

# The effect of blending high-density and linear low-density polyethylenes on slow crack growth

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(Received 7 August 1992; revised 8 October 1992)

A high-density polyethylene (HDPE) homopolymer was blended with a linear low-density polyethylene (LLDPE), i.e. an ethylene-hexene copolymer, over the composition range of 0–100%. The resistance to slow crack growth was measured by a notched tensile test under a constant load. The times to failure increased from about  $10^2$  min to  $10^8$  min as the composition increased from 0 to 100% of the copolymer. In the range of compositions below 50% of the copolymer, the time to failure increased relatively slowly with composition compared to the very rapid rate of increase for compositions greater than 50% of the copolymer. The results were explained in terms of a network formed by the crystals and tie molecules that contained short-chain branches. The network becomes continuous when the copolymer is the major component and consequently the resistance to slow crack growth increases rapidly.

(Keywords: high-density polyethylene; linear low-density polyethylene; blend; slow crack growth; network)

## INTRODUCTION

The resistance to slow crack growth (s.c.g.) of polyethylenes (PE), as measured by the time to failure, can vary by more than a factor of  $10^6$  depending on the molecular and morphological structure. This research was done in order to determine the effect on s.c.g. when a homopolymer with a low resistance to s.c.g. was blended with a copolymer of PE with a high resistance to s.c.g. Huang and Brown<sup>1</sup> investigated blends of a high-density polyethylene (HDPE) and an ultra-high-molecular-weight polyethylene (UHMWPE) whose resistances to s.c.g. differed by a factor of about  $10^3$ . Because the UHMWPE has such a high molecular weight, the blend was non-homogeneous so that the structure consisted of particles of UHMWPE in a matrix of the HDPE. The resistance to s.c.g. increased nearly linearly with the volume fraction in the composition range of 0–12% UHMWPE. The time to failure of the blend with 12% UHMWPE was about seven times that of the pure homopolymer.

In this investigation the composition of blends of HDPE and linear low-density PE (LLDPE), i.e. ethylene-hexene copolymer, varied from 0 to 100% and the molecular weight of the homopolymer was appreciably less than that of the copolymer in order to facilitate the blending. From the point of view of the d.s.c. measurements, the blends appeared homogeneous. The resistance to s.c.g., which will now be designated as  $t_f$ , time to failure, varied with composition in an extremely non-linear manner. In the range of compositions greater than 50% copolymer, a small amount of the homopolymer produced very large changes in  $t_f$ .

However, in the range of compositions below 50% copolymer,  $t_f$  varied slowly with composition.

These results could be partially explained by the change in the density of tie molecules with composition. The results suggest that the structure be viewed as a network whose resistance to s.c.g. increases rapidly when the network formed by the tie molecules of the copolymer becomes continuous.

## EXPERIMENTAL

The blends consisted of a linear homopolymer, Marlex 6060 ( $M_w = 66\,800$  and  $M_n = 19\,900$ ), and an ethylene-hexene copolymer, TR418 ( $M_w = 192\,000$ ,  $M_n = 12\,000$ ), with 4.8 butyl branches/1000C (Phillips Petroleum resins). The compositions of the blends were 0, 25, 50, 75 and 100% TR418. The blends are characterized in *Table 1*.

The pellets were first mixed manually and then blended in a twin co-rotation screw extruder (Werner and Pfideker 25K-30,  $L/D = 29$ ) at a feed of  $21\text{ lb h}^{-1}$  ( $\sim 9.5\text{ kg h}^{-1}$ ). The screw speed was  $150\text{ rev min}^{-1}$ ; the temperature in the screw ranged from 140 to  $210^\circ\text{C}$ ; the head pressure was 210–320 psi ( $\sim 1.45$ – $2.20\text{ MPa}$ ). The material was put through the blender twice.

The blends were compression moulded into 10 mm thick plaques. The plaques were cooled from the melt at rates of 0.5 and  $40^\circ\text{C min}^{-1}$  and these two states of the material will be designated slow-cooled (SC) and quenched (Q). The melting points were measured with a DuPont DSC.

The specimens for the s.c.g. test were  $25 \times 10\text{ mm}^2$  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

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**Table 1** Material parameters of the blends<sup>a</sup>

| Content of TR418 (wt%) | Density (g cm <sup>-3</sup> ) |       | Crystallinity (%)         |    |                          |    | $M_w \times 10^{-3}$ |
|------------------------|-------------------------------|-------|---------------------------|----|--------------------------|----|----------------------|
|                        |                               |       | From density <sup>b</sup> |    | From d.s.c. <sup>c</sup> |    |                      |
|                        | SC                            | Q     | SC                        | Q  | SC                       | Q  |                      |
| 0                      | 0.973                         | 0.962 | 84                        | 76 | 83                       | 78 | 66.8                 |
| 25                     | 0.966                         | 0.958 | 79                        | 73 | 78                       | 71 | 98.1                 |
| 50                     | 0.958                         | 0.952 | 73                        | 70 | 71                       | 64 | 129.4                |
| 75                     | 0.951                         | 0.946 | 69                        | 65 | 65                       | 63 | 160.7                |
| 100                    | 0.945                         | 0.940 | 64                        | 61 | 58                       | 53 | 192                  |

<sup>a</sup> SC and Q are slowly cooled and quenched conditions, respectively

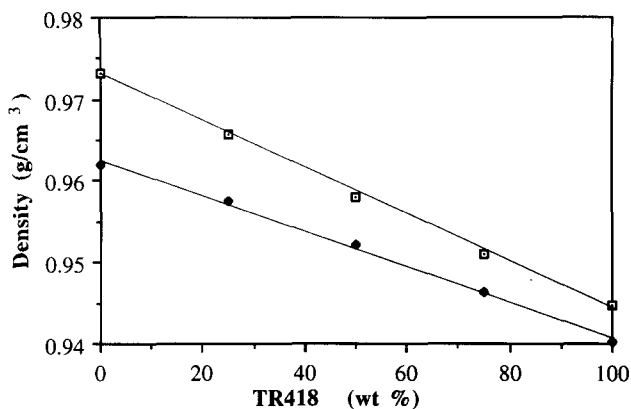
<sup>b</sup> Density crystallinity is based on an amorphous density of 0.86

<sup>c</sup> D.s.c. crystallinity is based on a heat of fusion = 289 J g<sup>-1</sup>

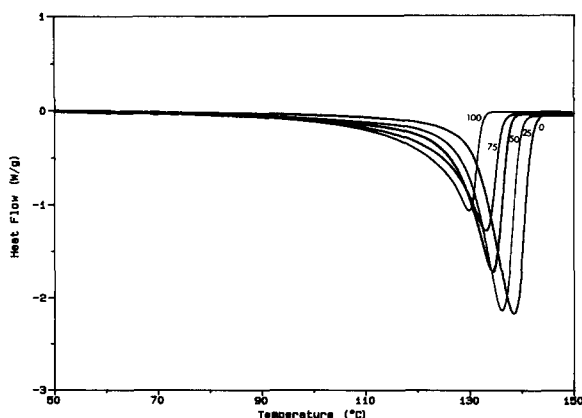
had two 1 mm deep side grooves. The constant-load tensile test was conducted under a 3 MPa stress at  $42 \pm 0.5^\circ\text{C}$  for all blends except for pure TR418. Since the pure TR418 has such a long time to failure it was tested at  $80^\circ\text{C}$  and 2.4 MPa where its time to failure was  $1.7 \times 10^6$  min. This failure time was adjusted to  $42^\circ\text{C}$  and 3 MPa by equations given in the 'Results' section. 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  $\pm 10\%$ .

## RESULTS

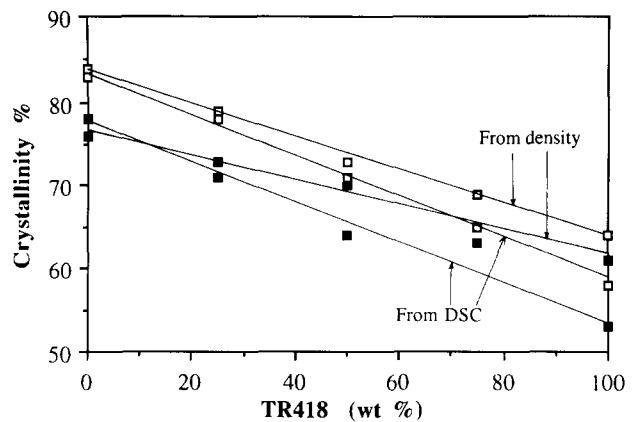
The densities of the SC and quenched states are linear functions of compositions as shown in Figure 1. Figure 2 shows the d.s.c. curves for the SC blends. No



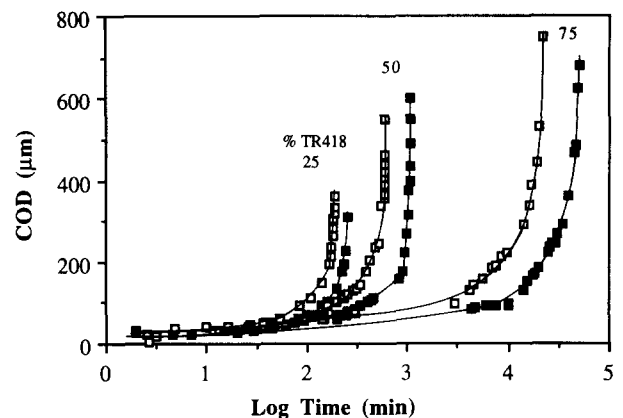
**Figure 1** Density versus composition for the quenched ( $\blacklozenge$ ) and slowly cooled ( $\square$ ) states



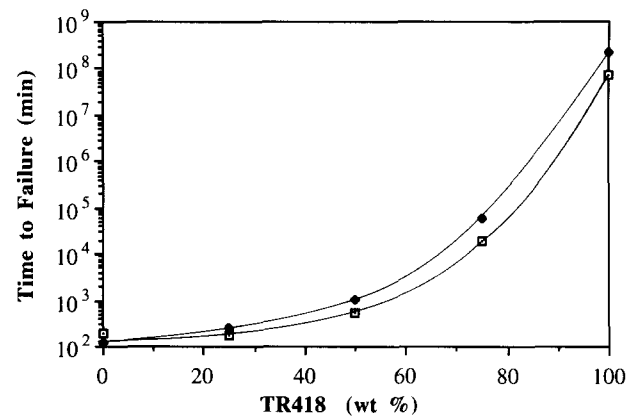
**Figure 2** D.s.c. curves for the slow-cooled state for the various compositions of the blends



**Figure 3** Crystallinity versus composition from the densities and from d.s.c. for the quenched ( $\blacksquare$ ) and SC ( $\square$ ) states



**Figure 4** Crack opening displacement versus log time for various compositions and for quenched ( $\blacksquare$ ) and SC ( $\square$ ) states



**Figure 5** Log of time to failure versus composition for quenched ( $\blacklozenge$ ) and SC ( $\square$ ) states

evidence of a double peak was detected. The d.s.c. curves for the quenched state were similar except that they occurred at somewhat lower temperatures. The crystallinities based on the d.s.c. curves and on the densities are listed in Table 1. Crystallinity is a linear function of composition for the SC and quenched states as shown in Figure 3.

The crack opening displacement (COD) versus time is shown in Figure 4 for several compositions. The initial linear part of the curves involves craze growth. The times when these curves accelerate correspond to the initiation of fracture. The log of time to failure,  $t_f$ , versus composition is shown in Figure 5 for the SC and quenched states. Note the rapid increase in  $t_f$  in the composition

range greater than 50% TR418 compared to the low rate of change below 50% TR418. The data in Figure 5 represent a double-exponential rate of increase in  $t_f$  with respect to composition. The effect of cooling rate on  $t_f$  is very small compared to the effect of composition. It is interesting to note that the quenched state has greater resistance to s.c.g. than the SC state except for the case of the pure homopolymer. Lu *et al.*<sup>2,3</sup> had previously observed, in the case of a homopolymer, that the SC state had a greater resistance to s.c.g. and, in the case of copolymers, that the quenched state better resists s.c.g.

The value of  $t_f$  for the pure TR418 was obtained from the value of  $1.7 \times 10^6$  min measured at 80°C and 2.4 MPa with a 3.5 mm notch by means of the following experimental equation by Brown *et al.*<sup>4</sup>, which is based on extensive experimental data from Brown and coworkers:

$$t_f = A e^{Q/RT} \sigma^{-n} a^{-m} \quad (1)$$

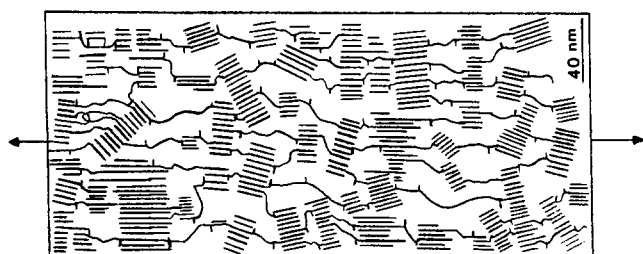
where  $A$  depends on the type of PE,  $Q = 110\,000$  J mol<sup>-1</sup>,  $n = 3.5$ ,  $m = 1.5$ ,  $\sigma$  is the stress and  $a$  is notch depth. To obtain  $t_f$  at 42°C and 3 MPa, the following calculation was used:

$$\begin{aligned} t_f(42^\circ\text{C}, 3.0 \text{ MPa}) &= 1.7 \times 10^6 \left(\frac{2.4}{3.0}\right)^{3.5} \exp\left[\frac{110\,000}{8.3} \left(\frac{1}{315} - \frac{1}{353}\right)\right] \\ &= 7.2 \times 10^7 \text{ min} \end{aligned}$$

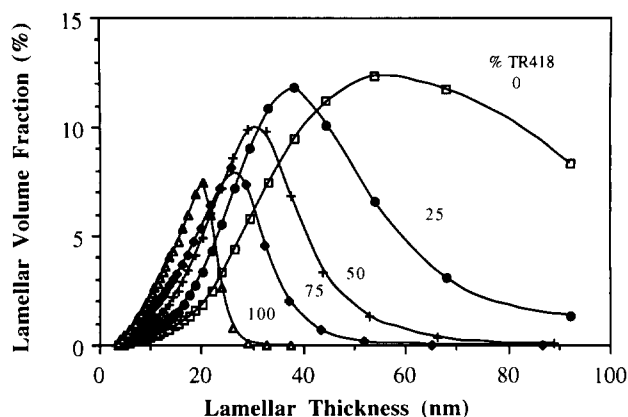
The above value is for the SC state. The work by Lu *et al.*<sup>3</sup> indicates that  $t_f$  for the quenched state is three times  $t_f$  for the SC state.

## DISCUSSION

The most important data in this investigation are in Figure 5. The purpose of the discussion is to explain the dependence of  $t_f$  on composition. The basis for the discussion is a schematic (Figure 6) of the molecular morphology of a fibril. Figure 6 was concocted from: (1) the distribution of lamella thickness derived from the d.s.c. curves; (2) a micrograph of a copolymer by Bassett<sup>5</sup>; (3) calculation of the density of the molecules by a theory of Huang and Brown<sup>6</sup>; (4) the assumption that the butyl branches are generally located outside of the crystal; (5) the known branch density of 4.8 branches/1000C; and (6) the fact that a fibril in the craze is oriented. It is assumed that the amorphous region offers no resistance to s.c.g. except that some molecules



**Figure 6** Schematic of the network structure within a fibril. The amorphous regions are blank. Arrows indicate direction of applied stress and the direction of orientation of the fibril. The tie molecules join the crystals. Note short-chain branches on the tie molecules. The structure is roughly to scale based on the per cent crystallinity values of crystal thickness, and a micrograph by Bassett<sup>5</sup>



**Figure 7** Volume fraction of lamella crystals versus thickness for slow-cooled state. Based on Figure 2 and equation (3)

in the amorphous region may function as tie molecules by being strongly entangled. Figure 6 represents our current view of the structure and is of course subject to change in the light of new experimental data. The distribution of lamella thickness was obtained from a d.s.c. curve and the equation proposed by Illers and Henders<sup>7</sup>:

$$L_c = \frac{0.62 \times 414}{(414 - T_M)} \text{ nm} \quad (2)$$

where  $T_M$  is the melting point. Figure 7 shows the distribution of lamella thickness for the slow-cooled state. The distribution function indicates that the crystallization of the homopolymer is related to the crystallization of the copolymer because there is no evidence of double peaks corresponding to each of the pure components.

The most important question with respect to s.c.g. is how the crystals are connected by tie molecules. The fact that pure TR418 has a resistance to s.c.g. that is  $10^6$  greater than that of the homopolymer suggests that the only effective tie molecules are provided by the TR418. The tie molecules represented in Figure 6 are branched molecules from the TR418. Thus, the crystals are the anchors for the tie molecules and the combination forms a network. The continuity of the network depends on the density of tie molecules.

The calculation for the density of tie molecules as depicted in Figure 6 comes from the theory by Huang and Brown<sup>6</sup>. The theory is based on the assumption that the probability of forming a tie molecule depends on the end-to-end distance of the random coil in the melt relative to the long period in the solid.

The following equation gives the probability of forming a tie molecule:

$$P = \frac{\int_0^L r^2 \exp(-b^2 r^2) dr}{3 \int_0^\infty r^2 \exp(-b^2 r^2) dr} \quad (3)$$

where  $r$  = end-to-end distance of the random coil,  $b^2 = (3/2)\bar{r}^2$  where  $\bar{r}$  is the root mean square of the end-to-end distances and  $L = 2L_c + L_a$  where  $L_c$  = lamella thickness and  $L_a$  = thickness of amorphous layer. The factor 3 in the denominator of equation (3) is based on the geometry of a lamella crystal since a tie molecule forms along one of the crystal dimensions. The value of

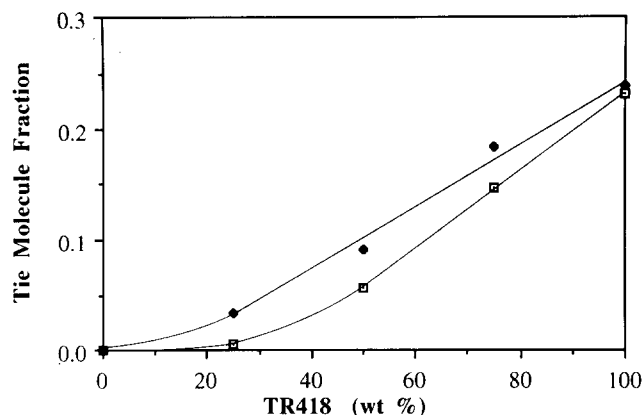
**Table 2** Data for calculation of tie molecule fraction (equation (3))<sup>a</sup>

| Content of TR418 (wt%) | $L_c$ (nm) <sup>b</sup> |      | $L_a$ (nm) <sup>c</sup> |     | $2L_c + L_a$ (nm) |      | $\bar{r}$ (nm) | Tie molecule fraction ( $10^3$ ) |       | Log[ $t_f$ (min)] |      |
|------------------------|-------------------------|------|-------------------------|-----|-------------------|------|----------------|----------------------------------|-------|-------------------|------|
|                        | SC                      | Q    | SC                      | Q   | SC                | Q    |                | SC                               | Q     | SC                | Q    |
| 0                      | 37.8                    | 25.8 | 8.4                     | 9.5 | 84.0              | 61.1 | 27.6           | 0.001                            | 0.682 | 2.27              | 2.09 |
| 25                     | 26.8                    | 19.8 | 8.3                     | 8.5 | 61.9              | 48.1 | 33.4           | 5.40                             | 33.8  | 2.25              | 2.40 |
| 50                     | 20.4                    | 17.4 | 8.8                     | 8.7 | 49.6              | 43.5 | 38.3           | 56.6                             | 92.0  | 2.72              | 3.0  |
| 75                     | 16.0                    | 13.8 | 8.4                     | 8.6 | 40.4              | 36.2 | 42.8           | 148                              | 184   | 4.31              | 4.79 |
| 100                    | 12.2                    | 11.5 | 8.0                     | 8.5 | 32.4              | 31.5 | 46.7           | 232                              | 238   | 7.86              | 8.33 |

<sup>a</sup> SC and Q are slowly cooled and quenched conditions, respectively

<sup>b</sup>  $L_c$  is a medium lamella thickness where 50% of the crystal volume has a thickness greater than  $L_c$

<sup>c</sup>  $L_a = L_c(1 - X)/X$  where  $X$  is the density crystallinity from Table 1

**Figure 8** Relative number of tie molecules versus composition for quenched (◆) and slow-cooled (□) states

$\bar{r}$  depends on the molecular weight and is given by  $\bar{r} = (Dnl^2)^{1/2}$  where  $D = 6.8$  for PE, the link length  $l = 0.153$  nm and  $n$  is the number of links in the molecule. Since there is a distribution of molecular weights and a distribution of long periods, the above equation can be modified to take these factors into account. However, detailed calculations by Huang and Brown<sup>6</sup> show that using  $\bar{M}_w$  and an average value for  $L$  in the above equation gives about the same results as does the detailed calculation. The results of the calculation of tie molecules is given in Table 2. The density of tie molecules versus composition is plotted in Figure 8; the relationship is approximately linear.

The central question in this paper is how can a relatively small change in the number of tie molecules account for such a large change in  $t_f$  as shown in Figure 5. This question will be answered by using Figure 6. The structure consists of a network of crystals connected by tie molecules. At a low concentration of tie molecules, the structure consists of isolated groups of strongly connected crystals, which are isolated within a matrix of weakly connected crystals. As the amount of TR418 is increased, the strongly connected crystals are joined together until a continuous network is formed. When the continuous network forms,  $t_f$  rises very rapidly. This process can be viewed as a gelation process where the system becomes very strong when a continuous network is formed. As long as the matrix is the weak component, the strength is low. When the strong component becomes the matrix the strength rises rapidly. The effect of thermal treatment on  $t_f$  is very small compared to the effect of changing composition. The slow-cooled state has thicker

crystals and consequently fewer tie molecules than the quenched state. However,  $t_f$  is influenced most by the degree to which the network of crystals and tie molecules becomes continuous. Again, it should be emphasized that the only significant tie molecules are those from the TR418 with the short-chain branches. The transition from a weak to a strong structure occurs when the TR418 network is greater than about 50% of the volume. Variations in morphology play a relatively minor role. This latter point has been demonstrated in previous work by Lu *et al.*<sup>3</sup>.

## SUMMARY

An HDPE homopolymer with a low resistance to s.c.g. was blended with an LLDPE with a high resistance to slow crack growth. The two resistances to s.c.g. differed by a factor of  $10^6$ .

The resistance to s.c.g. increased monotonically with the amount of the strong component and the rate of increase began to increase very significantly when the amount of the strong component became greater than 50%.

The results were explained in terms of a network consisting of crystals joined together by the tie molecules, which contain the short-chain branches from the LLDPE. The strength increases greatly when the network becomes continuous.

## ACKNOWLEDGEMENTS

The research was sponsored by the Gas Research Institute. The Central Facilities of the MRL supported by the National Science Foundation under Grant No. DMR88-19885 were most helpful. Dr Andrew McGhie's guidance with the d.s.c. is appreciated. The blending was done at the Rohm & Haas Company with the kind assistance of Mr Jose Reyes.

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