Role of molecular structure on the silane crosslinking of polyethylene: the importance of resin molecular structure change during silane grafting

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The degree of peroxide induced chain extension of polyethylene (PE) as a result of free radical silane grafting proves to be of vital importance to the rate of formation and also the final degree of crosslinking of the PE network structure upon moisture curing. The differences in solid state structure (which determines the moisture diffusion rate into the polymer) and silane grafting efficiency of various PE types have been shown to play an important but a secondary role in the crosslinking of the resins.

(Keywords: polyethylene; silane; peroxide)

INTRODUCTION

Crosslinked polyethylene (PE) has become widely adapted for a number of industrial applications which require withstanding high temperature environments. Examples of such applications include wire and cable coating, hot water tubing and steam resistant food packaging.

PE crosslinking which involves direct carbon–carbon interaction between different PE chains is carried out via the use of peroxide or β- and γ-radiation. Another process which involves the grafting of vinyl trimethoxy silane (VTMS) onto the polymer chain is becoming more popular nowadays due to the low investment cost and high production rate of such a process. VTMS molecules which normally graft onto PE polymer chains through free radical initiators can subsequently be condensed through moisture, leading to the formation of crosslinking. The details of the silane crosslinking technology and chemistry have been reported in a number of publications[1-3].

PE crosslinking generally enhances a number of properties such as impact strength, thermal performance, chemical, creep and environmental stress crack resistance. The degree of enhancement depends largely on the crosslink density of the sample. The effect of peroxide concentration[4], radiation dosage[5] or conditions of silane grafting[6], etc., on the crosslinking of PE have already been studied. In this paper, we intend to report the roles PE molecular structure and microstructure play on the crosslinking of PE through the silane crosslinking process. In particular, the importance of resin molecular structure change during melt grafting of silane is discussed.

EXPERIMENTAL

The polymers used in this study and their main characteristics are given in *Table 1*. The PEs shown in *Table 1* are of different types. The Eltex A 4019 is a linear high density PE (HDPE) with no or very little long and short chain branchings. The LL1004 is a linear low density PE (LLDPE) with a broad distribution of short chain branchings. The LD180 is a low density PE (LDPE) with both long and short chain branchings. These PEs have similar weight average molecular weight, M_w, in the range 69–88 K and molecular weight distribution in the range 3.5–4.6. The VTMS, dicumyl peroxide (Dicup) and dibutyltindilaurate (DBTD) catalyst were used as supplied.

The silane grafting of PE was carried out by first tumble blending the PE (pre-dried overnight at 70°C) with VTMS (1.2 wt%), Dicup (0.1 wt%) and DBTD (0.05 wt%) and then allowed to soak for 48 h before being extruded into a tape using a Haake single screw extruder coupled with a slit die. Similar samples were also made under the same conditions by extruding the neat resins or resins with only 0.1 wt% Dicup added. The conditions of extrusion were kept constant for the different sample preparations. The thickness of the extruded tape ranged from 1.25 to 1.45 mm depending on the resins used. The extruded samples were immediately kept in a desiccator to prevent premature moisture curing taking place. All moisture crosslinking was conducted within 2 days of sample preparation and was carried out by immersing the prepared sample strips in a water bath maintained at 80°C for different periods of time. The hot-set elongation after various curing periods was measured by subjecting the sample to a constant stress of 2.0 kg cm^{-2} inside an

Table 1 Main characteristics of the PEs used

Sample code	Eltex A 4019	LL1004	LD180
Polyethylene type	HDPE	LLDPE	LDPE
Melt index	2	2.8	2
Density (g cm^{-3})	0.953	0.918	0.9195
M_w ($\times$ 1000)	88.1	69.2	81.3
M_n ($\times$ 1000)	21.1	19.8	17.8
M_w/M_n	4.17	3.5	4.58

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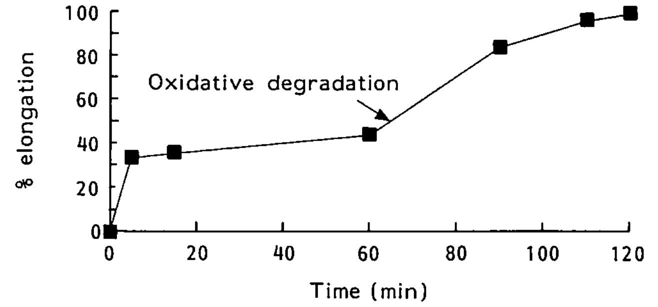

Figure 1 Creep elongation of LLDPE under conditions of hot-set elongation measurement

oven set at 200°C. The percentage elongation of the sample after equilibration at the above conditions for 15 min was recorded as the hot-set elongation. Since oxidative degradation of crosslinked PE to induce creep elongation under the above conditions only takes place after ~60 min (*Figure 1*), the hot-set elongation corresponds to the true mechanical response of the equilibrated crosslink network structure of the sample.

The amount of silane grafted was measured using a Mattson Cygnus 100 Fourier transform infra-red (*F*T*i.r.*) spectrometer. Measurements were made immediately after the samples were extruded and prior to moisture curing. Absorption peak heights at 1090 cm^{-1}, which corresponds to the Si-O-C stretching vibration of VTMS[7], were recorded. Correction was made for absorption at 1090 cm^{-1} by the PE matrix and any free vinyl silane which may still exist in the samples. This is carried out by subtracting the background signal at 1090 cm^{-1} of the pure PE resin and also that of the free silane back-calculated from the *F*T*i.r.* vinyl absorption peak at 1600 cm^{-1}. It happens that the free vinyl silane absorption is very insignificant (<1%) compared to the absorption of the grafted silane. This is probably due to the fact that most free vinyl silane has evaporated during the sample preparation for *F*T*i.r.* measurement which involves pressing the polymer at 120°C under a constant load of 3×10^3 kg for 3 min. The crosslink densities of the PE samples were calculated from the measured percentage elongation of the samples after equilibration at 200°C (above the melting temperature of PE) for 15 min and subjected to a tensile stress of 2.0 kg cm^{-2}. The calculation is based on an equation derived from the kinetic theory of rubber elasticity.

Dynamic shear viscosity measurements were conducted using a Rheometric mechanical spectrometer (RMS 800). Measurements were made at 180°C under nitrogen.

Transmission electron microscopy (TEM) was conducted using a Jeol 100C microscope. In order to reveal the details of the lamellar structure of the samples, a staining procedure similar to that pioneered by Kanig[8,9] was adopted.

RESULTS AND DISCUSSION

FT*i.r. determination of vinyl silane grafting onto PEs*

Figure 2 shows the *F*T*i.r.* absorption peaks at 1090 cm^{-1} of various silane-grafted PEs. The absorption peak at 1090 cm^{-1} corresponds to the Si-O-C stretching vibration of the silane group. The absorption peak heights which have been corrected for the background absorption of the PE matrices and the non-grafted (free) vinyl silane are shown in *Table 2*. It can be observed that the LL1004 and LD180 have comparable amounts of grafted silane, whilst the Eltex A 4019 has a much lower silane grafting efficiency.

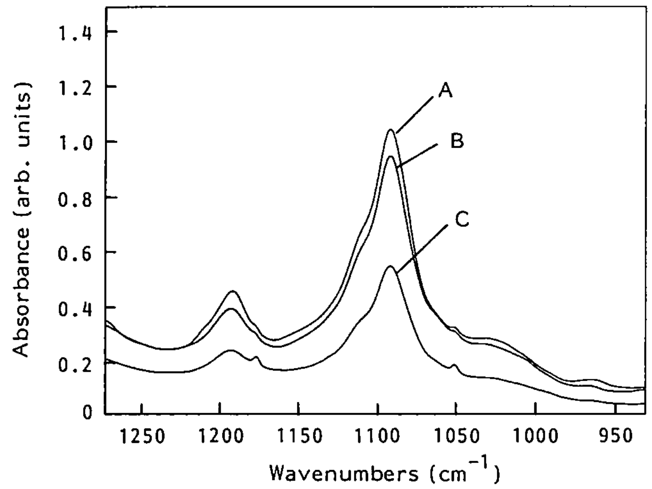

Figure 2 *F*T*i.r.* absorption peaks of VTMS grafted PEs: (A) LL1004; (B) LD180; (c) ELTEX A 4019

Table 2 Absorption peak height and peak area of different vinyl silane grafted PEs

Sample	Absorbance peak height[a] at 1090 cm^{-1} (per 100 μm film thickness)	Absorbance peak area[a] at 1090 cm^{-1} (per 100 μm film thickness)
LL1004	0.341	15.2
LD180	0.301	14.6
Eltex A 4019	0.163	7.1

[a] Corrected for non-grafted VTMS and PE matrix

Chain extension and degradation of PE during silane grafting

At the high temperature under which the extrusion grafting process is conducted, the peroxide dissociates to form unstable free radicals which readily abstract hydrogen atoms from the PE. The carbon free radicals which are then formed can have several reaction pathways: (1) they can disproportionate to form unsaturated species; (2) they can induce β-scissioning in the polymer chain; (3) they can recombine with another carbon free radical on a different chain to form a chain extension; (4) they can react with the vinyl unsaturation of the VTMS for grafting the molecule. The reaction pathways (1)–(3) listed above will no doubt alter the molecular structure of the resin which subsequently affects the crosslinking behaviour.

Dynamic shear viscosity change of various PE resins due to the effect of Dicup alone and also VTMS and Dicup together has been investigated. In order to confirm the large effect observed for LL1004, two other LLDPE resins have also been included in this study. *Figures 3–7* show the shear viscosity curves of the different PEs. In each figure, the shear viscosity over a range of shear rate of one of the unmodified resins, the same resin after peroxide treatment* and after peroxide and silane

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* Pre-dried PE resin mixed with 0.1 wt% Dicup and then extruded

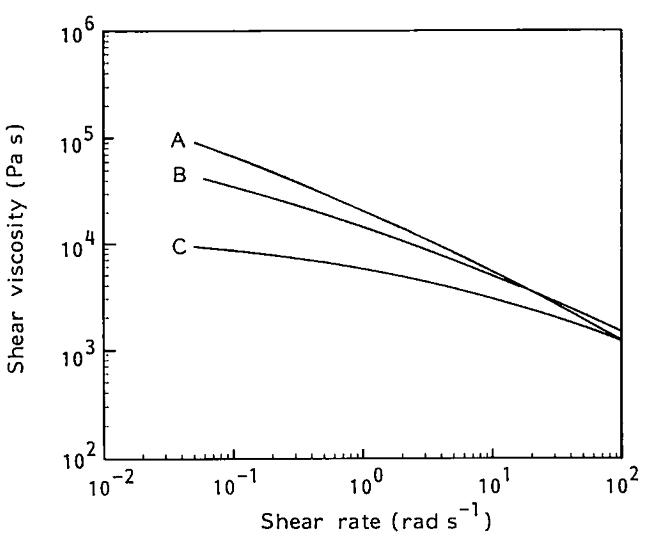

Figure 3 Shear viscosity curves of modified and unmodified Eltex A 4019: (A) peroxide and silane treated; (B) peroxide treated; (C) unmodified

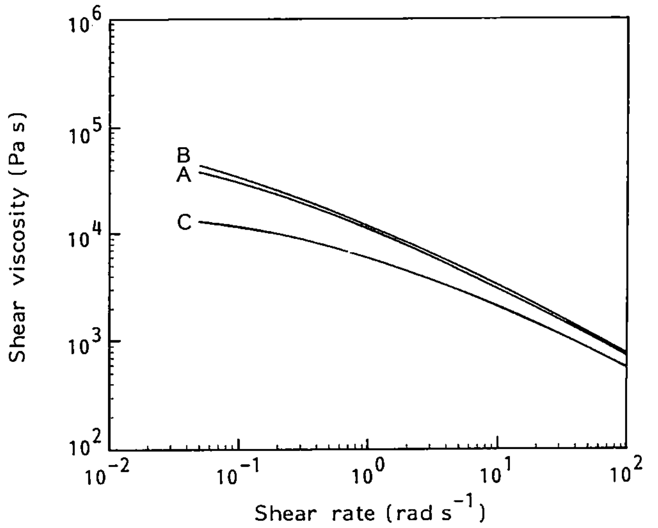

Figure 4 Shear viscosity curves of modified and unmodified LD180. Lettering as in *Figure 3*

treatment* are compared. It can be seen that, in all cases, the peroxide treatment causes a substantial increase in the zero shear viscosity of the resin. This increase is particularly significant for the LLDPE-type PE and less so for the LDPE and HDPE. The addition of silane does not seem to significantly change the zero shear viscosity of the PEs. The additional large increase in zero shear viscosity of the peroxide and silane treated LL1004 and Eltex A 4019 is most likely due to premature silane crosslinking.

The magnitude of the increase in zero shear viscosity of the PE resins studied is shown in *Table 3*. It is clear that the peroxide induces a very dramatic change in the molecular structure of the resin during the silane grafting process. The magnitude of the change, however, depends on the PE type. The LLDPEs which have, in most of their chains, a fair amount of randomly distributed short chain branches resulted in the highest degree of chain extension reaction. This is largely due to the formation of stable tertiary carbon free radicals[10] which can then recombine to form chain extensions. The LDPE, due to its more clustered short chain branches[11], suffers from β-scissioning[12] and therefore a lower degree of chain extension. The HDPE is also not very highly chain extended by free radicals, probably due to the lack of tertiary carbon atoms along its chains. The lack of tertiary carbon atoms probably also explains the low VTMS grafting efficiency of the Eltex A 4019 resin. It should be noted that for all the PEs studied so far, the peroxide treatment does not lead to detectable gel formation. All the peroxide treated samples can be completely dissolved in *o*-xylene at elevated temperature.

The above result no doubt indicates that the type of PE plays an important role in the silane crosslinking of the resin. The peroxide which is used primarily for grafting silane induces molecular changes in the resin

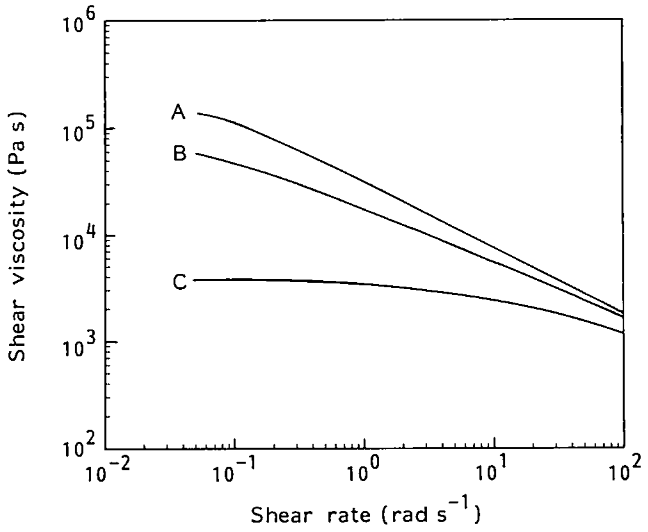

Figure 5 Shear viscosity curves of modified and unmodified LL1004. Lettering as in *Figure 3*

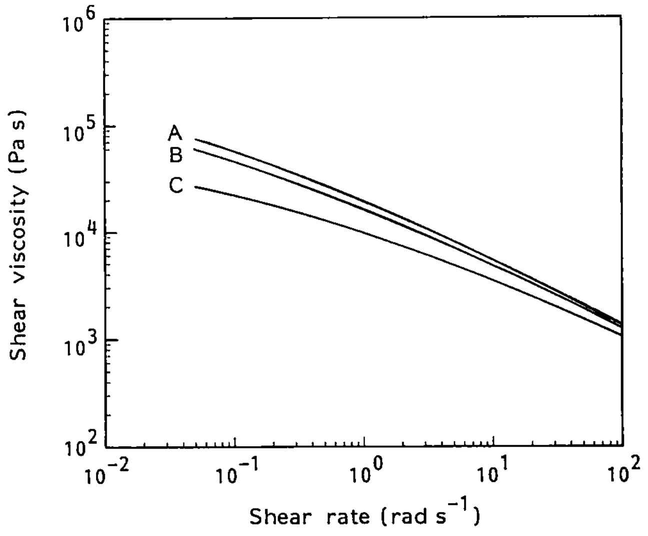

Figure 6 Shear viscosity curves of modified and unmodified LL4112. Lettering as in *Figure 3*

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* Pre-dried PE resin mixed with 0.1 wt% Dicup and 1.2 wt% VTMS and allowed to soak overnight and then extruded

during the grafting process. The peroxide-induced chain extension will enable the resins to be crosslinked more easily. Thus, a system of highly extended polymer chains will require much less silane crosslinking to form a highly crosslinked network structure.

Determination of crosslink density

The crosslink densities of the PEs listed in *Table 1* after silane crosslinking were determined. The number average molecular weight between crosslinks (M_c) of each sample was calculated from the stress elongation measurement carried out at 200°C by utilizing the following equation derived from the kinetic theory of rubber elasticity[13]:

$$M_c = dRT/F \times [L/L_u - (L_u/L)^2]$$

where d is the density (in g cm^{-3}) of the crosslinked sample (density of crosslinked sample at 200°C assumed equal to 0.73 that of the non-crosslinked sample at room temperature), R is the gas constant, T is the temperature (200°C), F is the tensile stress (2.0 kg cm^{-2}), L is the measured extended sample length (cm) and L_u is the measured unextended sample length (cm).

The plots of M_c *versus* curing period of the PEs are shown in *Figure 8*. The results clearly indicate that the PE type does play a strong role in the silane crosslinking of the resins.

It can be observed from *Figure 8* that LL1004 has the smallest M_c value (i.e. highest crosslink density) at very short curing period. This is followed by LD180. The Eltex A 4019, on the other hand, has a much higher M_c value at short curing period. Since the three PEs are of similar M_w, the result tends to suggest that the variation in the M_c value at short curing period is the consequence of the differences in chain extension during the silane grafting process. For the very short curing period, only a small fraction of the grafted silane was moisture-condensed to form crosslinks. The ability of the PE to form a crosslink network structure at this stage is therefore due to peroxide induced carbon–carbon chain extension during the silane grafting process. As mentioned above, the amount of peroxide used (0.1 wt%) was not enough to cause a crosslink network structure formation and no gel could be detected for all the samples prior to moisture curing. After a short curing period, the extra silane crosslinks effectively turn the chain-extended PE into a three-dimensional network structure – the crosslink density or M_c value of which must therefore reflect the degree of chain extension generated prior to the silane crosslinking. A high degree of peroxide induced chain extension during silane grafting means that the resin requires very little silane crosslinking and hence a short crosslinking period to generate a network with low M_c. On the other hand, if the resin has a low degree of peroxide induced chain extension or was degraded or scissioned during silane grafting, the small amount of silane crosslinking formed during the short curing period can only induce a crosslink network with low crosslink density or high M_c.

It can be seen from the plots of M_c *versus* curing period shown in *Figure 8* that a sharp turning point occurs at ~60 min curing period. This probably indicates the point where a uniform and stable network structure was formed. The steady decrease in M_c upon further moisture crosslinking therefore represents the progress of silane crosslinking which arises from the moisture condensation reactions between the grafted silane molecules within the solid sample. We can calculate the number of silane crosslinks formed per 20 000 number average molecular weight (M_n) of the network chain during a certain crosslinking period based on the decrease in the M_c value of the samples. The results are shown in *Table 4*. The number of silane crosslinks formed follows the order: LLDPE > LDPE > HDPE. This can be explained by the difference in the solid state microstructure of the various

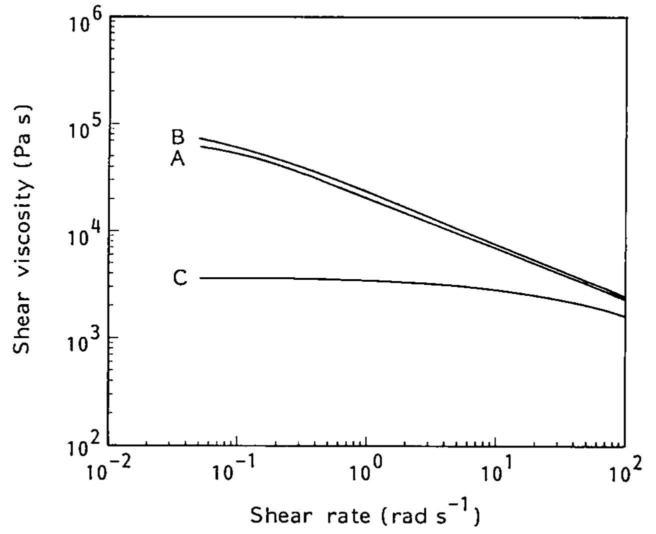

Figure 7 Shear viscosity curves of modified and unmodified Slp-1-0291. Lettering as in *Figure 3*

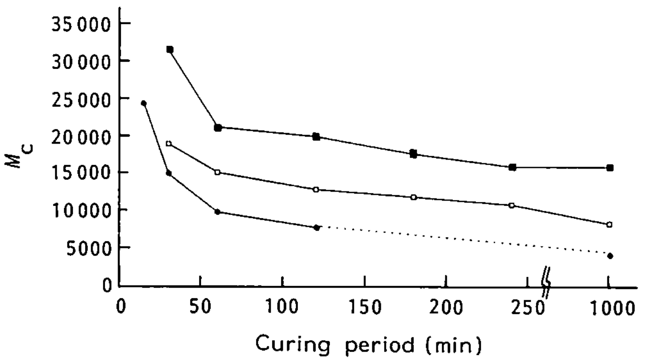

Figure 8 M_c *versus* curing period of various PE types: (■) Eltex A 4019; (□) LD180; (◆) LL1004

Table 3 Zero shear viscosity (Pa s) change of various PEs as a result of peroxide treatment and peroxide and silane treatment

Polyethylene type	HDPE	LDPE	LLDPE	LLDPE	LLDPE
Sample code	Eltex A 4019	LD180	LL1004	LL4112	Slp-1-0291
Unmodified resin	9500	14 000	3700	27 000	3700
Peroxide treated resin	33 000	45 000	60 000	61 000	72 000
Peroxide and silane treated resin	90 000	38 000	130 000	78 000	60 000

Table 4 Calculated number of silane crosslinks formed per 20 000 M_n of the network chain during different curing periods

Curing period (min)	Eltex A 4019	LD180	LL1004
60–120	0.006	0.56	1.59
60–1000	0.26	1.41	3.72

Figure 9 TEM micrograph of isothermally crystallized silane-grafted HDPE

Figure 10 TEM micrograph of isothermally crystallized silane-grafted LLDPE

PE types as well as the relatively low silane grafting level of the HDPE.

Effect of PE microstructure change on silane crosslinking

Crystallization of silane-grafted PE takes place prior to the moisture curing of the grafted silane molecules. The solid state microstructure of the crystallized polymer can affect silane crosslinking in two ways. It controls the moisture diffusion into the resin which is the rate determining step for moisture curing of the grafted silane. It also determines the distribution of the grafted silane molecules in the resin which affects the crosslink distribution. *Figures 9*, *10* and *11* are the TEM micrographs of silane-grafted HDPE, LLDPE and LDPE, respectively, which have been subjected to isothermal recrystallization prior to moisture curing. It can be seen that the silane-grafted LLDPE consists of short crystalline lamellae which distribute themselves in an almost continuous amorphous matrix. The silane-grafted HDPE, on the other hand, has much longer lamellae which are packed in stacks. The silane-grafted LDPE has a microstructure intermediate between that of the silane-grafted LLDPE and HDPE. The dramatic change in lamellae distribution and length of the silane-grafted LLDPE is likely the consequence of the higher degree of free radical induced carbon–carbon interaction between the polymer chains which interrupts chain folding and therefore lamella growth. The carbon–carbon interaction also renders lamella crystal growth initiated in a more random fashion resulting in a more 'diffuse' lamellar distribution. Gohil and Phillips[14] have also reported that crosslinking in PE produces a major increase in nucleation density. Besides the difference in silane grafting level, the big contrast in curing behaviour between silane-grafted LLDPE and HDPE is also due to the microstructural difference between the two resins. The former will be much more permeable to moisture due to the almost continuous amorphous region, while the latter will require a longer time for moisture to penetrate and facilitate the crosslinking reaction. The difference in the number of silane crosslinkings per 20 000 M_n of the network chains which occurs during the 60–120 min crosslinking period (*Table 4*) is therefore largely due to the different moisture diffusion rate of the various PEs and also the different amount of silane grafted onto the various PEs. Upon prolonged moisture-curing period (1000 min), all of the grafted silane molecules should be crosslinked. Since the amount of VTMS grafted onto the LL1004 and LD180 is about the same, we expect the number of silane crosslinks formed during the 60–1000 min curing period to be equal. *Table 4* shows that the number of silane crosslinks formed during the prolonged crosslink period differs by a factor of >2 between LD180 and LL1004. This suggests that a larger proportion of the silane molecules grafted onto the LD180 is not crosslinkable due to their physical separations upon crystallization. The microstructure of LL1004 may have contributed to the increased mobility of the grafted silane molecules in the amorphous phase and enhanced their chance of reacting with neighbouring silane molecules when cured at 80°C.

The very low number of silane crosslinks formed during prolonged moisture crosslinking of Eltex A 4019 is the result of the lower amount of grafted vinyl silane and also the lower mobility of the grafted silane. The final M_c value of the three PEs is also reflected in their gel contents which have been measured to be 64.8% (Eltex A 4019), 75.4% (LD180) and 81.8% (LL1104). It is also obvious that the final crosslink density of the fully moisture-crosslinked samples is very much determined

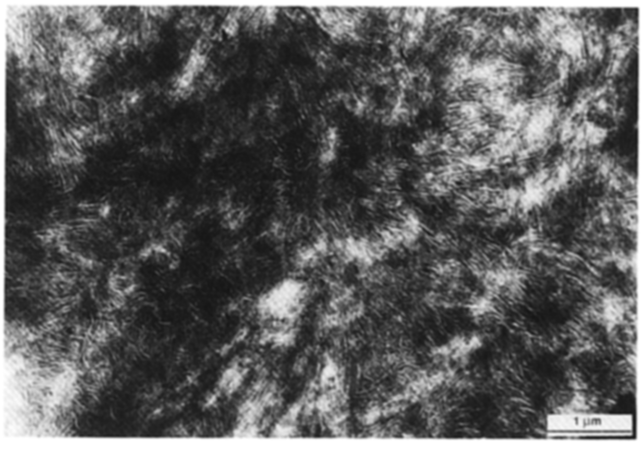

Figure 11 TEM micrograph of isothermally crystallized silane-grafted LDPE

by the carbon–carbon chain extension of the polymers. The relatively small decrease in M_c resulting from subsequent silane crosslinking indicates that the silane crosslinking only constitutes a small proportion of the network structure. Nevertheless, the silane crosslinking is essential for converting a highly chain-extended structure to a crosslinked structure. This is probably due to the fact that each silane molecule has three alkoxyl crosslinkable functional groups which will lead to the formation of polyfunctional branching points[10].

CONCLUSIONS

The process of extrusion grafting of VTMS onto the PE backbone will unavoidably alter the molecular structure of the PE resin. The molecular structure change varies according to PE type, with LLDPE exhibiting a much larger increase in free radical induced chain extension than LDPE or HDPE. The degree of chain extension of the PE as a result of the silane grafting process proves to be of vital importance to the rate of formation and also the final degree of crosslinking of the network structure upon moisture curing. The highly chain-extended LLDPE can be turned into a high crosslink density network without requiring much silane crosslinking. On the other hand, the less chain-extended HDPE or LDPE requires much more silane crosslinking, and therefore longer crosslinking times, to achieve a satisfactory network structure. The higher chain extension and also the intrinsic short chain branched structure of LLDPE mean that the resin crystallizes into a solid state structure of short crystalline lamellae highly dispersed in an almost continuous amorphous phase. Since grafted silane molecules only exist in the amorphous zone, a better silane crosslink distribution can be expected for the LLDPE. Furthermore, faster moisture diffusion into such a solid state structure will enable rapid moisture curing of the LLDPE resin. The relatively low level of silane grafting and free radical induced chain extension together with the tightly packed lamellar structure of HDPE render the resin difficult to crosslink rapidly to form a highly-crosslinked structure.

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