Slow crack growth of blends of high density and linear low density polyethylenes as influenced by morphology

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A high density polyethylene homopolymer was blended with a linear low density ethylene hexene copolymer over the composition range of 0–100%. The resistance to slow crack growth was measured by a notched tensile test under constant load at 42, 60 and 80°C. The morphology was varied by slow cooling, quenching and annealing at 129°C for 24 h. Whereas the resistance to slow crack growth increased by a factor of 10^6 over the composition range, the differences in morphology could only change the resistance to slow crack growth at the most by a factor of ~ 3. The effect of temperature was independent of the effect of composition on slow crack growth. The effects of molecular and morphological structure are discussed.

(Keywords: slow crack growth; blends; polyethylene)

INTRODUCTION

The slow crack growth behaviour of blends of a high density polyethylene (HDPE) homopolymer and a linear low density polyethylene (LLDPE) copolymer was investigated by Zhou *et al.*[1]. The resistance to slow crack growth (SCG) as measured by the time to fail under a constant load was 10^6 greater for the pure LLDPE than for the HDPE. It was found that when the content of LLDPE in the blend exceeded 50%, the resistance to SCG increased very rapidly. A small difference in the resistance to SCG was found between the quenched and slow cooled state when compared to the change with respect to composition. It was postulated that the large increase in resistance to SCG when the content of LLDPE exceeded 50% was associated with the formation of a continuous network formed by branched tie molecules and the crystals which anchored them. The d.s.c. data did not indicate that HDPE and LLDPE were separated after solidification. In order to improve our understanding of the relationship between blending and SCG additional work was carried out.

In this paper these same blends were studied. The effect of the morphology was further investigated by annealing below the melting point in order to partition the crystals according to their thickness. Also, the effect of temperature on the rate of SCG was investigated in order to determine how the activation energy varied with composition. It was found that by d.s.c. that the crystals could be partitioned but the effect on SCG was intermediate between that of the quenched and the slow cooled state. The activation energy did not vary with composition.

EXPERIMENTAL

The blends consisted of a linear homopolymer, Marlex 6060 ($M_w = 66\,800$; $M_n = 19\,900$) and an ethylene–hexene copolymer, TR418 ($M_w = 192\,000$; $M_n = 12\,000$, with 4.8 butyl branches/1000 C; Phillips Petroleum resins). The compositions of the blends were 0, 25, 50, 75 and 100% TR418.

The pellets were first mixed manually and then blended in a twin co-rotation screw extruder (Werner and Pfleiderer 25K-30, $L/D = 29$) at a feed rate of 9.5 kg h^{-1}. The screw speed was 150 rev min^{-1}; the temperature in the screw ranged from 140 to 210°C; the head pressure was 1.4–2.2 MPa. The material was put through the blender twice.

The blends were compression moulded into 10 mm thick plaques. Plaques were cooled from the melt at rates of 0.5 and 40°C min^{-1} and these two states of the material will be designated as slowly cooled (SC) and quenched (Q). The third state, which was produced by slowly cooling from the melt to 129°C and kept for 24 h and then cooled to room temperature at a rate of $\sim$2°C min^{-1}, is designated as the annealed (AN) condition. The melting points were measured with a DuPont DSC.

The specimens for the SCG test were 25 × 10 mm in cross-section with a 3.5 mm deep notch which was produced by slowly pressing a razor blade into the specimen. The notch length was 25 mm and the specimen had two 1 mm deep side grooves. The constant load tensile test was conducted under a 3 MPa stress at 42, 60 and 80°C ± 0.5°C for all blends except for pure TR418. Since the pure TR418 has such a long time to failure it was tested at 80°C and 2.4 MPa where its time to failure was 1.7×10^6 min. The failure time, after being adjusted

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to 42°C and 3 MPa by the equation used in reference 1, has the value of 7.2×10^7 min. The notch opening displacement was measured with an optical microscope by looking directly into the root of the notch. The times to failure were averages from duplicate tests with a scatter of ±10%.

RESULTS

The d.s.c. curves for the quenched and slow cooled states are shown in *Figure 1*. Since the melting point of a crystal is a function of its thickness the d.s.c. curves represent the distribution of crystals with respect to thickness. The general character of the d.s.c. curves is the same for the quenched and slow cooled states for all compositions. *Figure 2* shows the d.s.c. curves for the state annealed at 129°C where two regions of crystallinity are indicated. The annealing produced a definite partition between small crystals and large crystals except for the composition with 100% homopolymer. The partition is caused by the distribution of the branches in the copolymer. Some molecules in the copolymer have little or no branches so that thick crystals may form. Essentially, the distance between branches determines the crystal thickness.

The SCG behaviour is shown in *Figure 3* where crack opening displacement is plotted against time. From these curves the time for complete failure and the time to initiate fracture can be obtained. The time to initiate fracture corresponds to the time when the curves begin to accelerate. Previous work by Brown *et al.*[2] has shown that the time to initiate fracture is always related to the time for complete failure. *Figure 4* shows time to failure *versus* composition for the quenched, slow cooled

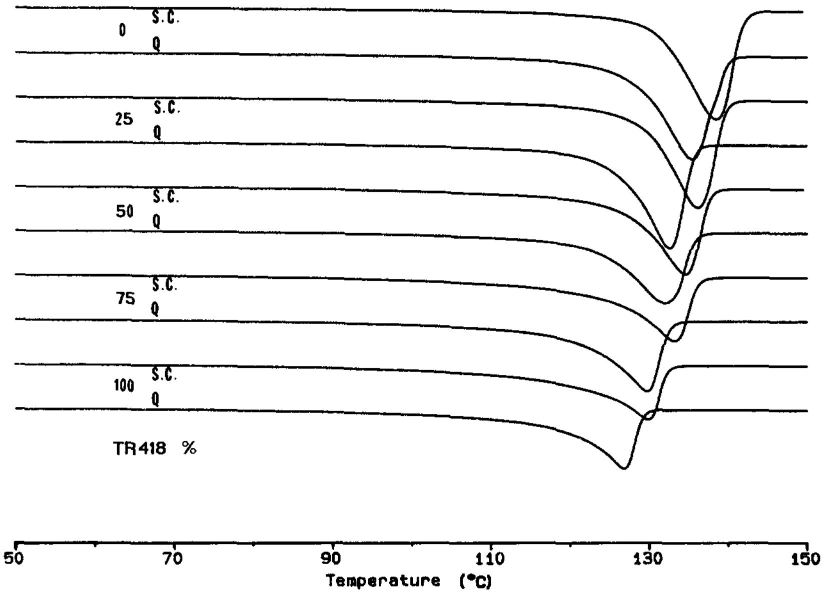

Figure 1 D.s.c. heating curves for slow cooled (SC) and quenched (Q) blends of various compositions. Cooling rate 5°C min^{-1}

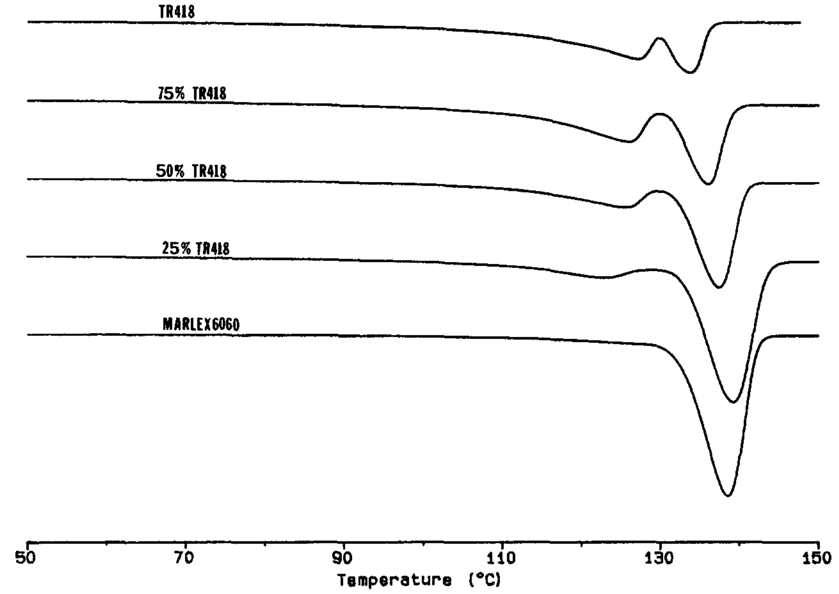

Figure 2 As for *Figure 1* for blends annealed at 129°C for 24 h and cooled at a rate of 2°C min^{-1}

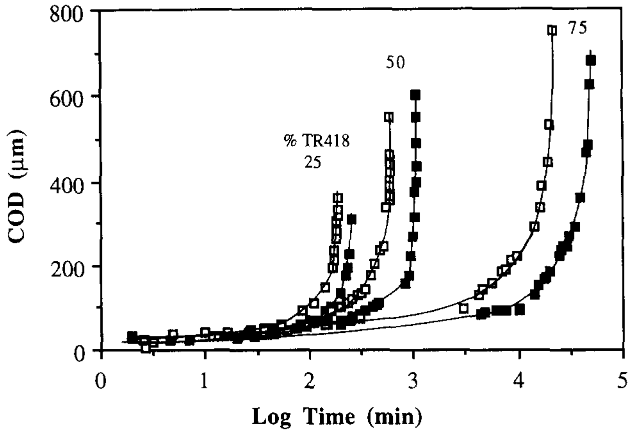

Figure 3 Crack opening displacement (COD) *versus* time at 42°C, 3 MPa, 3.5 mm notch for blends of different compositions: (□) slow cooled state; (■) quenched state

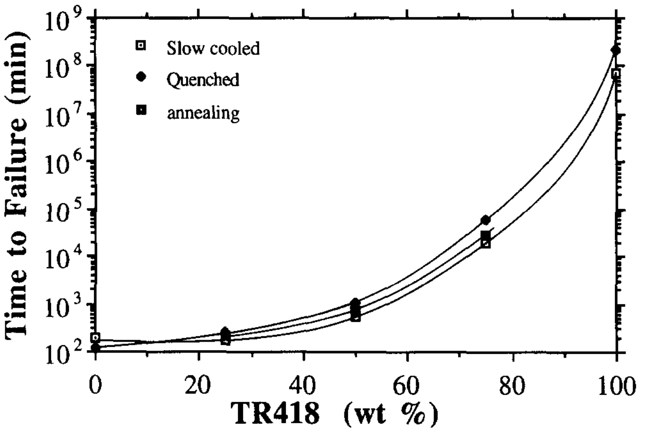

Figure 4 Time for failure *versus* weight per cent TR418 for different thermal histories tested at 42°C, 3 MPa and 3.5 mm notch

and annealed states. A most important point is that the annealed state is intermediate with respect to the quenched and slow cooled states. Although the annealing partitioned the structure with respect to crystal thickness, its failure time was between the most rapidly and most slowly cooled states. *Figure 5* shows the ratio of failure times for the quenched and slow cooled state. For the 100% homopolymer the failure time is greater for the slow cooled than for the quenched state. When the copolymer is added the quenched states have a longer failure time than the slow cooled state where the difference increases with the amount of copolymer. Time to failure *versus* composition is shown for the various temperatures of 42, 60 and 80°C. The same general trend with composition is shown at all temperatures where the rapid increase in failure time occurs for compositions with >50% copolymer. Using the data in *Figure 6*, the time to failure is plotted against $1/T$ in *Figure 7*. From these slopes an activation energy may be obtained. Within the accuracy of the experiment, the slopes are nearly independent of composition. The average value of the activation energy is ~100 kJ mol^{-1}.

DISCUSSION

The most important result is that the thickness of the crystals and the distribution of crystal thicknesses has a much smaller effect on SCG compared to the effect of composition (*Figure 4*). The extreme effects of morphology are associated with the slow cooled and quenched state. As shown in *Figure 5*, the ratio of times to failure for the quenched relative to the slow cooled state, increases from ~0.6 at 0% TR418 to ~3 for 100% TR418. Over this same composition range the failure times ranges from 10^2 to 10^8 min with the biggest change taking place for compositions >50% TR418.

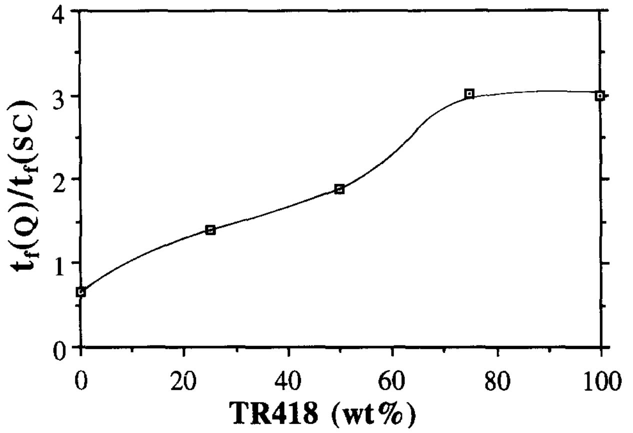

Figure 5 Ratio of time to failure of Q state over time to failure of SC state *versus* weight per cent TR418

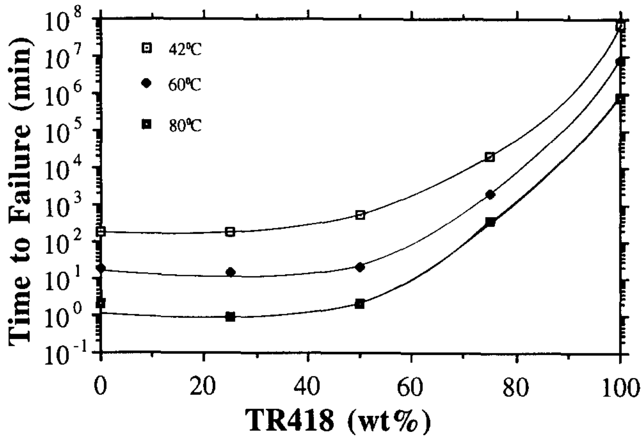

Figure 6 Same as for *Figure 4* for SC state at 42, 60 and 80°C

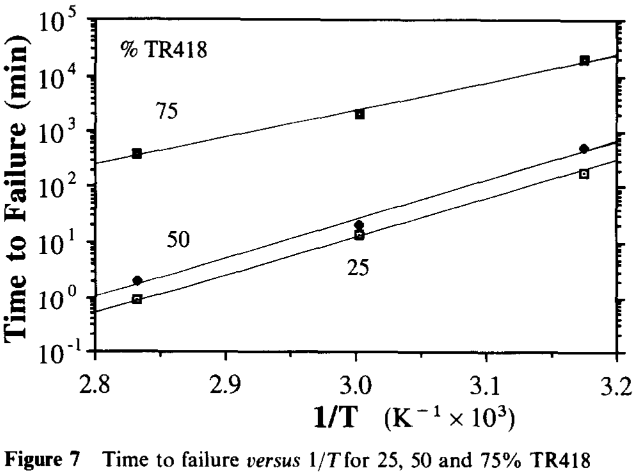

Figure 7 Time to failure *versus* $1/T$ for 25, 50 and 75% TR418

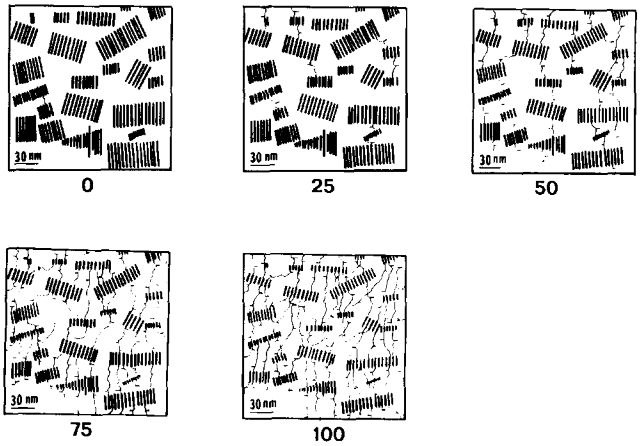

Figure 8 Quantitative rendition of the crystal–tie molecule network. Parallel lines represent crystal. Tie molecules density calculated by equation (2). Remaining area is amorphous

As shown in *Figures 6* and *7*, the dependence of the failure time for SCG on composition is about the same over the range of testing temperatures from 42 to 80°C. The temperature basically accelerates the rate of failure but only slightly modifies the compositional effect. Previous work by Lu *et al.*[3] showed that the effect of testing temperature is somewhat modified by the distribution of crystal thickness, but this effect is small compared to the effect of the composition. The fact that the activation energy does not vary appreciably with composition indicates that the fundamental process of disentanglement which produces fracture, is independent of composition. Huang and Brown[4] showed the activation energy was independent of branch density.

The question to be answered is how does the morphological and molecular structure account for the dependence of failure time on composition (*Figure 4*). The important differences between the molecular structure of the homopolymer and the copolymer are the difference in $M_w = 66\,800$ *versus* 192 000 and the existence of an average of 4.8 butyl branches/1000 C on the copolymer. As shown previously by Huang and Brown[5], the failure time increases with M_w. This effect is attributed to the increase in tie molecules with increasing molecular weight. The tie molecules join the crystals together to form a network. The short chain branches serve two purposes: (1) they reduce the average thickness of the crystals and thereby reduce the average distance between crystals so that the probability of forming a tie molecule is increased as pointed out by Huang and Brown[6]; and (2) the short chain branches inhibit the processes of disentanglement because a branched molecule is more difficult to disentangle than smooth molecules.

The question now arises as to why the failure time increases rapidly for compositions of >50% TR418. *Figure 8* was constructed to *quantitatively* conform to the following experimental and theoretical observations: (1) the relative volumes of the crystalline and amorphous regions are based on the density; (2) the average thickness and distribution of crystal thickness is derived from the d.s.c. data and calculated from the equation proposed by Illers and Hendus[7]:

$$L_c = \frac{0.62 \times 414}{(414 - T_M)} \tag{1}$$

where T_M is the melting point as obtained from the d.s.c. curves; (3) the number of molecules joining the crystals, the tie molecules, was obtained from the equation by Huang and Brown[6]:

$$P = \frac{\int_L^\infty r^2 \exp(-b^2 r^2)\,\mathrm{d}r}{3\int_0^\infty r^2 \exp(-b^2 r^2)\,\mathrm{d}r} \tag{2}$$

where P is the probability of forming a tie molecule, r is the end-to-end distance of the random coil in the melt, $b^2 = (3/2\bar{r}^2)$ where $\bar{r}$ is the root mean square of the end-to-end distance and $L = 2L_c + L_a$ where L_c is the crystal thickness and L_a is the thickness of the amorphous layer. The factor 3 in the denominator of equation (2) is based on the geometry of the lamella crystal, since a tie molecule forms along one of the crystal dimensions[4]. The overall dimensionality in *Figure 8* was guided by the microscopic observations by Bassett[8]. The changes in structure with composition shown in *Figure 8* indicate that the network consisting of the crystals and the tie molecules becomes appreciably more continuous when the composition is >50% TR418. It is suggested that, analogous to the gelation process, the strength of the network increases greatly at a critical degree of crosslinking.

When a stress is applied to the structures in *Figure 8*, the morphology suggests that the fundamental resistance to the disentanglement process is produced by the crystals. The structure comes apart as the tie molecules disengage from the crystals. The disengagement process is not known, but it may involve the pulling of a tie molecule through the crystal or a shredding of crystals as the tie molecule pulls them. Based on this model it is expected that the time to failure would be influenced mostly by the concentration of tie molecules since the force exerted by a tie molecule on the crystal is inversely proportional to the concentration of tie molecules. However, calculations of the concentration of tie molecules using equation (2) show that the tie molecule density increases only by a factor of 2×10^2 as the composition goes from 0 to 100% TR418 whereas the time to failure changes by a factor of 10^6. An additional factor to be taken into account is the presence of the short chain branches.

It is generally agreed that especially in the slow cooled state short chain branches, longer than a methyl branch, occur outside of the crystals. Thus, if the disentanglement process involves the pulling of a tie molecule through the crystal, it is expected that the short chain branch would severely impede the motion. More recent work by Qian *et al.*[9] on the effect of a solvent on SCG in polyethylenes suggests that entanglements in the amorphous region also contribute to the resistance to the process of disentanglement. It is now suggested that, when two molecules that emanate from adjoining crystals become strongly entangled, a tie molecule is found. The presence of a short chain branch is expected to increase the strength of such a random entanglement. *Figure 9* shows the conventional tie molecule as predicted by equation (2) and two other molecular interactions that perform the function of a tie molecule. This resistance in the amorphous region is associated with the usual resistance to the disentanglement of a craze as widely discussed by Kramer[10] for amorphous polymers.

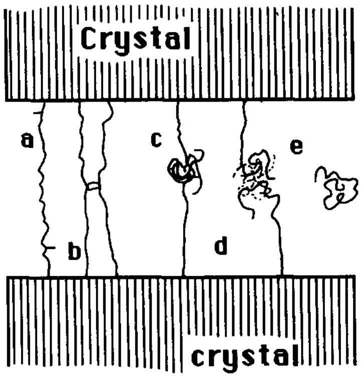

Figure 9 Various molecular arrangements: (a) conventional tie molecule as predicted by equation (2); (b) effective tie molecule produced by an interloop; (c) effective tie molecule produced by a strong entanglement associated with a branch; (d) weakly entangled molecules; (e) molecule with no attachment to a crystal

However, in the case of a branched molecule, the resistance to disentanglement is greatly enhanced by the short chain branches.

It is known that for ethyl, butyl and hexyl branches, the length of the branch is a minor factor compared to the branch density. An extremely important factor that determines the resistance to SCG is the placement of the branches. The work by Scholten and Rijpkema[11] has shown definitively that it is most important to place the branches on the high molecular end of the molecular weight distribution. Probably, the branches are effective if they work in concert with the tie molecules. The concept of the network should be generally extended to include the probability of forming strong entanglements in the amorphous and crystalline regions.

CONCLUSIONS

- Variations in crystal thickness and the distribution of crystal thickness by thermal treatment has a relatively small effect on the resistance to SCG when compared to the effect of composition.
- The activation energy for SCG growth is practically independent of composition.
- The resistance to SCG increases rapidly when the composition of the blend is $>50\%$ copolymer.
- The fundamental resistance to the process of molecular disentanglement that produces SCG comes from the crystals and from the entanglements in the amorphous region.
- When the entangled network, which is formed by the crystals and the branched molecules in the amorphous region, becomes continuous, the resistance to SCG increases rapidly.

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