

Influence of the Method of Mixing on Homogeneity and Crystallization Kinetics of Blends of Linear and Branched Polyethylene

B. Neway, U. W. Gedde

Royal Institute of Technology, Department of Fiber and Polymer Technology, SE-100 44 Stockholm, Sweden

Received 18 March 2004; accepted 25 May 2004

DOI 10.1002/app.21092

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The influence of mixing method—solution and melt mixing—on the homogeneity and crystallization kinetics of a series of blends of single-site materials of linear polyethylene and ethyl-branched polyethylene was studied by differential scanning calorimetry. Data obtained for heats of melting and crystallization, melting and crystallization peak temperatures, and melting and crystallization temperature profiles were essentially the same for the samples obtained by the two mixing methods. The results obtained can be interpreted as indicating that melt mixing is capable of producing homogeneous melts of these relatively low molar mass polymers, given that solution mixing is considered to give perfectly homogeneous blends. The heat asso-

ciated with the high temperature melting peak after crystallization at 125°C of the blend samples, obtained by the two preparation methods, was higher than that of the linear polyethylene included in the blends, suggesting that a part of the branched polyethylene crystallized at 125°C. The unblended branched polyethylene showed no crystallization at 125°C. Samples obtained by powder mixing showed independent crystallization and melting of the linear and branched polyethylene components. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1730–1736, 2004

Key words: polyethylene (PE); blends; mixing; homogeneity; crystallization

INTRODUCTION

Polyethylene (PE) blends based on high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and ultra-high molecular weight polyethylene (UHMWPE) have attracted a growing interest because of the potential for obtaining low-cost materials with improved mechanical properties and better processability than those of the pure constituents involved. The advantages in the mechanical properties of blends have been demonstrated in several reports.^{1–3} Other studies concerned with these blends report thermal properties,^{4,5} rheological properties,^{4,6,7} and mechanical properties,^{8,9} and the state of segregation.¹⁰ Some thermal and mechanical properties are intermediate between those of the pure polymers, although the rheological properties exhibit a more complex behavior. Recently, Yamaguchi and Abe⁵ studied the miscibility of LDPE and LLDPE produced by a metallocene catalyst. They found, based on rheological measurements, that LDPE and LLDPE were miscible in the molten state, and that

the apparent activation energy of the flow process increased monotonically with increasing LDPE content. Mixing two polymers is indeed intended to improve the material properties, but there is also a risk: poor mixing may result in separate crystallization of the components⁶ and poor mechanical properties.¹¹

Vadhar and Kyu⁶ found that the mechanical properties were significantly affected by the mixing method used for LLDPE–UHMWPE blends. They also observed by differential scanning calorimetry that cocrystallization of the two components depended on the conditions of mixing, where poor mixing leads to a clearly visible separate crystallization, whereas systems with good mixing showed cocrystallization of the two components. According to Gedde and Jansson,¹¹ a fracture propagates in PE with a broad molar mass distribution preferentially through domains of segregated low mass material. In other words, the state of phase separation existing before, or developing during, crystallization has possible implications on the fracture properties.

Physical-mixing methods, such as melt mixing and solution mixing, are used in the preparation of polymer blends. In solution blends, the two polymers can be mixed to a homogeneous state because polymer chains in the solution state diffuse and disperse easily. During melt mixing, the dispersion of the components is controlled by the shear viscosity of the two polymer

Correspondence to: U. Gedde (gedde@polymer.kth.se).

Contract grant sponsor: Borealis AB, Sweden.

Contract grant sponsor: Swedish Agency for Research Co-operation with Developing Countries (SAREC/SIDA).

components as well as by factors such as temperature, time of mixing, and rotor speed. Solution mixing may be regarded as a "laboratory method," whereas the vast majority of methods used in industry are melt-mixing methods. In this article, we present a comparative study of the degree of homogeneity achieved by melt- and solution mixing and the thermal properties of blends based on linear and branched PE produced by metallocene technology. Comparison is also made with blends prepared by powder mixing; these resemble poorly mixed blends. Differential scanning calorimetry was used to compare the melting and crystallization behavior of the blends and thus the state of mixing of the components. In addition, information about the state of mixing of the components after crystallization is presented.

EXPERIMENTAL

Materials

A linear polyethylene (LPE) and an ethyl-branched polyethylene (BPE), both produced by Borealis AB (Stenungsund, Sweden) by metallocene technology, were used. Characteristics of these polymers are as follows: LPE: $\bar{M}_n = 7100 \text{ g mol}^{-1}$; $\bar{M}_w = 29,000 \text{ g mol}^{-1}$; density at $23^\circ\text{C} = 976 \text{ kg m}^{-3}$; melt index (MI_2) = $88 \text{ g (10 min)}^{-1}$ according to ISO/R 292. BPE: $\bar{M}_n = 14,000 \text{ g mol}^{-1}$; $\bar{M}_w = 64,000 \text{ g mol}^{-1}$; butene-1 comonomer content = 2.5 mol %, density at $23^\circ\text{C} = 927 \text{ kg m}^{-3}$; melt index (MI_2) = $5.4 \text{ g (10 min)}^{-1}$. The density values refer to granules after compounding.

Blend preparation

Blends containing 20, 40, 60, and 80 wt % of LPE were prepared by solution mixing (samples denoted LxS), melt mixing (samples denoted LxM), and powder mixing (samples denoted LxP), where x represents the weight percentage of LPE in the blend.

The solution-mixed blends were obtained by dissolving LPE and BPE in hot xylene (1 wt % polymer in solution), with stirring for 30 min under a nitrogen atmosphere, followed by rapid precipitation of the blended polymers by pouring the xylene solution into an excess of cold methanol. The precipitated blends were filtered and dried under vacuum until a constant mass was reached. The pure polymers (LPE and BPE) were also given the same treatment as that for the blends.

Melt mixing was accomplished in a 2- to 3-g single-screw mixer by melting the linear PE and branched PE at a temperature of 180°C . The rotor speed of the mixer was 136 rpm and the melt was mixed for about 40 min under a nitrogen atmosphere. The pure samples (LPE and BPE) were given the same treatment.

Powder mixing was performed by manual mixing of powders of LPE and BPE for 2–3 min before direct transfer to 40- μL aluminum pans used for thermal analysis. The diameter of the individual polymer particles was about 300 μm .

Methods

A Model DSC 820 differential scanning calorimeter (Mettler-Toledo, Zurich, Switzerland), with nitrogen as purge gas, was used to measure thermal properties on $5 \pm 0.5 \text{ mg}$ samples in 40- μL aluminum pans. The heats of melting and crystallization were determined from the peak areas under the endo- and exothermic traces. The calibration was checked against the onset melting temperature and enthalpy of fusion of pure indium.

The samples were heated at $10^\circ\text{C min}^{-1}$ from -10 to 170°C . The sample was maintained for 3 min at this temperature to ensure complete melting, before cooling at either 1 or $20^\circ\text{C min}^{-1}$. The samples were again heated at $10^\circ\text{C min}^{-1}$ from -10 to 170°C . Thermograms were recorded during cooling and during the second heating scan.

Isothermal crystallization at 125°C for time periods shorter than 3 h was carried out in the DSC apparatus. The samples were heated at $10^\circ\text{C min}^{-1}$ from -10 to 170°C , held at this temperature for 3 min, and then cooled at $80^\circ\text{C min}^{-1}$ to 125°C . The samples were finally heated directly from 125 to 170°C at $10^\circ\text{C min}^{-1}$. Crystallization experiments longer than 5 h were performed in a temperature-controlled silicone oil bath. Samples sealed in 40- μL aluminum pan and further wrapped with aluminum foil were rapidly transferred from the 150°C oil bath to a 125°C oil bath and kept in the latter for different periods of time (≥ 5 h) before rapid cooling in a water-ice mixture. The sample was heated from -10 to 170°C at a rate of $10^\circ\text{C min}^{-1}$ while recording the endothermic melting traces. The high temperature melting peak was attributed to the material crystallizing at 125°C .

The densities at 23°C of the pure and blended samples were determined using the Archimedean principle, that is, by weighing the samples in air and in ethanol (density = 790 kg m^{-3} at 23°C). A top-loaded Mettler AE balance with pan diameters of 80 and 130 mm, equipped with the ME-33360 kit, was used. The samples studied were compression molded at 170°C for 10 min followed by cooling at $0.2^\circ\text{C min}^{-1}$ to room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the strictly linear relationship between the heats of melting and crystallization and the LPE content of the blends. The differences between the heat of melting and the heat of crystallization were

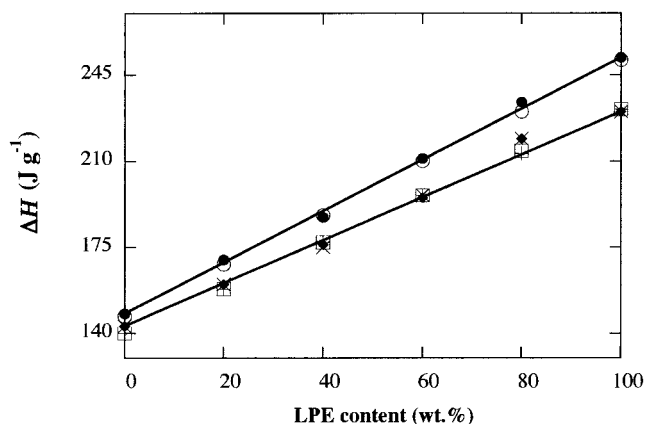


Figure 1 Heat of melting and crystallization as a function of LPE content of blend. Heat of melting for melt-mixed samples cooled at: $1^{\circ}\text{C min}^{-1}$ (●); $20^{\circ}\text{C min}^{-1}$ (◆). Heat of melting for solution-mixed samples cooled at $1^{\circ}\text{C min}^{-1}$ (○); $20^{\circ}\text{C min}^{-1}$ (□). Heat of crystallization of samples cooled at $20^{\circ}\text{C min}^{-1}$ for melt-mixed samples (×) and solution mixed samples (+).

small. At the same LPE content and the same cooling rate, the maximum difference in the heat of melting (crystallization) attributed to the mixing method was only 4%. The linear relationship between melting/crystallization heat and LPE content together with the small deviation between single data points and the regression line suggest that homogeneous mixing of the two polymers, at least at the 5 ± 0.5 mg level, was achieved by both mixing methods. Similar results have been reported for solution-mixed binary LDPE-HDPE blends^{1,12} and solution-mixed ternary blends of LDPE, MDPE, and HDPE.¹² Consonant data, a linear relationship between a quantity proportional to the degree of crystallinity, the density, and the LPE content are presented in Figure 2. The densities of the blends obtained by the two mixing methods were practically the same.

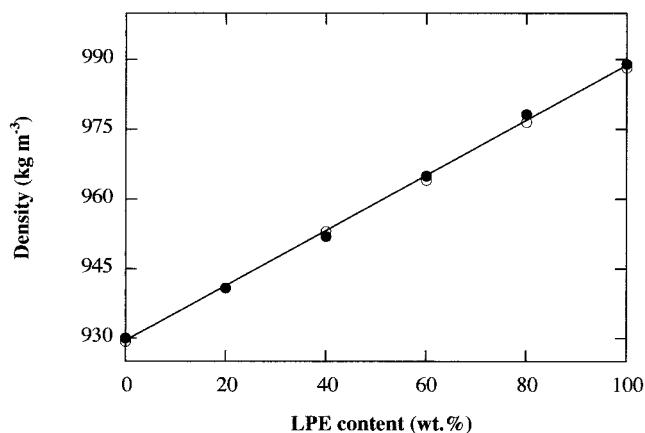


Figure 2 Density as a function of LPE content for melt-mixed (●) and solution-mixed (○) blends.

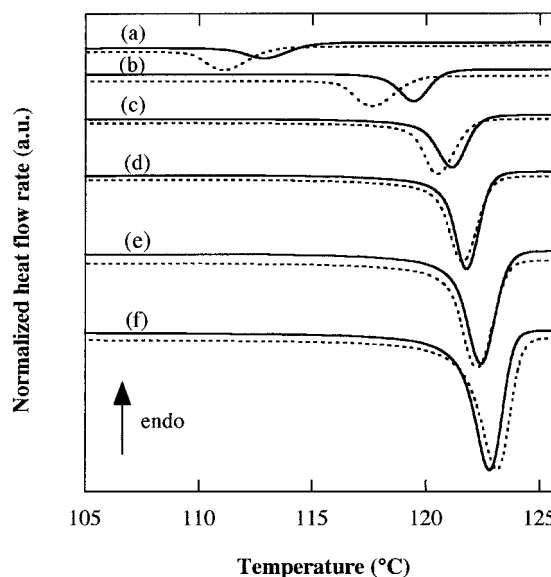


Figure 3 Crystallization exotherms of samples cooled at $1^{\circ}\text{C min}^{-1}$ from the melt: (a) L0; (b) L20; (c) L40; (d) L60; (e) L80; (f) L100. Continuous and broken lines indicate melt- and solution-mixed samples, respectively.

The crystallization exotherms obtained during cooling at $1^{\circ}\text{C min}^{-1}$ for LPE, BPE, and their blends are shown in Figure 3. Both the crystallization peak temperature and the heat of crystallization showed a continuous increase with increasing LPE content. The continuous change in peak crystallization temperature and the unimodal crystallization peaks suggest miscibility of the components, even after crystallization. Similar arguments were earlier presented by Nishi and Wang.¹³ The solution-mixed samples, rich in BPE, showed a shift of almost 2°C toward lower temperatures with respect to the crystallization traces of the corresponding melt-mixed samples (Fig. 3). It may be that solution mixing affects the concentration of primary nucleation sites, and that this in turn influences the onset of crystallization.

The melting traces recorded after the slow cooling ($1^{\circ}\text{C min}^{-1}$) crystallization resembled the crystallization exotherms (Figs. 3 and 4). Only the three compositions with the lowest LPE content (≤ 40 wt % LPE) showed a lowering of, at the most, 2°C in the peak melting temperature of the solution-mixed sample with respect to that of the melt-mixed samples. The melting traces of the melt- and solution-mixed samples with higher LPE content showed a complete overlap (Fig. 4). Similar results were obtained for the samples crystallized at the higher cooling rate ($20^{\circ}\text{C min}^{-1}$) (Fig. 5).

Figures 6 and 7 show the influence of blend content and temperature on the fraction of crystals converted to the molten state of the pure components and their blends, cooled at a rate of $1^{\circ}\text{C min}^{-1}$. At a given melting temperature, more crystals were converted to

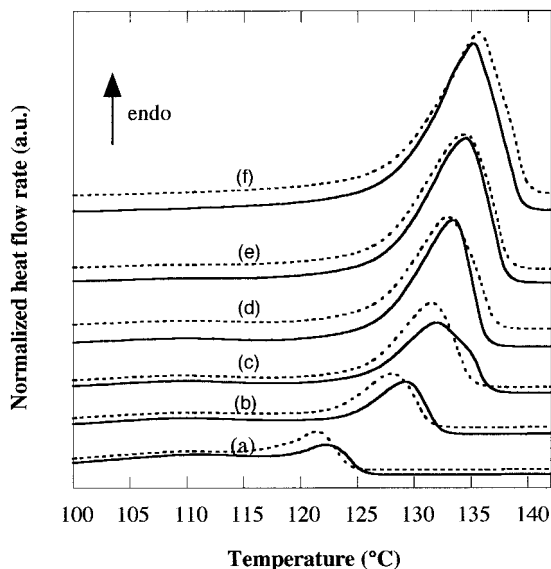


Figure 4 Melting endotherms of samples crystallized during a 1°C min^{-1} cooling: (a) L0; (b) L20; (c) L40; (d) L60; (e) L80; (f) L100. Continuous and broken lines indicate melt- and solution-mixed samples, respectively.

the molten state in a blend with a low LPE content than those in a blend with a high LPE content. Moreover, the final or complete melting temperature shifted to higher temperatures with increasing LPE content. The cumulative melting curves presented in Figures 6 and 7 are practically identical. This is illustrated more clearly in Figure 8, in which the difference

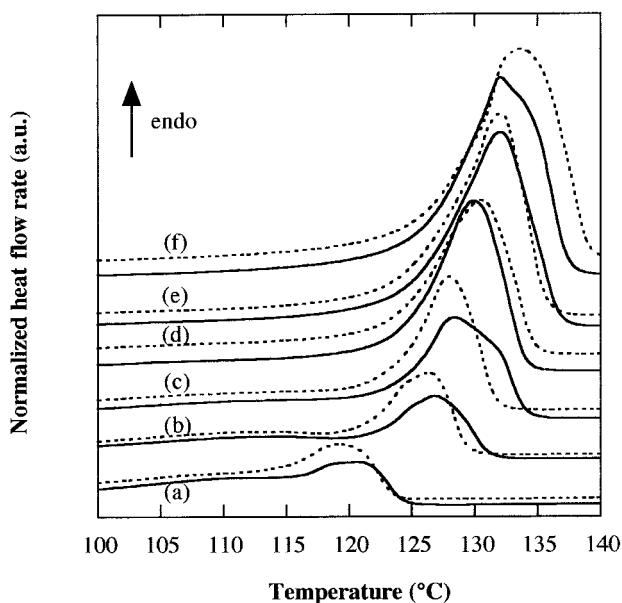


Figure 5 Melting endotherms of samples crystallized during cooling at $20^\circ\text{C min}^{-1}$: (a) L0; (b) L20; (c) L40; (d) L60; (e) L80; (f) L100. Continuous and broken lines indicate melt- and solution-mixed samples, respectively.

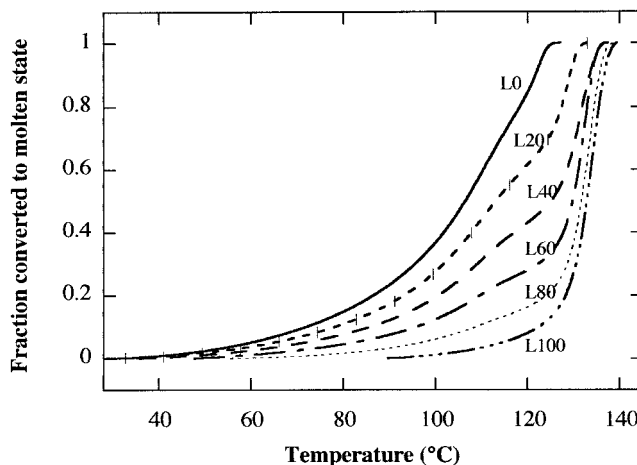


Figure 6 Fraction of crystals converted to molten state versus temperature for melt-mixed samples crystallized during cooling at 1°C min^{-1} from the melt.

in the normalized cumulative heat of melting (Q_n) between melt-mixed and solution-mixed samples is shown as a function of temperature. Q_n is calculated as $[\Delta H_m(M) - \Delta H_m(S)]/[\Delta H_m(M) - \Delta H_m(S)]_{\text{max}}$, where (M) and (S) refer to melt- and solution-mixed methods, respectively, and $\{[\Delta H_m(M) - \Delta H_m(S)]_{\text{max}}\}$ refers to the maximum difference in enthalpy between the two blends. The maximum difference was obtained near the melting peak. With respect to the absolute value of the difference between the two methods over the whole temperature spectrum, it can be said that the conversion to the molten state was not very sensitive to the mixing method. Similar results were obtained for the blends crystallized at $20^\circ\text{C min}^{-1}$.

The blends obtained by powder mixing showed a different behavior: the crystallization exotherms and

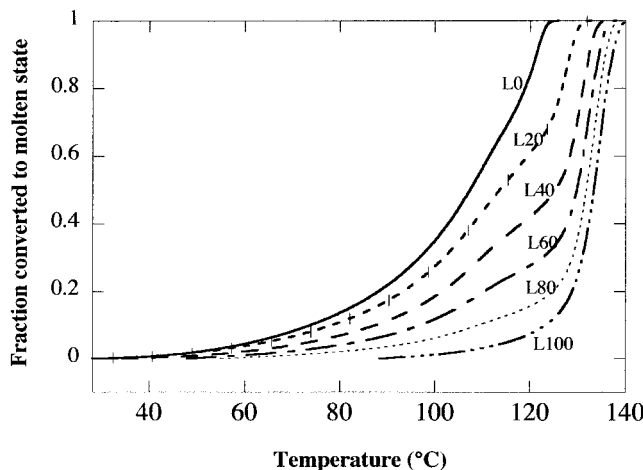


Figure 7 Fraction of crystals converted to molten state versus temperature for solution-mixed samples crystallized during cooling at 1°C min^{-1} from the melt.

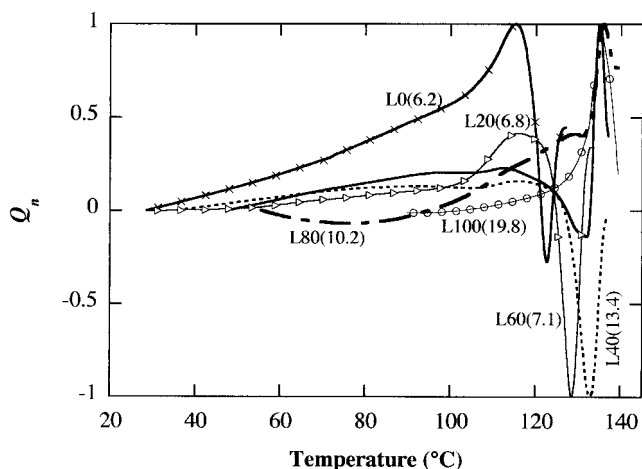


Figure 8 Difference in normalized cumulative heat of melting (Q_n) between melt and solution mixed samples as a function of temperature. Q_n is given by $[\Delta H_m(M) - \Delta H_m(S)]/[\Delta H_m(M) - \Delta H_m(S)]_{\max}$, where (M) and (S) refer to melt- and solution-mixed methods, respectively. The maximum difference value $\{[\Delta H_m(M) - \Delta H_m(S)]_{\max}\}$ between the two mixing methods is indicated on the corresponding curve in brackets after the sample name. All samples were crystallized during cooling at 1°C min^{-1} .

the melting endotherms associated with LPE and BPE remained at the same temperatures, independent of the blend composition [Figs. 9(a) and (b)]. These data imply that the relatively large particles, $300\ \mu\text{m}$ in diameter, of the different polyethylenes in the powder mixture and the relatively short time available for interdiffusion of the components in the molten state form the basis for separate crystallization of the components in the powder-mixed systems.

Figure 10 shows the melting endotherms of the pure LPE and of the blends after crystallization at 125°C for 72 h, followed by fast cooling in ice water. Pure BPE showed no crystallization at 125°C . LPE showed bimodal melting, a high-temperature peak at 135.6°C , and a low-temperature peak at about 120°C . The latter was associated with the melting of segregated low molar mass species, $M < 5000\ \text{g mol}^{-1}$.^{14,15} Details about the basic phenomenology of molecular weight segregation in linear polyethylene can be found in Mehta and Wunderlich,¹⁴ Gedde et al.,¹⁵ Wunderlich and Mehta,¹⁶ and Gedde and Jansson.¹⁷ The segregated material crystallizes at low temperatures in subsidiary lamellae located between the dominant lamellae and sometimes also preferentially near the spherulite boundaries.^{18,19} The relative size of the low-temperature peak decreased with increasing LPE content, that is, the low-temperature melting peak is mainly attributed to the branched polymer. Similar findings were reported by Norton and Keller,²⁰ who noticed segregation of the branched component in a 50/50 blend of HDPE and LLDPE crystallized at different temperatures between 121 and 130°C . Hu et al.³

and Edwards,²¹ on the other hand, presented evidence in favor of cocrystallization of LPE and BPE. In fact, both schemes apply in the present case. Clearly the low-temperature peak became more intense in the blends rich in BPE. Thus a significant fraction of BPE segregated and crystallized late at lower temperatures. A careful analysis of the enthalpy associated with the high-temperature peak showed that part of the BPE crystallized at 125°C . This does not prove, however, that LPE and BPE cocrystallized. It is still

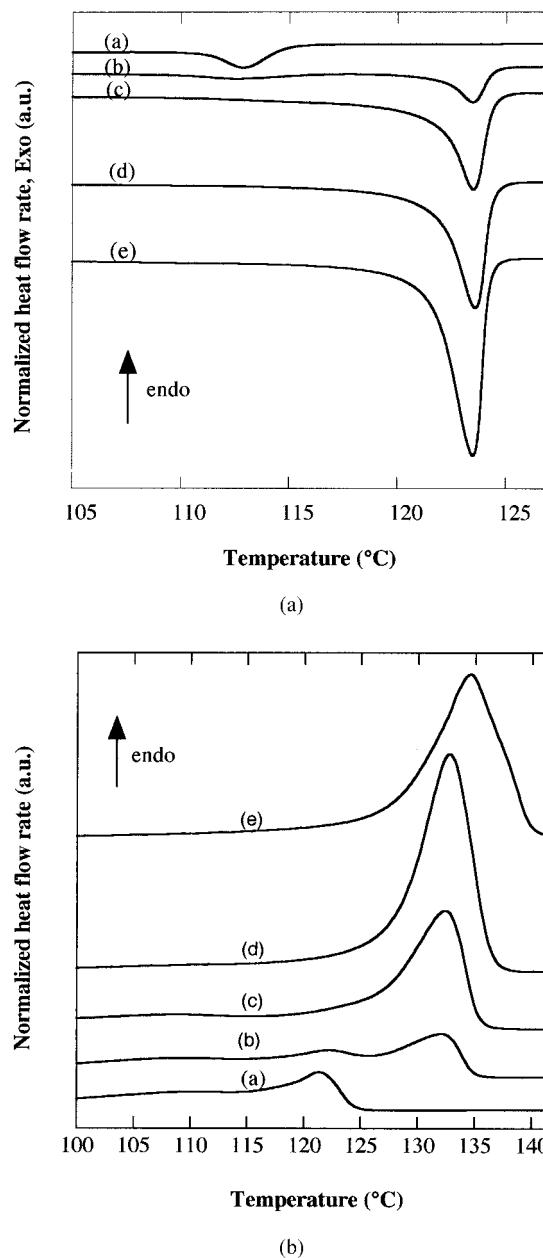


Figure 9 (a) Crystallization exotherms of powder-mixed samples cooled at 1°C min^{-1} from the melt: (a) L0; (b) L20; (c) L40; (d) L80; (e) L100; (b) Melting endotherms of powder-mixed samples crystallized during a 1°C min^{-1} cooling: (a) L0; (b) L20; (c) L40; (d) L80; (e) L100. The melting traces were obtained at a $10^\circ\text{C min}^{-1}$ heating scan.

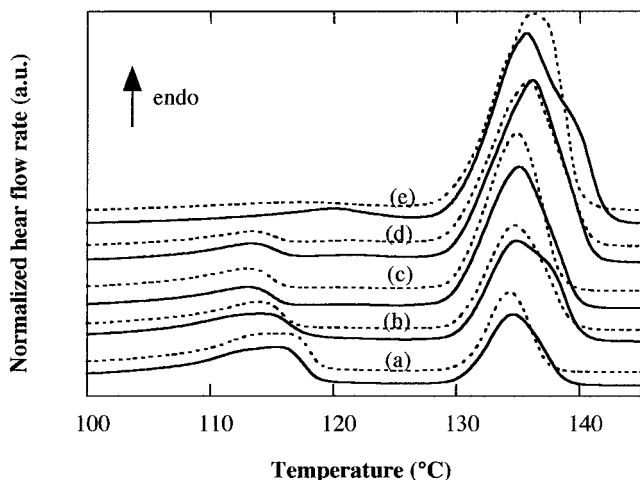


Figure 10 Melting endotherms of: melt- and solution-mixed samples after crystallization at 125°C for 72 h followed by rapid cooling: (a) L20; (b) L40; (c) L60; (d) L80S; (e) L100S. Continuous and broken lines indicate melt- and solution-mixed samples, respectively.

possible that they crystallized in different crystal lamellae. Conde Braña and Gedde²² showed, using transmission electron microscopy, that low molar mass LPE cocrystallized with higher molar mass BPE, in a combination of polyethylene similar to that reported in the present article.

The temperature of the high temperature peak was relatively constant, that is, independent of LPE content (Fig. 10). The melting traces of the melt-mixed blends were essentially identical with those obtained by solution mixing (Fig. 10).

Figure 11 shows the heat associated with melting

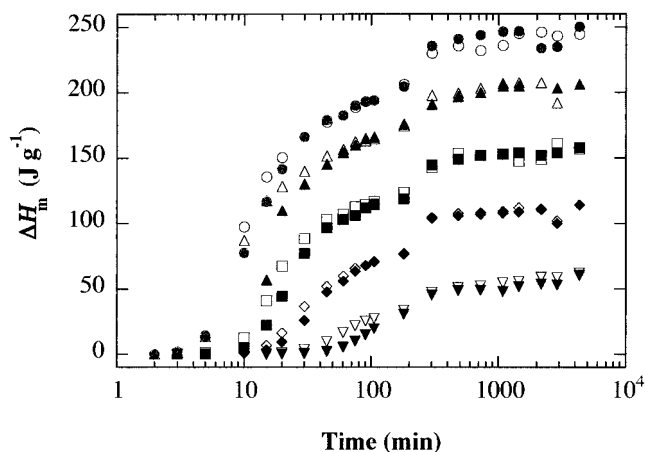


Figure 11 Heat of melting of the material crystallized at 125°C as a function of crystallization time at 125°C for the following samples: L20M (∇); L20S (▼); L40M (◇); L40S (◆); L60M (□); L60S (■); L80M (△); L80S (▲); L100M (○); L100S (●). Note that the small discontinuities in the curves are attributed to a change in the method of crystallization (see experimental section).

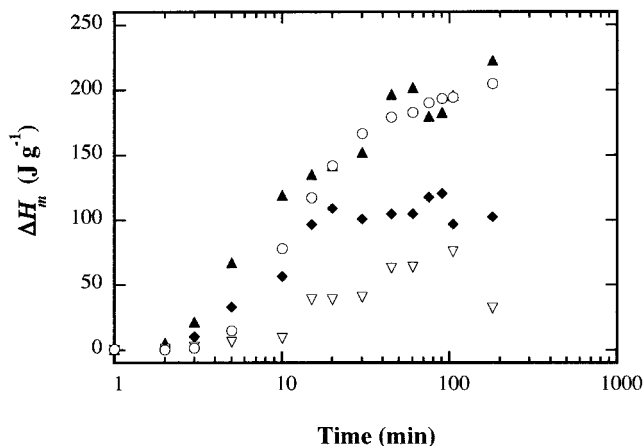


Figure 12 Heat of melting of the material crystallized at 125°C as a function of crystallization time at 125°C for the following powder-mixed samples: L20P (∇); L40P (◆); L80P (▲); L100P (○).

after different periods of time of crystallization at 125°C for the different blends. This quantity is proportional to the degree of crystallinity; the coefficient between the two is the heat of fusion of 100% crystalline material at the equilibrium melting point, 293 kJ (kg)⁻¹.²³ The blend with 20% LPE blends started to crystallize late, approximately one decade in time later than did the pure LPE. The onset time of crystallization for the blends showed a gradual increase with decreasing LPE content (Fig. 11). Long et al.²⁴ made a similar observation and proposed that BPE dilutes the crystallizable fraction and that this delays diffusion and crystal nucleation. Most important, no measurable differences in the crystallization kinetics were found between the blends prepared by melt mixing and solution mixing. However, L20M crystallized slightly more slowly than did L20S (Fig. 11). The small variation in the position of the high temperature peak after 72 h crystallization is attributed to the small variation in crystal-thickening time; the plateau crystallinity was reached within 1–3 h (shortest time for LPE). This means that the crystal-thickening time varied between 69 and 71 h.

Figure 11 also shows that LPE promotes crystallization of BPE. After 72 h of crystallization, the heats of melting were 60 (L20S), 114 (L40S), 158 (L60S), 206 (L80S), and 250 J g⁻¹ (L100S). If we assume that only LPE was crystallizing, then the melting enthalpy associated with LPE would be: 302 (L20S), 286 (L40S), 263 (L60S), 258 (L80S), and 250 kJ kg⁻¹. Thus, the values for the blends are higher than those for L100S, 250 J g⁻¹. It can be concluded that part of the BPE crystallized at 125°C in the melt- and solution-mixed samples.

The blends prepared by powder mixing showed no delay of crystallization in the systems rich in BPE (Fig. 12). The larger scatter in the data points is attributed to

the greater compositional variations in these samples, compared to the samples obtained by the other mixing procedures. However, the data suggest separate crystallization of the pure LPE component.

CONCLUSIONS

Melt mixing produced samples of basically the same degree of homogeneity as that of solution-mixed blends. The molar masses of the studied polymers were relatively low and the conclusion cannot be generalized to include high molar mass polymers. However, the methodology used to reveal heterogeneity can be very useful for assessing the homogeneity of a wider range of polyethylene blends. It was shown that the linear polyethylene promoted crystallization of the branched polyethylene. Segregation of low molar mass and/or more highly branched species was discovered. The crystallization and melting characteristics of the pure components was evident in the poorly mixed systems (powder-mixed samples).

This work was sponsored by Borealis AB, Sweden and by the Swedish Agency for Research Co-operation with Developing Countries (SAREC/SIDA) through the joint collaboration of the University of Asmara, Eritrea and the International Science Programs of Uppsala University, Sweden. M. Palmlov and C. Lind, Borealis AB, Sweden are thanked for valuable discussions.

References

1. Shishesaz, M. R.; Donatelli, A. A. *Polym Eng Sci* 1981, 21, 869.
2. Sakellarides, S. L.; Muchugh, A. J. *Polym Eng Sci* 1985, 25, 1179.
3. Hu, S.-R.; Kyu, T.; Stein, R. S. *J Polym Sci Polym Phys Ed* 1987, 25, 71.
4. Bhateja, S. K.; Andrews, E. H. *Polym Eng Sci* 1983, 23, 888.
5. Yamaguchi, M.; Abe, S. *J Polym Sci Polym Phys Ed* 1999, 74, 3153.
6. Vadhar, P.; Kyo, T. *Polym Eng Sci* 1987, 27, 202.
7. Lee, H. S.; Denn, M. M. *Polym Eng Sci* 2000, 40, 1132.
8. Kyo, T.; Hu, S.-R.; Stein, R. S. *J Polym Sci Polym Phys Ed* 1987, 25, 89.
9. Siegmann, A.; Nir, Y. *Polym Eng Sci* 1987, 27, 1182.
10. Hill, M. J.; Barham, P. J.; Keller, A.; Rosney, C. C. A. *Polymer* 1991, 32, 1384.
11. Gedde, U. W.; Jansson, J.-F. *Polymer* 1985, 26, 1469.
12. Donatelli, A. A. *J Appl Polym Sci* 1979, 23, 3071.
13. Nishi, T.; Wang, T. T. *Macromolecules* 1975, 8, 909.
14. Mehta, A.; Wunderlich, B. *Colloid Polym Sci* 1975, 253, 193.
15. Gedde, U. W.; Eklund, S.; Jansson, J.-F. *Polymer* 1983, 24, 1532.
16. Wunderlich, B.; Mehta, A. *J Polym Sci Polym Phys Ed* 1974, 12, 255.
17. Gedde, U. W.; Jansson, J.-F. *Polymer* 1983, 24, 1521.
18. Bassett, D. C.; Hodge, A. M.; Olley, R. H. *Proc R Soc London A Phys Sci*, 1981, A377, 39.
19. Gedde, U. W.; Jansson, J.-F. *Polymer* 1984, 25, 1263.
20. Norton, D. R.; Keller, A. *J Mater Sci* 1984, 19, 447.
21. Edwards, D. R. *Br Polym J* 1986, 18, 88.
22. Conde Braña, M. T.; Gedde, U. W. *Polymer* 1992, 33, 3123.
23. Wunderlich, B. *Macromolecular Physics*, Vol. 3: Crystal Melting; Academic Press: New York, 1980; p. 49.
24. Long, Y.; Shanks, R. A.; Zbigniew, H.; Stachurski, Z. H. *Prog Polym Sci* 1995, 20, 651.