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An investigation of co-crystallization in LDPE/HDPE blends using DSC and TREF[1]

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Abstract

A number of differential scanning calorimetry (DSC) experiments were performed to investigate the melting behavior of blends of low density polyethylene (LDPE) and high density polyethylene (HDPE). Results revealed three endothermic peaks which suggested that, upon fast cooling, a ‘‘co-crystalline’’ phase is formed. The same feature was found using Temperature Rising Elution Fractionation (TREF), which fractionates semi-crystalline polymers based on relative crystallizability of molecules. Isolation of the ‘‘co-crystallized’’ fraction was possible using TREF in a preparative mode. Analytical TREF and DSC were then used to identify polymeric components in the ‘‘co-crystalline’’ phase. © 1998 Elsevier Science B.V.

Keywords: Blend; Co-crystallization; Polyethylene; TREF

1. Introduction

In melting studies of mixtures of linear and branched (high pressure) polyethylenes, some investigators reported that DSC/DTA experiments revealed three endothermic peaks [1–4]. An intermediate peak between the higher temperature high density polyethylene (HDPE) and the lower temperature low-density polyethylene (LDPE) peaks has been associated with the fusion of a co-crystal, formed from linear and branched polyethylenes.

In the present study, the melting behavior of blends of LDPE and HDPE was investigated using DSC. Results revealed three endothermic peaks which suggest that, upon fast cooling, a ‘‘co-crystalline’’ phase is formed. The same feature was found using a special form of Temperature Rising Elution Fractionation (TREF), which separates semi-crystalline polymer chains based on relative crystallizability of molecules. In regular/normal TREF, the polymer is dissolved in a solvent at high temperatures. A heated inert support is added, and the mixture is then slowly cooled, allowing polymer molecules to crystallize on the support according to their crystallizabilities. After crystallization, the temperature is raised continuously with solvent flowing through the column. As a result, chains which crystallized with difficulty are eluted first (at lower temperatures). As the temperature rises, less defective and more perfect chains are eluted. In quench TREF, the solution is rapidly crystallized prior to elution, as opposed to slow crystallization. On the

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elution of a quench TREF sample a "co-crystallized" peak is seen. Successful isolation of the "co-crystallized" fraction was possible using TREF in a preparative mode. Analytical TREF and DSC were then used to identify polymeric components in the "co-crystalline" phase.

2. Experimental

The polymers used in this work are DOW Chemical products (HDPE 12165 and LDPE 526). A 1%(w/v) solution was prepared by dissolving the appropriate polymer composition in 1,2,4-trichlorobenzene. After crystallizing by allowing solutions to cool to room temperature, the polymers were filtered, washed with methanol, and dried in a vacuum oven. Films were formed using a Carver press at 160°C for 5 min. These film samples were used for DSC and TREF experiments.

DSC analysis was performed on 1–4 mg samples using a DuPont2000 unit at 10°C/min heating rate from 0–160°C. The instrument was calibrated with indium. After melting, samples were cooled in two different ways: quenched – using liquid nitrogen; or slowly cooled at ≈3°C/min.

TREF was performed on pure LDPE, HDPE and a LD/HD 75/25 blend. Polymers were dissolved at 160°C in 1,2,4-trichlorobenzene and then loaded onto a heated inert support (Chromosorb ®P.) Samples were either crystallized by quenching the hot slurry in an ice-water bath, or they were slowly crystallized in a microprocessor-controlled crystallization oven on reducing the temperature from 130 to 30°C at a rate of 1.5°C/h. Subsequently, the mixture was loaded into a column, and placed in an elution oven. A controlled heating rate of 40°C/h was applied simultaneously with an eluent flow rate of 4 ml/min.

A preparative mode TREF experiment was performed on the LD/HD 75/25 quench-crystallized blend. The "co-crystallized" fraction was collected from 80–90°C and, subsequently, studied using analytical TREF and DSC.

3. Results and discussion

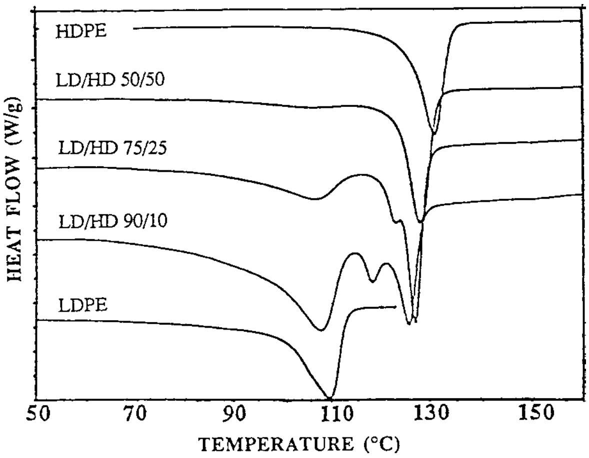

Fig. 1. DSC of different composition LDPE/HDPE blends.

In some of the various composition LDPE/HDPE blends investigated, three endothermic peaks were observed in DSC as illustrated in Fig. 1. The intermediate peak shifted to higher temperature with increasing amount of HDPE. For all compositions examined, the peak associated with HDPE shifted to lower temperatures relative to pure HDPE. This shift to the lower temperatures increased as the amount of LDPE increased.

The melting behavior of a LDPE/HDPE 90/10 blend, previously crystallized using a variety of cooling conditions, is shown in Fig. 2. The intermediate peak is clearly observed after rapid cooling and it shifts toward the highest temperature endotherm (HDPE) as the cooling rate is reduced. At the slowest cooling rate an intermediate peak is not seen.

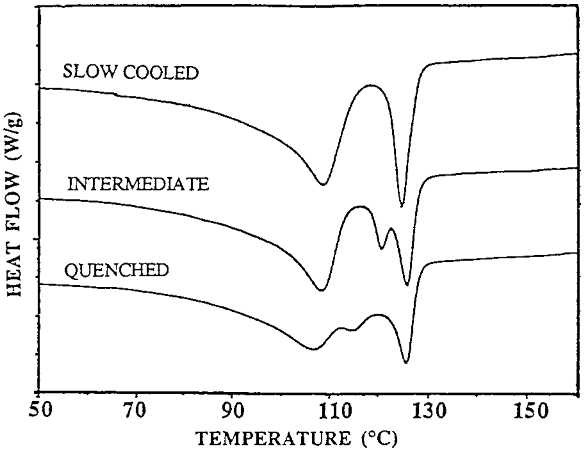

Fig. 2. Effect of cooling rate in a LDPE/HDPE 90/10 blend.

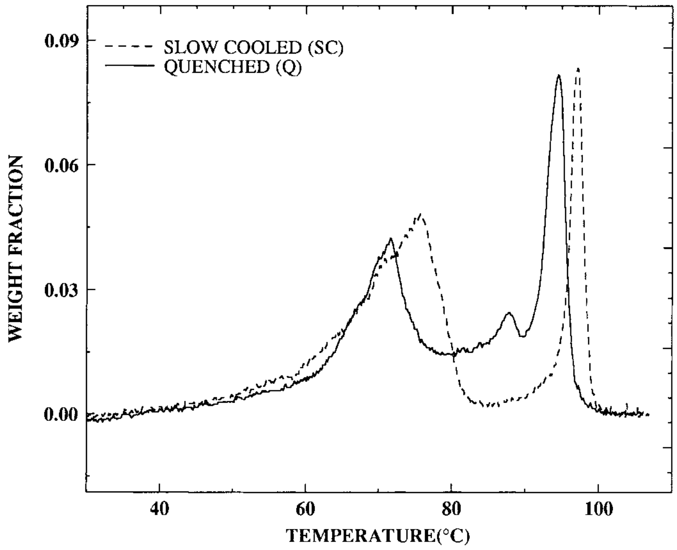

Fig. 3. Analytical TREF of a LDPE/HDPE 75/25 blend.

In Fig. 3, we can see that a phenomenon, which appears to be co-crystallization, can also be detected with TREF. A solution of a LDPE/HDPE 75/25 blend, when quenched prior to TREF elution, showed three dissolution peaks as did melt crystallized DSC. LDPE and HDPE separate quite cleanly on slow cooled TREF of the blend; and the area in the 80°–90°C range represents only ~4% of total curve area. In contrast, on quenched TREF the co-crystal region from 80–90°C contains ~20% of the total eluted material. Based on shape of the curve, much of this co-crystal material appears to be LDPE which is eluting at higher temperatures than usually seen with standard crystallization.

The composition of co-crystal material obtained from preparative TREF on a quenched sample, can be determined more directly using slow cooled TREF. Results are shown in Fig. 4 with pure LDPE and HDPE included for comparison. Co-crystalline material seems to contain both, a fraction of the original LDPE and a fraction of HDPE. Pure LDPE has an absolute upper temperature limit of dissolution of 85°C. Pure HDPE has an upper limit of ~105°C, but a low temperature "tail" that may extend as low as ~75°C. Assuming that everything below 82°C is LDPE, the approximate composition of co-crystal is LD/HD/70/30.

Analytical TREF of the co-crystal, prepared using a quenched TREF procedure is shown in Fig. 5, together with LDPE and HDPE also quenched. The co-crystal quenched TREF position lies between quenched TREF curves for LDPE and HDPE. The LDPE quenched curve is significantly narrower than a regular TREF curve of the same material (cf. Fig. 4). In contrast the quenched HDPE TREF curve shows marked broadening and splits into two clearly defined peaks. The origin of the two peaks in quenched HDPE TREF curves is discussed elsewhere [5].

The DSC curve of TREF derived co-crystal material is shown in Fig. 6, after being slowly crystallized from the melt. Slowly crystallized pure LDPE and HDPE are also shown for comparison. Two endothermic peaks are observed for the co-crystal material and seem to be associated with linear and branched polyethylene. The linear component appears to melt somewhat lower than regular HDPE and the branched material melts higher than normal LDPE.

The DSC curve of TREF derived co-crystal material after fast cooling from the melt can be seen in Fig. 7; fast cooled LDPE and HDPE are also included. Co-crystalline material melts over a broad range of temperatures, including part of the LDPE melting region

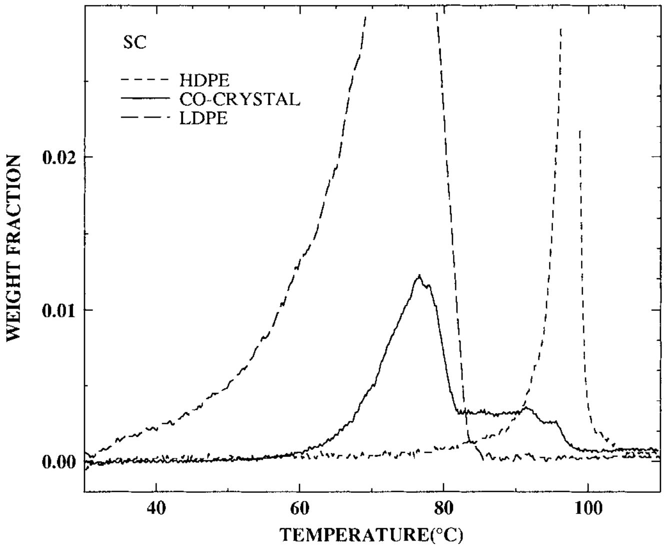

Fig. 4. Analytical TREF of slow cooled co-crystal material obtained from preparative TREF.

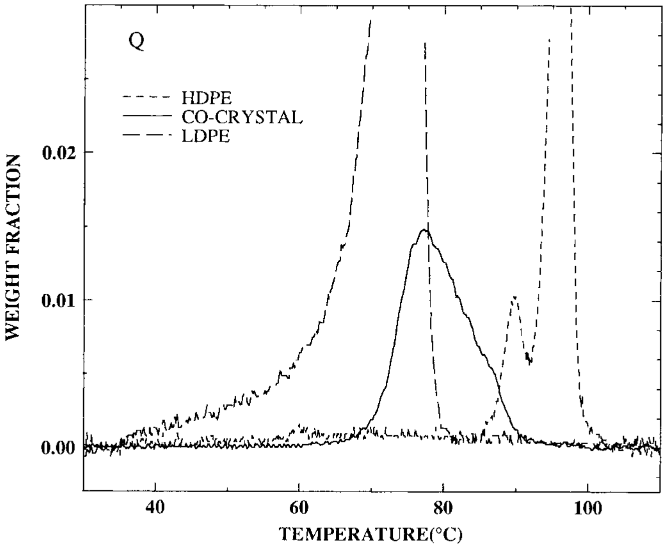

Fig. 5. Analytical TREF of quenched co-crystal material obtained from preparative TREF.

and some of the HDPE melting range. The co-crystal melting peak is observed at an intermediate temperature between those of LDPE and HDPE.

One possibility is that both, DSC and TREF data presented are showing a melting–recrystallization–melting phenomenon. Therefore, the "co-crystal" is a result of crystallites melting, recrystallizing and melting again during the heating cycle of a DSC or TREF run. However, in previous studies from our laboratory [4], DSC experiments were performed on a similar blend, and there was little difference in the ratio of the areas of the higher temperature and "co-crystal" peaks with increasing heating rate. If reorganization was taking place, this ratio should have changed; faster heating rates allow less time for reorganization.

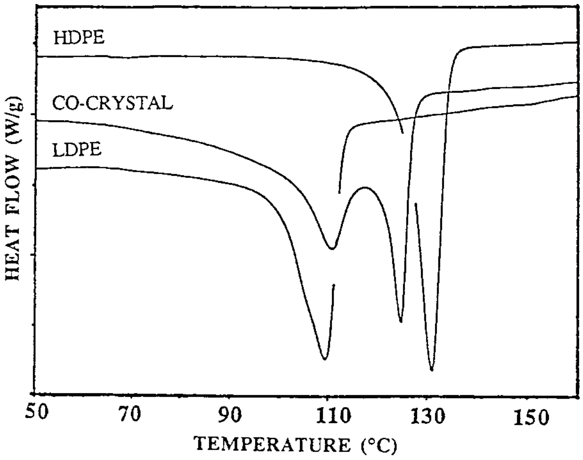

Fig. 6. DSC of slow-cooled co-crystal material from TREF.

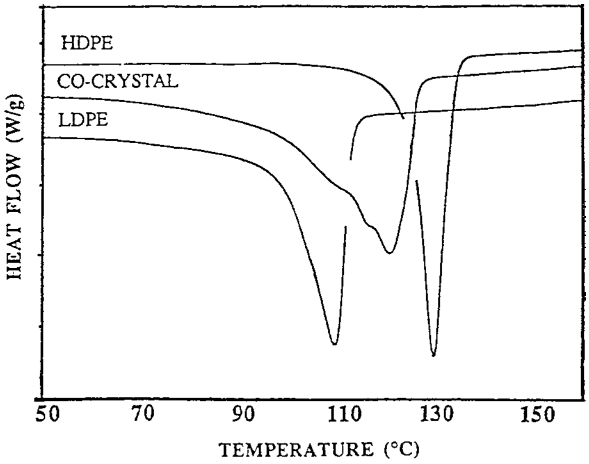

Fig. 7. DSC of quenched co-crystal material from TREF.

Another possibility is that the interaction between the two components is due to the formation of a co-crystallite from HDPE and LDPE which occurs during fast cooling crystallization due to the slower diffusion and segregation of HDPE from LDPE. From Figs. 4 and 6, it is clear that selective portions of LDPE and HDPE are involved. The co-crystal consists of material normally associated with the higher temperature portion of LDPE and the lower temperature tail of HDPE. Remarkably (cf. Fig. 5), approximately 1/2 of the co-crystal material dissolves at temperatures significantly higher than LDPE normally dissolves when quenched. Given that the co-crystal contains a major portion of LDPE ($\sim$70%), some of the LDPE appears to dissolve at higher temperatures than pure LDPE normally dissolves. Such behavior seems to be evidence that co-crystallization takes place. Therefore, the co-crystallized portion of LDPE elutes off the TREF column only after the co-crystallite has dissolved.

4. Conclusion

DSC and TREF of LDPE/HDPE blend manifest co-crystallization behavior when crystallization rates are high. The unique advantage of TREF is that it permits, for the first time, separation and analysis of those materials involved in the co-crystallization stage for those systems showing partial co-crystallization (multiple dissolution/melting peaks). In this case, it is possible to determine not only the relative composition of a LDPE/HDPE co-crystal, but also to demonstrate that only selected portions of the pure homopolymers are involved in co-crystal formation.

Acknowledgements

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