Crystallinity in chemically crosslinked low-density polyethylene: 5. Annealing behaviour of XLPE-2

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The annealing behaviour of lightly crosslinked low-density polyethylenes having various levels of extractable non-crosslinked polyethylene present has been studied. Three separate processes can be identified, which are (a) solid-state annealing, (b) recrystallization and (c) gel–sol separation in the molten state. Unlike linear or linear low-density polyethylene, annealing for long times does not result in crystallization of all crystallizable material; there is always a component present that crystallizes only on cooling if the annealing temperature is in excess of 90°C. The multiple melting peaks observed are not associated with macroscopic morphological features but arise largely from differences in the perfection of crystals or in the character of the amorphous phase in the vicinity of the crystal.

(Keywords: morphology; polyethylene; crosslinking; annealing; ageing)

INTRODUCTION

In the first two papers in this series the influence of crosslink density on the crystallinity[1], melting point[1] and crystallization kinetics[2] of low-density polyethylene, crosslinked using dicumyl peroxide, was reported. Morphological studies of the XLPE-2 system[3] and the variation of morphology with crosslink density[4] were discussed in the second two papers. It was noted that the dominant morphology for systems of low to moderate crosslink density was sheaflike. When crystallized at high to moderate supercooling, the sheaves were non-banded; however, crystallization at low supercooling produced banded sheaves. Differential scanning calorimetry showed that samples crystallized isothermally[1] tended to show multiple melting peaks. Morphological studies of samples stained with chlorosulphonic acid at a temperature between the two major melting peaks showed that both resulted from lamellae present in the same sheaf. Although the sheaves tended to be non-impinging, the lamellae between the sheaves were indistinguishable from those within the sheaves on the basis of the staining experiment.

The melting ranges of these crosslinked polymers are broad, usually beginning at 60°C and extending to 105°C. Since they contain, in addition to the crosslinked or gel network, a sizeable component of low-molecular-weight uncrosslinked molecules[1] usually referred to as the sol fraction, their crystallization behaviour is quite complex. The limited experimentation on annealing effects first reported[3] clearly demonstrated complex annealing behaviour. In this contribution a detailed study of annealing effects and the kinetics associated with those effects will be reported. It will be demonstrated that several melting peaks can be produced in slow cooling experiments and that one of those is associated with separation of the sol from the gel fraction in the melt over a narrow temperature range above the melting point.

EXPERIMENTAL

In this experiment, specimens were taken from commercially produced transmission cables of insulation wall thickness 12 to 22 mm. Because of different heat transfer media used[5] in the crosslinking process, specimens from different cables showed differences in the sol content, even though manufactured from the same base material (Union Carbide HFDE-4201). The characteristics of the specimens used are listed in *Table 1* (data for cable A1 being given for the section closest to the conductor (A1-8) and for the section furthest from the conductor (A1-1)).

Annealing experiments were carried out in Haake thermostatting baths with specimens sealed and in contact with a reference thermocouple. Differential scanning calorimetry was carried out using a Perkin–Elmer DSC2 or DSC7 instrument at a heating rate of 10°C min^{-1}, unless otherwise stated. Determination of sol content, swelling ratios, etc., were carried out exactly as described earlier[1].

High-temperature wide-angle X-ray diffraction studies were carried out using a Rigaku Geigerflex diffractometer with the specimen placed in a specially designed cell. In this cell, the film specimen was placed between beryllium windows. Temperature control was achieved by using cartridge heaters to offset liquid circulating, at a temperature slightly lower than that desired, through the interior channels of this aluminium-bodied cell. Dynamic experimentation was carried out using complete scans.

RESULTS

Two specific samples have been chosen for most of the data to be presented, since they differ considerably in sol

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Table 1

Specimen	Heat transfer medium	Insulation wall thickness (mm)	Sol fraction (wt %)	Peak melting temperature (°C)	Return to baseline (°C)	Crystallinity (%)
E1	Steam	23–24	14.2	101.7	105.6	49
C1	N_2 gas	20–21	13.2	104.6	108.5	53
A1-1	Liquid PEO	11–14	15.8	100.9	106.5	49
A1-8	Liquid PEO	11–14	28.0	103.3	108.2	51

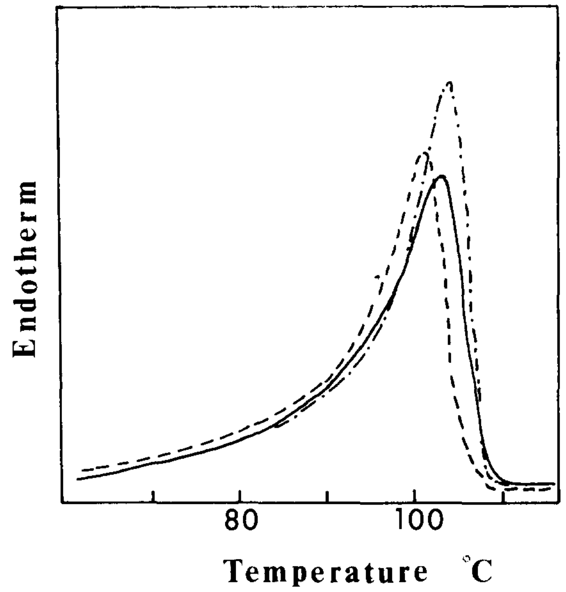

Figure 1 Typical d.s.c. scans of unannealed specimens: (———) A1-8; (-·-·-) C1; (– – –) E1

fraction. Specimens of cable A1 were taken from the section closest (A1-8) to the conductor, where a sol fraction of 28% occurred due to incomplete crosslinking[5]. Cable E1 has a relatively uniform sol fraction (14%); however, specimens were always taken adjacent to the conductor for consistency.

The base curves for all annealing experiments are the d.s.c. melting curves of the as-received quenched specimens (*Figure 1*). It can be seen that the curves are typical of low-density polyethylenes, showing a relatively broad curve peaking in the vicinity of 103°C and returning to the baseline between 105 and 108°C. It should, however, be noted that there are minor differences between specimens. Particularly significant is the temperature at which the curve returns to the baseline. This temperature tends to be slightly higher for specimens with higher sol fractions[5] and indicates an influence of the sol content on the melting temperatures of the best-formed crystals.

Annealing studies were carried out for various time intervals at temperatures of 90, 92, 95, 97, 100, 103, 105 and 107°C. The behaviour can conveniently be classified in terms of three regions: (a) 90–103°C, below the melting peak; (b) 103–107°C, above the melting peak but below the return-to-baseline temperature; and (c) above the return-to-baseline temperature.

First some general comments on the appearance of the d.s.c. thermogram and how it varies with annealing temperature. It should be recalled that the melting peak of the quenched original materials is over by 106–108°C and peaks in the vicinity of 100–105°C dependent on sol content. For the lowest annealing temperature used (92°C) only about 10% of the material has melted. Roughly speaking, therefore, polymers annealed below 100°C are being primarily solid-state annealed whereas for temperatures above 100°C much of the activity may be associated with crystallization of molten material.

General behaviour

The specimen (A1-8) taken from close to the conductor of cable A1 and having a sol fraction of 28% will be dealt with first. Annealing in the low-temperature range (*Figure 2a*) produces a pair of overlapping peaks together with a low-temperature shoulder. The double peak is believed to arise from two sources. First, there is material not molten at the annealing temperature, which was able to anneal, thereby producing an increase in the melting point and a narrowing of the melting range. Some of the molten material may also have recrystallized into a more stable form than that in which it was originally produced during quenching, thereby producing the bimodality. The remainder of the crystallizable material was unable to crystallize at the annealing temperature and crystallized on cooling, producing the low-temperature shoulder.

Curves similar to the one just described occur for annealing temperatures up to 100°C. However, the temperature of onset of the bimodal peak increases also, tending to be located at or close to the annealing temperature.

For specimens crystallized at 100°C and above, there tends to be one large peak with an onset temperature corresponding to the annealing temperature. Since an increasingly larger fraction of the material is unable to recrystallize at the annealing temperature, the low-temperature shoulder becomes a considerable peak resembling, in shape, the melting curve of a quenched sample, but having a narrower melting range (*Figure 2b*). It is possible that the large high-temperature peak is a pair of peaks which now overlap so closely that they cannot be resolved. Another, perhaps more likely, explanation is that crystals now being grown at the annealing temperature are able to anneal sufficiently rapidly that they achieve a melting point as high as that of pre-existing crystals which have simply annealed.

Specimens annealed at a temperature close to the return-to-baseline temperature show quite distinct behaviour (*Figure 2b*). A very sharp peak is observed generally close to 112°C together with a large peak at lower temperatures typical of material which could only crystallize on cooling from such a high annealing temperature. It has already been demonstrated[6] through studies of the gel fraction that this behaviour occurs only

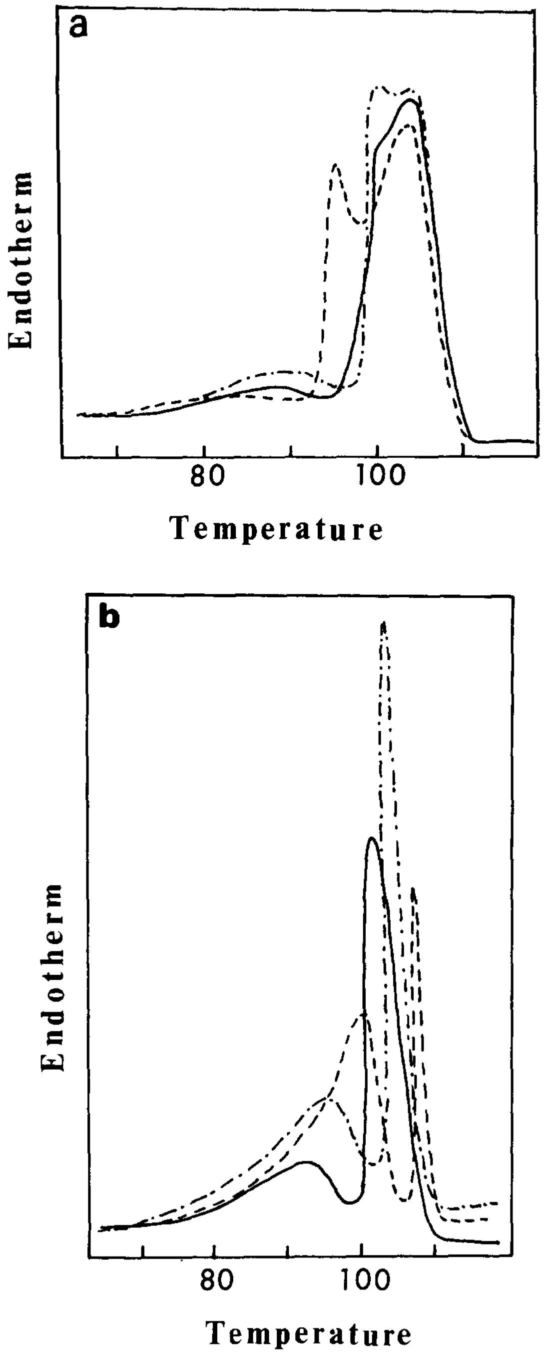

Figure 2 Melting curves of A1-8 after annealing for 2 h (a) at 92°C (---), 95°C (———) and (97°C) -·-·-) and (b) at 100°C (———), 103°C (-·-·-) and 107°C (---)

when sol is present. It was recently demonstrated[7] that it may be directly attributable to the production of separate sol crystals due to melt immiscibility of the sol and gel components.

Effect of sol content on annealing at 100°C and above

Studies of specimens having different sol levels have been enlightening. Here we will compare the two specimens referred to earlier: (a) cable A1 with 28 % sol fraction and the subject of the general review; and (b) cable E1 having 14% sol fraction. Since major differences are observed only for high temperatures of annealing, the temperature range over which comparisons will be made is restricted to 100°C and above. Comparative curves are presented in *Figure 3* for 60 min annealing, at 100, 103 and 107°C for the two materials. At 100°C specimen E1, having less sol, exhibits a larger peak, whereas for higher temperatures cable A1 shows the largest peak. The return-to-baseline temperatures of the two materials are 105.6 (E1) and 108.2°C (A1). Annealing at 107°C produces a minor peak for sample E1, yet a substantial peak for sample A1. Clearly the size of the peak depends on both sol fraction and the fraction of non-molten material present at the annealing temperature. However, it should be remembered that the d.s.c. scans are carried out at 10°C min^{-1} and the temperature data are dynamic. X-ray diffraction studies show both specimens to be completely molten at 107°C.

Similar differences in annealing behaviour can be observed for specimens of different sol fractions taken from cable A1. Results for 60 min annealing at 100, 103 and 107°C can be seen in *Figure 4* for the specimen previously considered (28 % sol) together with a specimen taken from the fully cured part of the cable close to the outer shield (15.8 % sol). Although, comparatively, the general trend in behaviour for this 15.8 % sol material resembles that of the 14 % sol material from cable E1, there are significant differences. In particular, the high-

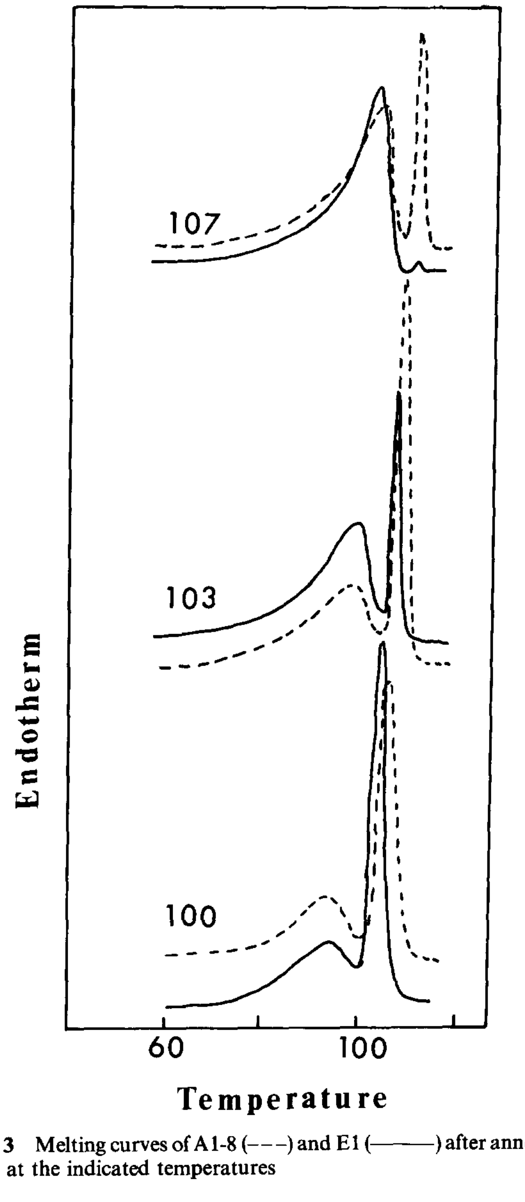

Figure 3 Melting curves of A1-8 (---) and E1 (———) after annealing for 1 h at the indicated temperatures

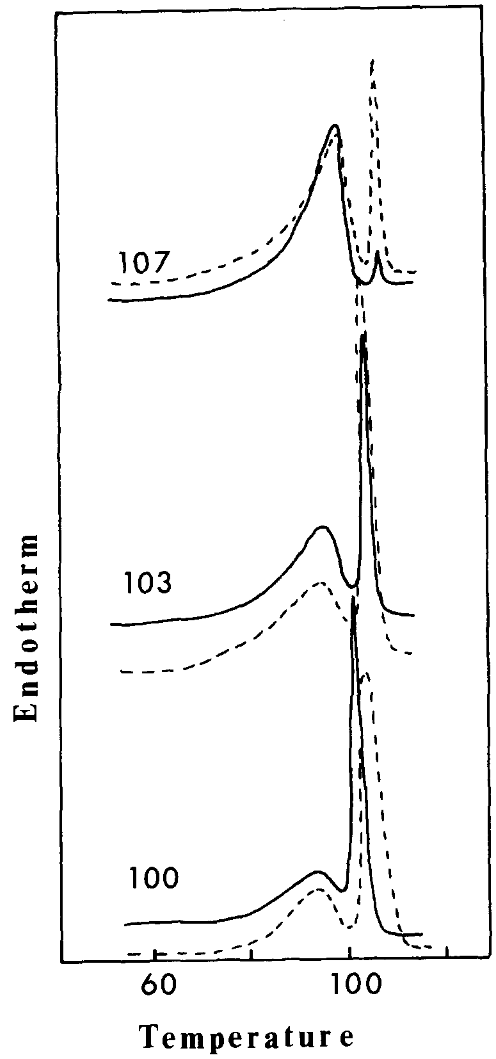

Figure 4 Melting curves of A1-8 (28% sol) (– – –) and A1-1 (15.8% sol) (———) after annealing for 1 h at the indicated temperatures

temperature peak of E1 is larger for a 100°C anneal but significantly lower for higher-temperature annealings. This is a result of the slightly different shape of the original melting curve. Specimens from cable E1 tend to have a narrower peak and a somewhat higher onset of melting temperature. Cable E1 was steam-cured at a different temperature from cable A1, which was subjected to an experimental heat transfer method[5]. Both were quenched in water after manufacture and so differences in their melting curves may also reflect their different cooling rates as well as differences in sol fraction. Specimens from both cables melted and quenched in water to give an identical thermal history have more similar melting curves, but still differ because of their different sol levels.

Effect of cooling rate on high-temperature annealing results

The character of the process giving rise to the sharp high-temperature peak at high annealing temperatures has been investigated through the use of different cooling rates from the annealing temperature. Materials annealed at both 97 and 107°C were studied for comparison. Data are presented in *Figures 5* and *6*, the curves for the 97°C anneal not being unusual. The lower-temperature peak of the two occurs at higher temperatures and merges with a higher one, for the case of the slow cool. Material has had time to crystallize and anneal at higher-than-normal temperature as the sample was cooling. For the 107°C anneal, the small high-temperature peak is higher for the liquid-nitrogen quench and does not merge with the lower-temperature peak as in the slowly cooled sample. If the material giving rise to this peak were crystalline at the annealing temperature then the peak should have merged with the low-temperature peak, since similar material would have crystallized during slow cooling. Also, a quench cool should not have influenced its height. Both observations can be explained in terms of a liquid–liquid

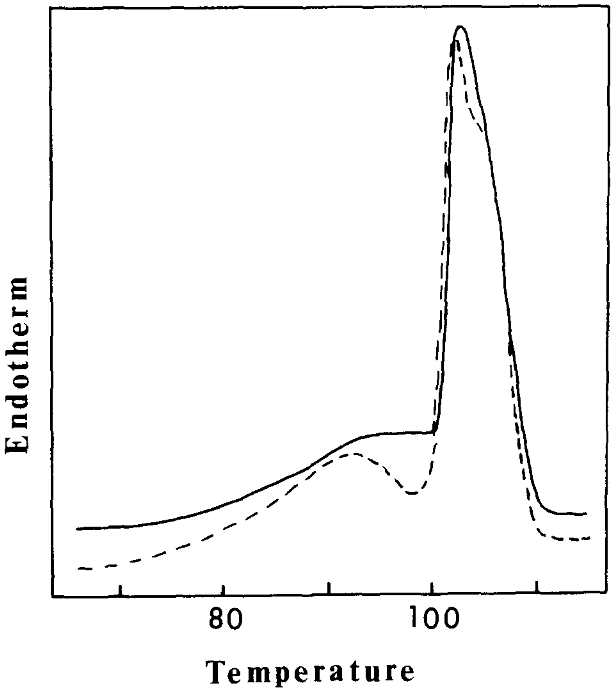

Figure 5 Melting curves of A1-8 cooled to ambient temperature at 0.2°C min^{-1} (– – –) and quenched (———) after annealing at 97°C for 30 min

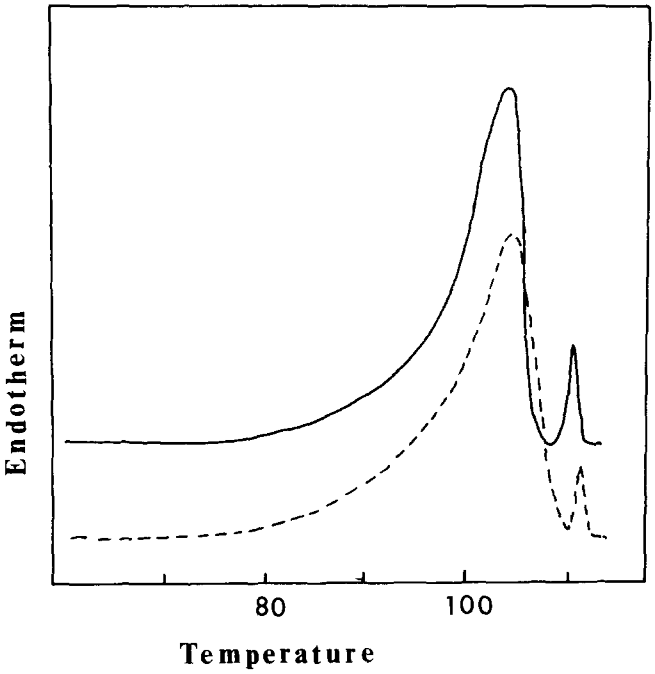

Figure 6 Melting curves of A1-8 cooled to ambient temperature at 0.2°C min^{-1} (– – –) and quenched (———) after annealing at 107°C for 30 min

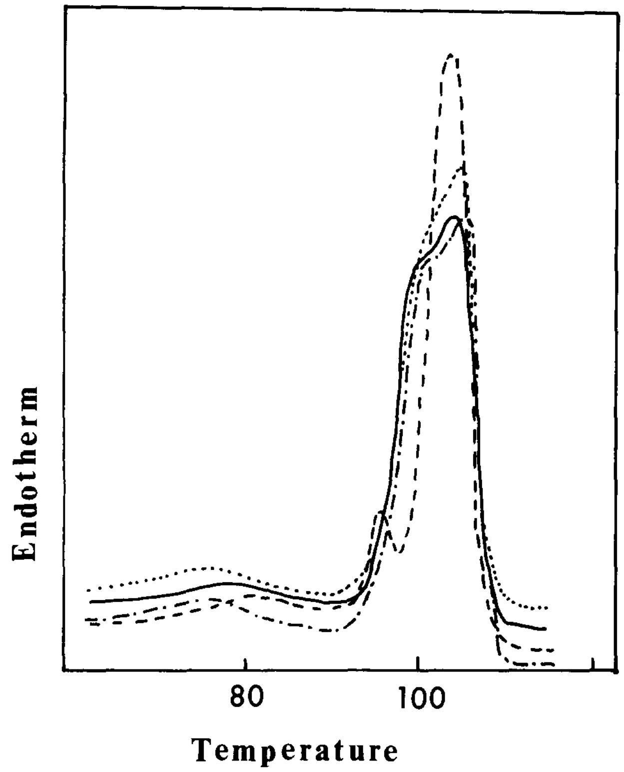

Figure 7 Melting curves of E1 after annealing at 90°C for 8 days (– – –), 16 days (———), 24 days (–·–·–) and 60 days (·····)

separation of sol from gel at 107°C (ref. 8). The separated molten sol would crystallize on cooling but would have a higher melting point because of its more perfect, possibly thicker, crystals. Cooling slowly would permit the molten sol to remix into the molten gel if a lower critical solubility limit existed and was reached during slow cooling. This would result in a diminution of the amount of sol crystallizing alone. Annealing at a temperature of 110°C results in a cruve typical of quenched material, indicating that the miscibility gap is narrow, occupying only a few degrees in the vicinity of 105–110°C. Holding a specimen at 107°C after heating to 110°C also produces a melting curve typical of quenched material, although a minute peak is produced after one week at 107°C.

The above observations indicate that the separation of sol from gel occurs on melting of the crystals and is retained if the sample temperature is not raised by more than 1–2°C. Such an observation would lead to the inference that the sol was already separated from the gel in at least some of the crystals.

Effect of time on high-temperature annealing

It was noted early in our studies that the annealing effects discussed above were time-dependent. In order to study this effect further and to quantify the rate of appearance of these changes, experiments were carried out as a function of annealing time. Results of annealing at 90°C of cable E1 (14% sol) followed by quenching to ambient temperature are shown in *Figure 7*. The annealing times here were 8, 16, 24 and 60 days. It is clear that a steady state has been achieved by 16 days for this sample. For the eight-day sample it can be seen that there is one large single peak centred at 375 K (102°C) together with a very small peak at 368 K (95°C). For times of 16 days and greater, the curve is always bimodal with the larger peak of the two situated at 377 K (104°C).

For specimens crystallized at 90°C after being held for various times at 110°C, the behaviour is similar. When the dwell time at 110°C was increased to several hours prior to crystallization at 90°C, an additional effect was observed. Data are shown in *Figure 8* for 4 and 8 days at 110°C followed by four days at 90°C. Again double peaks occur; however, in this case it can be seen by comparison with *Figure 7* that effects occur at twice the rate observed for direct crystallization at 90°C. One more effect was detected. If the high-temperature baseline is observed (*Figure 9*) for quenching after holding at 110°C, it will be seen that a small peak occurs in the region of 385 K (112°C). This region is characteristic of the melting point of sol crystals. Results for specimens held at 110°C for periods of up to eight days and then quenched to ambient temperature also show the same small peaks (*Figure 9*). The magnitude of this small peak increased with dwell time at 110°C. Since it is common to specimens crystallized at 90°C as well as to those that were quenched, it has to result from something that has occurred at 110°C in the melt as well as from sol crystals. As mentioned earlier, there are two ways in which this could occur: (a) the sol molecules actually crystallize at 110°C; or (b) the sol molecules diffuse together forming droplets at 110°C and crystallize on cooling.

DISCUSSION

In this paper we will discuss only the high-temperature range of 90°C and above, i.e. within the melting region. Low-temperature annealing from 60°C upwards results in what is essentially retarded crystallization of material that could not crystallize in the original specimen preparation. This behaviour has been reported in another publication[7].

The crosslinked low-density polyethylene considered

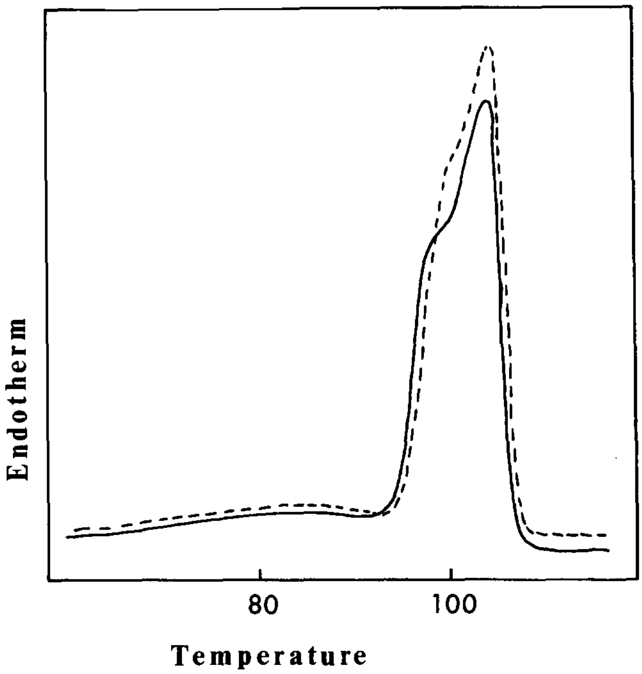

Figure 8 Melting curves of E1 after holding at 110°C for 4 days (———) and 8 days (– – –) followed by 4 days at 90°C

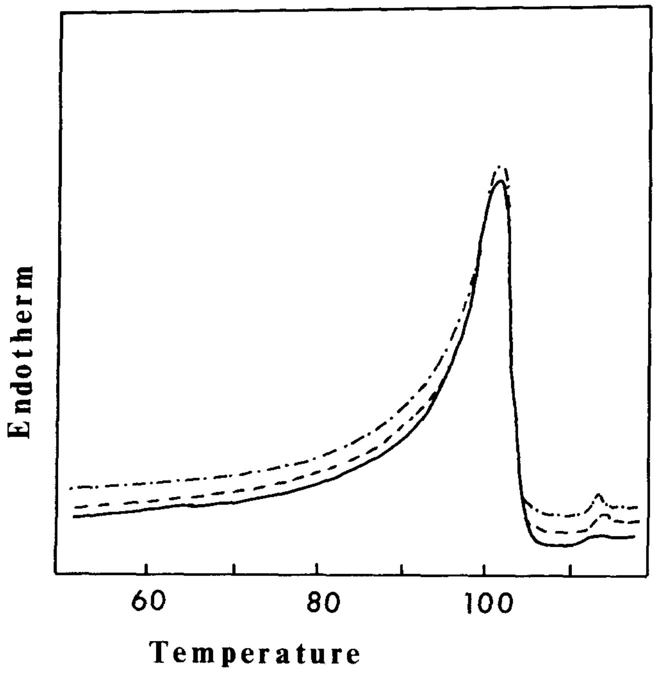

Figure 9 Melting curves of E1 quenched to ambient temperature after holding at 110°C for 1 day (———), 4 days (– – –) and 8 days (–·–·–)

here, and earlier[1–4], has 16 branches per 1000 carbon atoms and only 0.4 crosslinks per 1000 carbon atoms. It can therefore be expected that the lamellar thickness will be controlled by the branching concentration. For such an amount of branching, most common thickening processes are suppressed. Solid-state annealing mechanisms involving the perfecting of crystals and the relaxation of stresses associated with the gel network or the surface structure are therefore to be expected. The extractable fraction is slightly less branched than the original uncrosslinked material and has a lower molecular weight, being comprised essentially of molecules from the lower end of the molecular-weight distribution.

The initial state of the polymer, prior to annealing, is not well understood in terms of the distribution of sol molecules between crystals. It has been established that the isolated gel crystallizes in regime III and the isolated sol in regime II. Kinetic studies showed that the unextracted polymer exhibited mixed regime growth[2]. No significant changes in morphology exist between the gel and its unextracted analogue. Both are sheaflike and there is no evidence for a separate sol morphology in the unextracted material, except for crystallization at the highest temperatures, where some evidence for small stacks of sol crystals exist, being no more than a few hundred angstroms in size. For the initial material considered here, all the crystallizable sol and gel is believed to be present in the same sheaves.

On a lamellar level, during crystallization, there is no evidence available on how a molecule (or section of a molecule) which crystallizes in a particular regime will react to a nucleus generated by another regime. There should be no major differences between a sol molecule or a section of gel between crosslinks in their likelihood of addition to a preformed niche, except that caused by their differences in mobility. The existence of a particular growth regime is directly related to the relative values of the rates of nucleation and spreading. The rate of deposition by spreading of sol molecules is likely to be higher than that of gel sections because of their ability to reptate. There is also the additional problem of whether or not a crosslink could be incorporated into a crystal. The answer to this question has to depend on the structure of the crosslink. Chemical crosslinking of polyethylene results in the production of a single carbon–carbon bond joining two chains. Such a crosslink may be incorporated into a crystal of crosslinked linear polyethylene[9]; however, in crosslinked low-density polyethylene the situation is complicated. Tertiary carbons, such as those found at branch points, are more reactive to free radicals than are secondary carbons (e.g. methylene groups) and so the crosslink junction points may be quaternary carbons. In the small space of a crosslink, five or six subchains may come together. It seems unlikely that such a large defect would be incorporated into the crystal. Should such a unit be deposited on the surface it would need to be rejected, thereby temporarily poisoning a growth site. It seems likely, therefore, that the sol molecules would preferentially attach to a crystal regardless of how the nucleus was formed. This would lead to a segregation of the sol molecules from the gel sections on a microscale in any crystal. Since the chemical potential for mixing of polyethylene molecules of different lengths is not very great, it seems likely that a severe sol concentration depletion would be generated, leading to preferential gel section crystallization until the sol concentration were restored by the diffusion process.

Hence, with the exception of rapid quenching conditions, where the mobility of the sol molecules would be severely reduced, a microscale separation of sol molecules from gel sections within each crystal seems likely. Therefore, when annealing mechanisms are discussed it may be appropriate to consider the likely effects on both unsegregated and segregated crystals. It should also be remembered that the melting curves of the initial materials were broad, with no evidence of multiple melting peaks.

The low-density polyethylene resin contained 16 branches per 1000 carbon atoms, i.e. on average about 60 methylene groups between branch points. There will, of course, be a considerable distribution spectrum of subchain sections present. The addition of the crosslinks barely changes the concentration of microstructural defects to be rejected by the crystal growth process. It seems likely therefore that the lamellar thickness will not be affected in any significant manner, if it is assumed that the branch points are rejected from the crystal. The major differences to be expected between regions of crystals comprising sol molecules and regions comprising gel sections are in the fold surface structure of each region and the way in which they exist in the amorphous phase. Sol molecules would be expected to be relaxed and not subjected to as much frozen-in strain as gel subchains. Since sol molecules have fewer branch points than the original material[10], it seems that the more highly branched chains are preferentially incorporated into the network.

Since annealing behaviour is usually dependent on the difference between the melting and annealing temperatures, it is necessary to consider the likely melting temperatures of sol regions and gel regions. The equation is, of course, well known[11]:

$$T_m = T_m^\circ\left(1 - \frac{2\sigma_e}{\Delta H_f l}\right)$$

Since the lamellar thickness l will be essentially constant, as it is determined by the high degree of branching in the original polyethylene, as will the equilibrium melting point T_m°, only the heat of fusion ΔH_f and the fold surface free energy σ_e may vary in a significant manner. Studies[1] have shown that the latent heat of fusion after crosslinking remains at the value typical of the uncrosslinked polymer. Major differences might be expected in the values of σ_e characteristic of the two regions. The surface structure of sol molecular regions would be comprised largely of adjacent re-entry folds, many containing branch points, together with some tie-chain material. Since the molecular weight is still fairly high, end-groups (cilia) probably are a very minor component, but would be totally absent from gel sections. The concentration of crosslink points is only 3% of the concentration of branch points, so a large change in surface structure is unlikely between the sol and the gel regions. The important difference will lie in the fact that the gel sections are part of the rubber elastic network. There are likely to be fluctuations in the crosslink density from point to point and probably different amounts of amorphous chain orientation in different regions. This is likely to result in a larger amount of what is now becoming known as 'rigid amorphous phase' in the interfacial regions.

As temperature is raised the rubber elastic network will become more mobile and any sections of random subchain will tend to contract. However, sections of chain not able to crystallize during the initial quench preparation may acquire enough mobility to be able to crystallize. The latter behaviour is not unique to XLPE and is simply an example of retarded crystallization. It does occur here when a temperature of 60°C is achieved and prior to any significant melting. An increased degree of crystallinity is generated.

It is likely that gel regions begin to anneal first. The melting point of pure sol is 110–112°C and its melting curve is quite sharp[1], whereas the gel gives rise to a broad curve which peaks at 103–105°C. Since the possibility of significant lamellar thickening is remote for both regions because of the branch content, annealing processes activated are probably related to perfection of crystals through elimination of dislocations, or by changes in surface free energy caused by changes in surface structure and/or interactions with the gel network. Only the latter will be unique to the gel sections, all others being common, although they may occur with differing degrees of intensity in the two regions. This observation seems to be generally correct since both the unextracted polymer and the gel, when studied separately, show essentially the same behaviour as long as the annealing temperature is less than ~ 103°C. The phenomenology is unchanged by removing the sol for such annealing conditions, identical numbers of and general shapes of multiple melting curves being common. There are small differences in the temperatures of the peaks produced by annealing at the same temperature and small differences in the rates at which the peaks are generated. For annealings at temperatures up to 97°C the gel tends to produce the new peak more rapidly and it approaches its ultimate temperature location more rapidly. It appears that the effect of increasing temperature on the amorphous sections of the gel network is to enhance the annealing process without causing substantial changes in the mechanisms.

Two processes are generally operating. Material that melts on approach to and at the annealing temperature recrystallizes, giving rise to the new lower-temperature peak of *Figure 2a*. Material not molten anneals through a perfecting or surface structure change mechanism and its melting point is increased. Some of the melted material cannot crystallize at the annealing temperature, but does so on cooling, giving rise to the low-temperature hump of *Figures 2a* and *2b*. The latter behaviour is shown by all fractions, even isolated sol[3], and is caused by highly branched material. The magnitude of this low-temperature hump is increased as the annealing temperature is increased, being of considerable magnitude for annealing temperatures in excess of 100°C. For the gel it becomes the only melting peak for an annealing temperature of 105°C and above.

For the unextracted material, when annealing temperatures of 100°C and above are used, the high-temperature melting peak sharpens and moves to higher temperatures, decreasing in magnitude in the process (*Figure 2b*). As is shown in a separate publication[8] this is caused by the separation of molten sol from gel and its subsequent separate crystallization on cooling, if the quench rate is sufficiently fast. At 100°C the peak is probably caused by a combination of annealing of crystals containing sol molecules and gel sections of low branching, together with the partial melt separation of material from mixed crystals. At 103°C the increased sharpness is probably due to the enhanced annealing temperature resulting in predominantly sol crystals remaining. Annealing at 107°C occurred essentially in the molten state and both peaks were produced on quenching of two melt-separated phases[8].

It is suggested that, on melting, instead of remixing, the segregated sol microdroplets coalesce because of an immiscibility gap in the sol–gel phase diagram. Treating the kinetics of growth of the high-temperature peak at 107°C using an Avrami analysis led to an exponent of 0.28 (ref. 8). Such a value of the exponent is not predicted by any models and indicates that the growth process is not one of conventional nucleation. However, since the process is very slow, when the polymer is cooled rather than heated as indicated by *Figure 9*, for example, it is clear that the separation is enhanced if the polymer had previously crystallized. This suggests that some microseparation occurs during the quench crystallization but not on such a scale as to generate separate melting peaks.

CONCLUSIONS

Crosslinked low-density polyethylene shows complicated annealing behaviour, involving at least three distinct processes.

Unique to the crosslinked system is a liquid–liquid separation process, which occurs in a narrow range of temperature close to and above the melting peak.

As the annealing temperature is raised, an increasingly larger fraction of the material is unable to recrystallize.

Other than the melt separation process, annealing mechanisms are not changed by this level of crosslinking. They do, however, occur at somewhat more rapid rates in the gel than in the unextracted material, suggesting that the gel network exerts an accelerating effect.

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