, taking all blends into account, only 6.8% of the initial vinyl content.

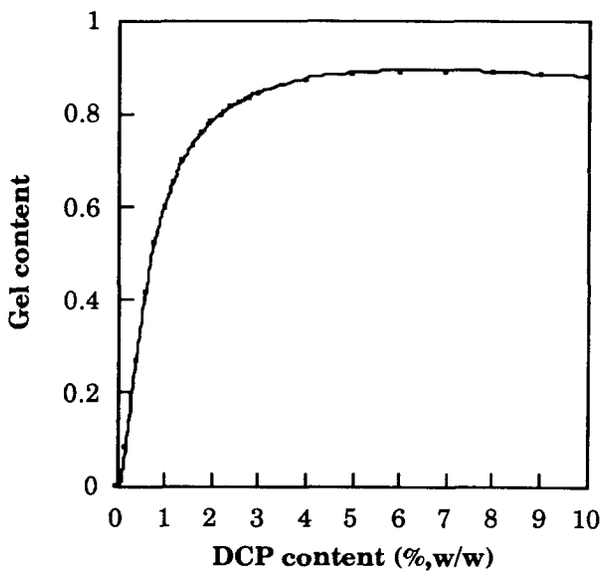

Figure 6 Predicted gel content (from equation 13) as a function of dicumyl peroxide content assuming 100% crosslinking efficiency and $x = 1$

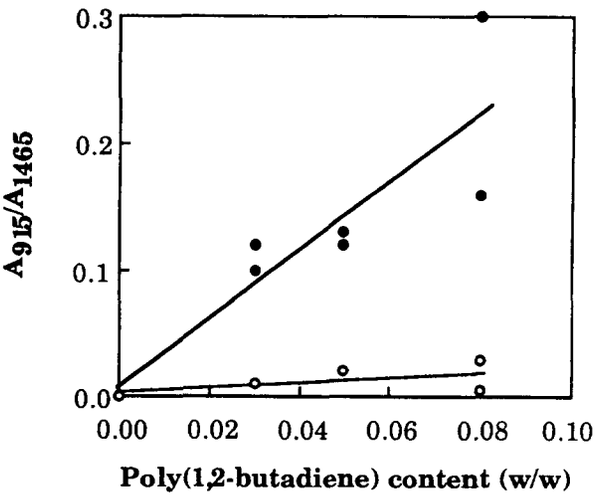

Figure 7 Vinyl content expressed as relative infra-red absorbance (A_{915}/A_{1465}) as a function of the poly(1,2-butadiene) content: (●) before crosslinking; (○) after crosslinking

Table 1 Activation energy of crosslinking reaction

Poly(1,2-butadiene) content (% w/w)	Activation energy[a] (kJ mol^{-1})
0	156.7 ± 7.6
3	132.8 ± 17.0
5	142.4 ± 14.9
8	135.1 ± 23.8

[a] Average value and standard deviation

The kinetics of the crosslinking reaction was measured dynamically and the data were analysed according to the method proposed by Barton[9]. *Table 1* shows that the activation energy of pure PE was relatively similar to the 142 kJ mol^{-1} reported by Sen *et al.*[15]. The decrease in activation energy with increasing poly(1,2-butadiene) content amounted to approximately 2 ± 1 kJ mol^{-1} (%poly(1,2-butadiene))$^{-1}$ which may be compared with 0.7 kJ mol^{-1} (%EPDM)$^{-1}$ reported for mixtures of PE and poly(ethylene-*co*-propylene-*co*-dicyclopentadiene) (EPDM)[15]. The difference may be attributed to the higher degree of unsaturation of poly(1,2-butadiene) than of EPDM.

The results of the d.s.c. simulation of the extrusion process presented in *Table 2* indicate that 7.4% of the reaction heat was evolved for the pure polyethylene and only 4.5% for the blend with 5% of poly(1,2-butadiene). No detectable gel was found in either of the two samples.

The melting peak temperature and mass crystallinity decreased with increasing poly(1,2-butadiene) content (*Figures 8a* and *9*). The melting temperature (T_m (K)) was transformed into crystal thickness (L_c) using the Thompson–Gibbs equation:

$$L_c = \frac{2\sigma T_m^0}{(T_m^0 - T_m)\Delta h \rho} \quad (15)$$

Table 2 Heat of crosslinking

Poly(1,2-butadiene) content (% w/w)	ΔH^a ($J\,g^{-1}$)	ΔH^b ($J\,g^{-1}$)
0	12.6	13.6
5	31.9	33.4

[a]Heat of crosslinking in post-extrusion period
[b]Total heat of crosslinking

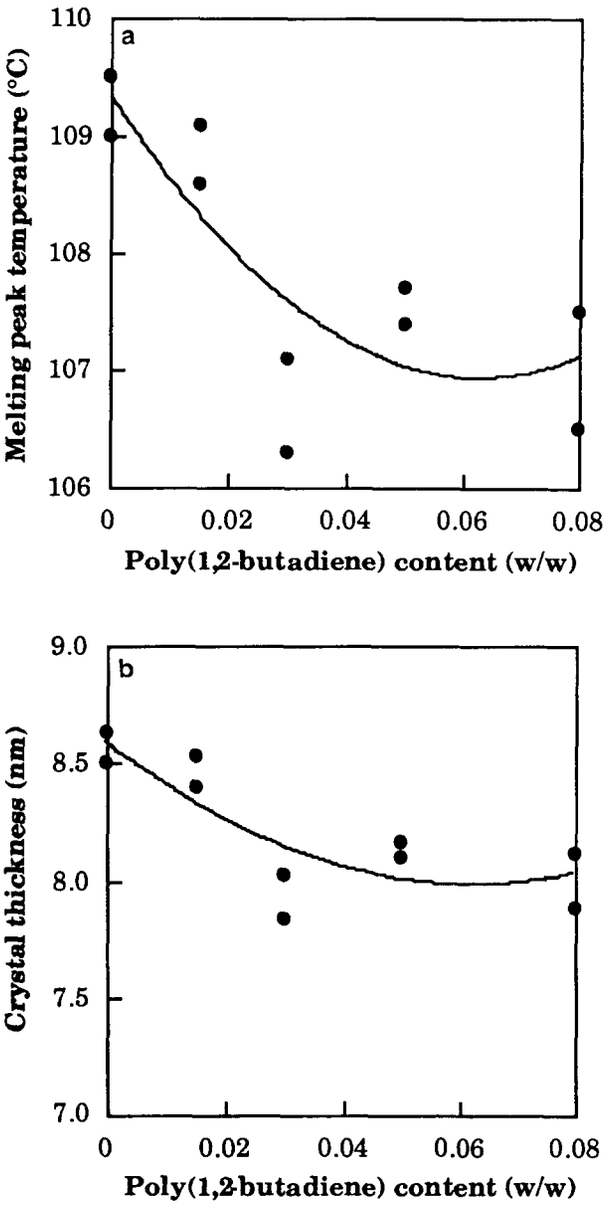

Figure 8 (a) Melting peak temperature as a function of poly(1,2-butadiene) content. (b) Crystal thickness from melting peak temperature data according to equation (15) as a function of poly(1,2-butadiene) content

where σ is the fold surface free energy (93 mJ m^{-2}; ref. 11), T_m^0 is the equilibrium melting temperature (414.6 K; ref. 11), Δh is the heat of fusion (280 kJ kg^{-1}; ref. 11) and ρ is the crystal phase density (1000 kg m^{-3}; ref. 16). No correction was made for crystal thickening since the crosslinked nature of the studied samples was believed to inhibit any crystal thickening occurring during the heating scan in the d.s.c.

Figure 8b shows that the crystal thickness decreased with increasing poly(1,2-butadiene) content from about

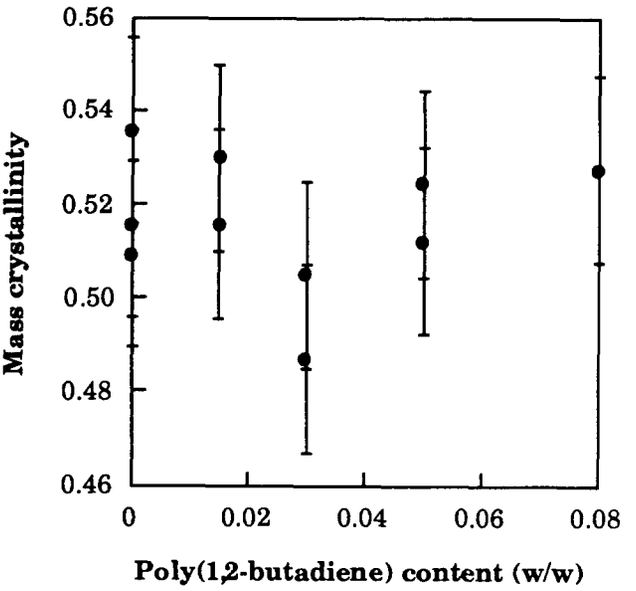

Figure 9 Mass crystallinity of the crosslinked polyethylene component by d.s.c. (equation (2)) as a function of poly(1,2-butadiene) content

8.6 nm at 0% poly(1,2-butadiene) to about 8.0 nm at 6% poly(1,2-butadiene). The exact position of the minimum in crystal thickness is uncertain due to the scatter in the data. The uncrosslinked polyethylene given the same thermal treatment as the crosslinked samples exhibited a peak melting temperature of 112.5°C corresponding to a crystal thickness of 9.5 nm. The crystal thickness data were compared with the data for the crosslink density and it was observed that L_c decreased roughly linearly with $\bar{M}_c^{-1}$, which indicates that each 'newly' formed network chain leads to a certain incremental reduction in crystallinity. The maximum lowering in mass crystallinity compared with the reference sample with no poly(1,2-butadiene) amounted to 7.5% (relative value), which is similar to that calculated from crystal thickness data (7%). The uncrosslinked polymer had a mass crystallinity of 0.55. The magnitude of the crystallinity reduction is in agreement with earlier data of Kao and Phillips[17].

In conclusion, the addition of different percentage portions of poly(1,2-butadiene) to branched polyethylene containing 2% (w/w) of dicumyl peroxide has a significant effect on the crosslinking process, indicating semi-compatibility of the two polymers. The strong increase in gel content and the strong decrease in molar mass of the soluble fraction of the crosslinked polymer confirm the enhancing effect of poly(1,2-butadiene) on the crosslinking of polyethylene. Both gel content data and the entire molar mass distributions of the soluble fractions were used to fit a two-adjustable-parameter model for the crosslinking reaction. It was shown that the major adjustable parameter, the crosslinking efficiency, increased from 0.86 in pure polyethylene to 1.3 at 5% (w/w) of poly(1,2-butadiene). It is suggested that the crosslinking efficiency increases because, in addition to the normal hydrogen abstraction followed by combination of two alkyl radicals producing a crosslink, other reactions leading to crosslinks must occur in the poly(1,2-butadiene)-containing systems. Free-radical chain reactions involving the vinyl groups in poly(1,2-butadiene) and in polyethylene may account for the observed increase in crosslink density. The levelling-off tendency in the gel content increase and

molar mass decrease observed at 3–4% poly(1,2-butadiene) content indicates a saturation of polyethylene–poly(1,2-butadiene) solution at this composition. For blends with a higher concentration of poly(1,2-butadiene), a separate poly(1,2-butadiene) phase is most probably formed and no further enhancement of polyethylene crosslinking occurs. The observed decrease in crosslinking efficiency with increasing poly(1,2-butadiene) content observed in this poly(1,2-butadiene) range may be due to a lowering of the dicumyl peroxide concentration in the polyethylene-rich phase. The strong decrease in vinyl content in the blends accompanying vulcanization indicates that poly(1,2-butadiene) is involved in the crosslinking of the polyethylene component and that further crosslinking of segregated poly(1,2-butadiene) occurs in the blends having a higher concentration of poly(1,2-butadiene).

ACKNOWLEDGEMENTS

This study has been sponsored by the Swedish Board for Technical Development (STU), grant 89-02294P. The authors thank Dr S. Holding, RAPRA Technology Ltd, UK, for the s.e.c. analyses.

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