

Advances in Polymer Blends and Alloys Technology



VOLUME 5

Edited by Kier Finlayson

Advances in Polymer Blends and Alloys Technology

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EDITOR'S NOTE: The progress of new plastic materials by compounding of polymer blends and alloys continues to be an active area of science and engineering.

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Thermal Characterization of Low Density and Linear Low Density Polyethylene Blends

A. J. MÜLLER*¹ and V. BALSAMO*

ABSTRACT: The complex calorimetric behavior of Linear Low Density Polyethylene (LLDPE), Low Density Polyethylene (LDPE), and their blends was studied using Differential Scanning Calorimetry (DSC). The results suggest that the blends are partially miscible and can phase separate either in the melt (liquid-liquid phase separation), depending on the composition and temperature, or during cooling (liquid-solid phase separation), depending on the cooling rate used. The possibility of remixing during cooling can help to explain some of the observed results. The relevance of the cooling rate is crucial since it regulates the competence between thermodynamically driven phase transformations and kinetically controlled molecular segregation during crystallization. The degree of interaction between the phases formed is very good since the tensile properties of the blends (reported on a previous study and conducted on the same samples used here) conformed to a rule of mixtures or positive deviations from it.

KEY WORDS: linear low density polyethylene, low density polyethylene, blends, miscibility, phase diagram.

INTRODUCTION

MISCIBILITY DETERMINATION OF semicrystalline polymer blends by DSC is not an easy task because multiple melting transitions can occur even in homopolymers. In branched polyethylenes this is commonly due to chain branching or molecular length segregation effects. Therefore, kinetic factors are always present and true equilibrium phase diagrams are very difficult to obtain.

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This work is part of a series of investigations on the rheology, structure, and properties of LLDPE/LDPE blends [1–5]. The motivation for the production of these blends stems from the fact that LLDPE has better mechanical properties than LDPE (higher modulus, tensile strength, and even higher elongation at rupture than LDPE); on the other hand, LDPE is easier to process than LLDPE. A blend of both polymers could then result in a very interesting material for practical applications; however, this outcome is not evident because an additive rule of mixture is more often the exception rather than the rule when two polymers are mixed. The mechanical success of the blend will depend on the homopolymer's molecular interaction (i.e., on its particular phase diagram). Such interactions can be revealed by calorimetric studies, if careful interpretation of the results can be provided [6–8].

EXPERIMENTAL

The materials used in this study were a Dowlex 2045 1-octene LLDPE ($M_w = 1.3 \times 10^5$) and a LDPE FD-0348 ($M_w = 1.1 \times 10^5$) manufactured in Venezuela by POLILAGO C.A. The polymers were melt mixed at 190°C by twin screw extrusion (Werner and Pfleiderer ZSK-30). A Perkin-Elmer DSC-7 was used to determine the calorimetric behavior of the homopolymers and their blends. Further experimental details can be found elsewhere [1–4]. An important modification was introduced in this work in the way the samples labeled “unmixed” were prepared. These are samples that are not mixed; in previous investigations [2] they were prepared by placing the desired weight by weight ratio of both homopolymers in the same DSC pan without any prior mixing. Here the procedure was nearly identical except for the fact that an aluminium thin sheet was placed in between the two polymers (and correspondingly in the reference pan) in order to guarantee the total lack of contact between the homopolymers in the pan. The fast quenching applied to some samples was performed manually by transferring the sample as quickly as possible from the DSC oven at the appropriate temperature into a beaker that contained acetone at the freezing point.

RESULTS AND DISCUSSION

Melting Behavior

Figures 1 and 2 show heating scans of the homopolymers and their blends after slow cooling (at approx. 2.5°C/min) and fast quenching (immersion in acetone at freezing point) from the melt (190°C). It is well known that slow cooling promotes molecular segregation during crystallization of the LLDPE homopolymer due to its heterogeneous chain branching distribution along the chain, hence, the double melting peak in Figure 1(h) [9–11].

Since the first endotherm of the LLDPE homopolymer occurs at nearly the same temperature of that of pure LDPE, it is difficult to consider the blend's miscibility under these circumstances. However, if the peak values of the endotherms are plotted versus composition (Figure 3) it can be seen that most of them do not change with composition [Figures 1 and 4(d)–4(g)]. This result is not surprising

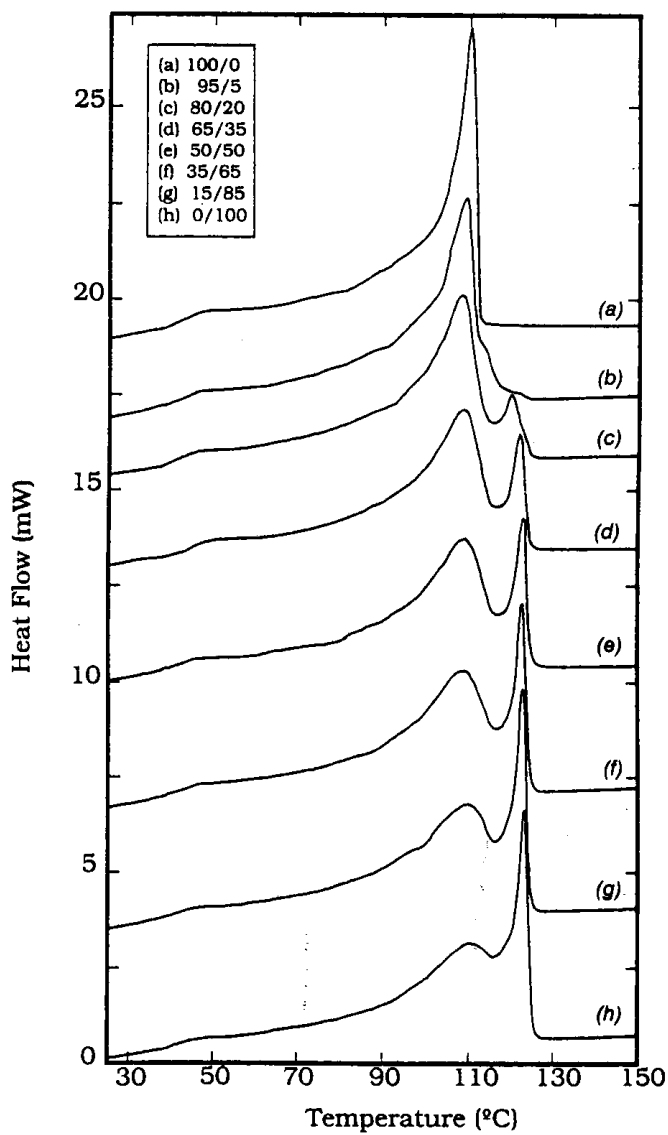


FIGURE 1. DSC heating curves (heating rate = 10°C/min) after slow cooling at 2.5°C/min for the homopolymers and the melt mixed LDPE/LLDPE blends.

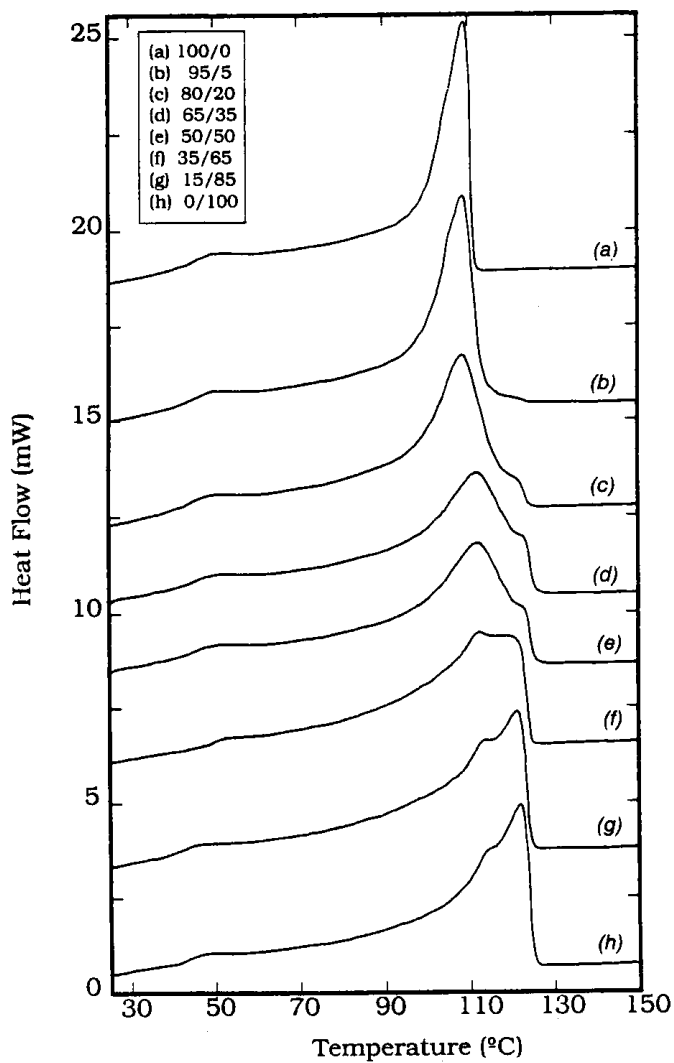


FIGURE 2. DSC heating curves (heating rate = 10°C/min) after rapid quenching in acetone at freezing point for the homopolymers and the melt mixed LDPE/LLDPE blends.

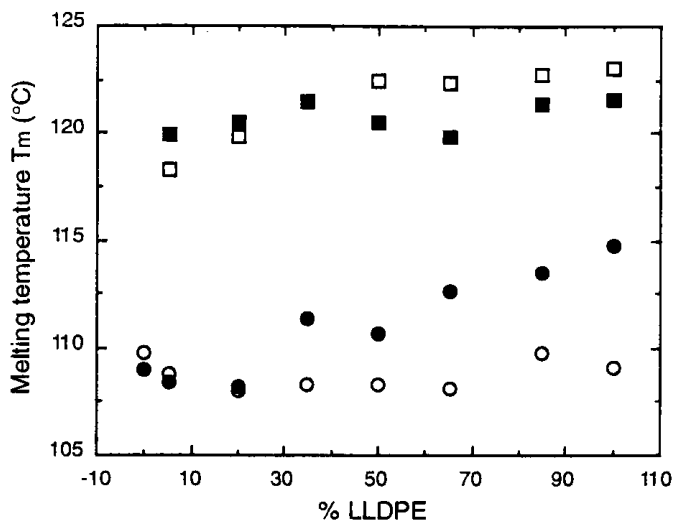


FIGURE 3. Melting temperature versus composition for the homopolymers and the melt mixed LDPE/LLDPE blends, corresponding to a heating scan after the following cooling procedure: slow cooling at 2.5°C/min, T_{m1} (open circles), T_{m2} (open squares); and quenching in acetone at freezing point, T_{m1} (filled circles), T_{m2} (filled squares).

since slow cooling is promoting segregation during crystallization. It should be noted that the blend 95/5 LLDPE/LLDPE may be showing signs of miscibility because it exhibits a complex endotherm that is not what would be expected for complete phase segregation during crystallization. A comparison with Figure 4(b) strengthens this latter point.

The DSC thermograms of the blends that were rapidly quenched from the melt (Figure 2) can be interpreted as indirect evidence of the partial miscibility of the blend in the melt. The term partial miscibility in this context means that the blend will show one or two phase regions in the melt depending on the exact shape of its phase diagram.

When the blends prepared here are rapidly quenched from the melt (190°C), two endotherms are observed for compositions up to 85% LLDPE. The melting points of both endotherms are displaced towards intermediate values when compared with the homopolymer's melting points. The displacement of the peak temperature of the low melting endotherm to higher values is particularly noticeable (Figure 3). The fact that the melting temperatures of the partially miscible phases do not stay constant with composition could indicate that the cooling could not have been completely effective in stopping the molecular segregation and/or phase separation during quenching (it should be remembered that the samples were 1 mm thick and that the quenching was performed manually). Another possible explanation for the shifting of the endotherms with composition involves the presence of an Upper Critical Solution Temperature (UCST) in the phase diagram of the system; this possibility will be examined later on (see below).

A totally different situation to the one described above is shown in Figure 5 for

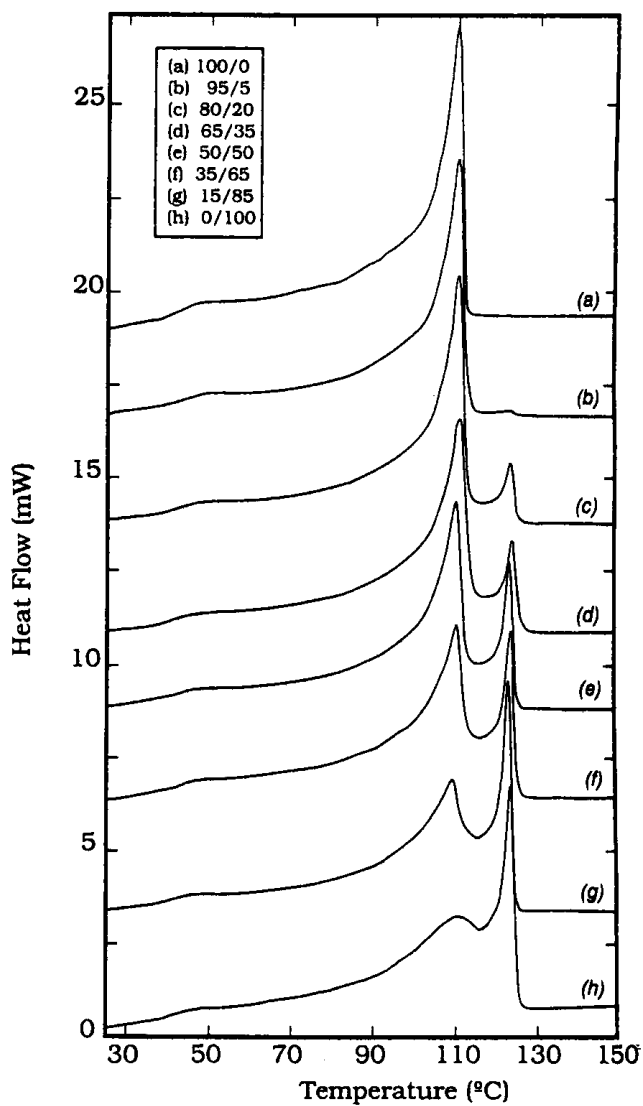


FIGURE 4. DSC heating curves (heating rate = 10°C/min) after slow cooling at 2.5°C/min for the homopolymers and the “unmixed” LDPE/LLDPE blends.

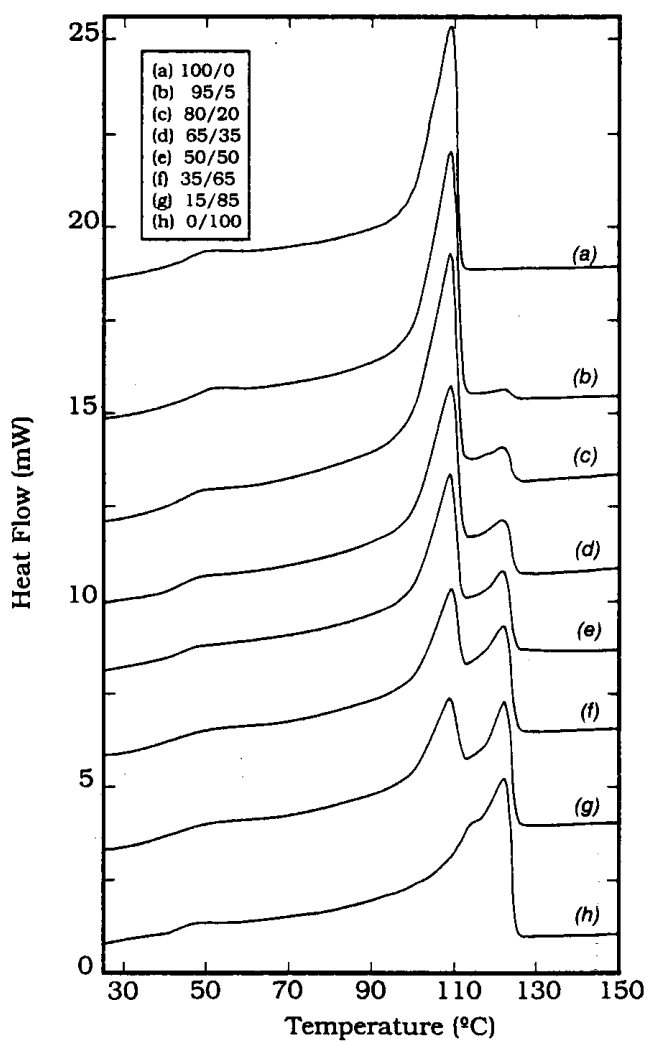


FIGURE 5. DSC heating curves (heating rate = 10°C/min) after rapid quenching in acetone at freezing point for the homopolymers and the “unmixed” LDPE/LLDPE blends.

“unmixed” samples (with no interaction whatsoever, see experimental) where the two endotherms are very distinct and their peak values do not shift at all from the values exhibited by the homopolymers. In this figure it can also be seen that when the LLDPE is rapidly quenched from the melt, most of the molecular segregation during crystallization is halted (but not all, in fact a small shoulder remains of the low temperature melting endotherm) and the polymer now shows in a subsequent melting run [Figure 5(h)] one main endotherm.

More evidence on molecular interactions is obtained when isothermal heights are examined as a function of composition. Three temperatures were chosen to measure the height with respect to the baseline, they correspond to the peak melting temperature of the LDPE homopolymer (Y1), the first melting endotherm of the LLDPE homopolymer (Y2) and the second melting peak of the LLDPE (Y3). Figure 6 shows these isothermal height variations for the rapidly quenched samples. Y1 does not decrease linearly (the “unmixed” samples are not represented in the figure but the height variation was perfectly linear with composition, as one would expect for non-interacting or immiscible blends) with composition, it decreases faster at low LLDPE content. Correspondingly Y2 increases faster than a linear dependence at the same composition range. Y3 does vary linearly with composition. These results indicate that a LDPE rich phase must be present after melt mixing, since the LDPE peak is being depleted and the material that should be melting at Y1 is now melting at higher temperatures (Y2).

Even in the slow cooled samples, where the endotherms are more separated in peak temperatures and do not change much with composition (see Figure 3), other evidence of differences with the “unmixed” blends can be found. Figure 7 shows how the endotherm width varies with composition for the homopolymers

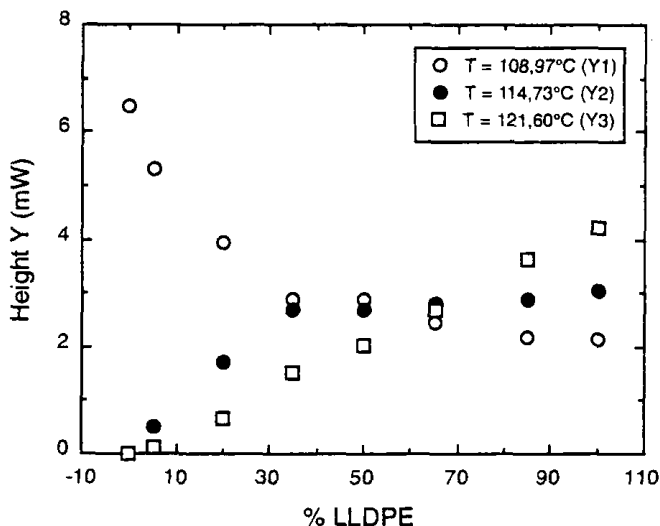


FIGURE 6. Isothermal height variation at the indicated temperatures versus composition for the homopolymers and the melt mixed LDPE/LLDPE blends after fast quenching, corresponding to the melting endotherms of Figure 2.