Isothermal crystallization of high density polyethylene with monomodal and bimodal molar mass distribution

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Abstract: The isothermal crystallization behavior of two different high density polyethylene grades with monomodal and bimodal molar mass distribution was investigated by means of differential scanning calorimetry. The results indicate that extensive cocrystallization between linear short chains and long chains with short branches in bimodal polyethylene grade occurred. In contrast, polymer chains of different lengths in monomodal polyethylene exhibit different tendency to crystallize. This finding was explained qualitatively based on a general discussion of the effect of molar mass and branch content/length on crystallization tendency of polymeric chains.

Introduction

High density polyethylene (HDPE) is the simplest polymer in terms of its chemical structure and is used in many applications, with special importance in the field of pipes for water, gas and oil distribution. It has been long established in industry that HDPE grades for pipe applications should preferably possess a bimodal molar mass distribution with linear short chains and long chains with few short branches. HDPE materials with similar average molar mass and a broad molar mass distribution may yield similar crystallinity, crystalline lamellar thickness and thus similar short term mechanical properties as, e.g., modulus and yield stress, but they differ significantly from bimodal grades with respect to the long term stability in pipe applications, namely, slow crack growth resistance. Despite the large amount of literature discussing the reasons for this difference, the actual mechanisms are still under discussion [1-7]. It is well accepted that in semi-crystalline polymers all macroscopic properties have their microscopic structural basis; but the goal of many studies is still to unravel unequivocally the links between microscopic features ranging from chain architecture, via crystallite sizes and the arrangement of crystallites to the length scale of spherulites. These studies comprise the whole machinery of polymer science. A special branch of these approaches comprises thermoanalytical methods where information about structural aspects of the material is derived from the measurement of materials properties while varying temperature according to specific protocols. Within this framework a thorough examination of the solidification behavior of the HDPE samples with varying composition will enhance the understanding of their
mechanical properties. In this paper, we describe an isothermal crystallization study on monomodal and bimodal HDPE samples. It was found that in the case of the bimodal polyethylene extensive cocrystallization of the short linear and long branched chains occurs during isothermal crystallization even at relative high crystallization temperatures. The reason for this behavior is explained.

Results and discussion

Crystallinity values of samples subjected to isothermal crystallization for given time intervals are presented in Figure 1. It must be mentioned that in the two samples no phase separation between differently branched species on the micron-scale occurs in the molten state [10-17].

Fig. 1. Evolution of crystallinity during isothermal crystallization measured at different temperatures for PE1 (top) and PE2 (middle) as well as isothermal crystallization temperature dependence of the crystallinity recorded after crystallization for 5 minutes (bottom).
To understand the above experimental results, we present in Figure 2 a tentative explanation. The PE samples in this study exhibit a broad molar mass distribution implying the presence of molecules with different typical crystallization temperatures when considered separately. For the sake of simplicity, the crystallization temperature (Tc) under certain given conditions was chosen as a measure for the aptness of classes of molecules with different molar masses and architectures to crystallize. It is known that crystallization temperature increases with the increasing molar mass in the molar mass range considered here (sketched in the left part of Figure 2). Incorporation of branches in molecules of certain length reduces the crystallization temperature (see right part of Figure 2). In bimodal PE, it is to be assumed that an optimum situation is realized. Linear short chains possess a lower crystallization temperature than linear long chains. This difference is effectively removed by long chains, containing a certain amount of short branches, acting as nucleating promoters and agents. Thus extensive cocrystallization prevents phase separation of the two components during crystallization resulting in a continuous distribution of different polymeric chains throughout the crystals. In the case of monomodal PE, incorporating of branches in short chains further lowers their crystallization temperature making it difficult to cocrystallize with other, longer chains unless sufficiently low crystallization temperatures are applied (e.g., 40 °C in Figure 1). Figure 2 thus provides a general scheme for designing bimodal polyethylene materials since one must consider solidification process of the final products in addition to the melt miscibility.

![Fig. 2. Schematic illustration of the effect of molar mass and branch content/length on crystallization temperature Tc. Tc denotes, e.g., the onset of crystallization in cooling experiments. Optimized condition for a bimodal polyethylene is met when both components crystallize in a similar temperature range.](image)

**Conclusions**

In summary, we have shown that bimodal HDPE used for pipe applications form phase separation free structure due to the well balanced crystallization ability between linear short chains and long branched chains. This finding may provide a better understanding on the superior long term performance of the bimodal polyethylene in pipe application.

**Experimental part**

**Materials**

Two HDPE samples used in this study were supplied by BASELL Polyolefins GmbH, Frankfurt, Germany. The samples are characterized in Table 1. The samples differ
with regard to their molar mass distribution and branch type and distribution. In PE1, branches are preferentially distributed on the shorter molecules regardless of the length of the chains whereas in PE2 branches are distributed predominantly along chains with high molar mass [8]. PE2 is typical material for pipe applications exhibiting excellent crack growth resistance.

**Tab. 1.** Characterization of the samples examined.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$M_w\times10^5$</th>
<th>$M_w/M_n$</th>
<th>MWD</th>
<th>Branch type</th>
<th>Branch content 1/1000C</th>
</tr>
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<tbody>
<tr>
<td>PE1</td>
<td>3.9</td>
<td>22</td>
<td>monomodal</td>
<td>C$_4$H$_9$-</td>
<td>2</td>
</tr>
<tr>
<td>PE2</td>
<td>4.4</td>
<td>44</td>
<td>bimodal</td>
<td>C$_4$H$_9$-</td>
<td>3.1</td>
</tr>
</tbody>
</table>

**Differential scanning calorimetry**

The isothermal crystallization behavior of the samples was studied with a DSC 2920 (TA Instruments) using a temperature program illustrated in Figure 3.

![DSC diagram](image)

**Fig. 3.** Schematic representation of the procedure used for isothermal crystallization studies with DSC. The inset shows a typical DSC melting curve after isothermal crystallization from where the value for crystallinity was derived.

Samples were first heated up to 190 °C at a heating rate of 20 K/min. They were then kept at this temperature for 5 min to eliminate thermal history before being cooled down to the desired crystallization temperature at a rate of 30 K/min. Samples were heated up again after a certain preset isothermal crystallization time and the corresponding crystallinity was estimated by relating the integrated heat to the melting enthalpy of hypothetical 100% crystalline polyethylene of 293 J/g [9]. Crystallinity values can also be evaluated from the isothermal DSC curve when the crystallization temperature is relatively low, resulting in a fast crystallization process. However, when the crystallization was carried out at high temperatures, it became
difficult to deduce crystallinity values as a function of time directly from the DSC curve. This effect is easy to understand because crystallization becomes very slow resulting in a widespread distribution of the released heat over long time at high crystallization temperatures making it impossible to distinguish. For this reason, isothermal processes were stopped after a certain time when according to prior experience no further significant contribution to the signal is expected and a heating run was performed to yield crystallinity value.

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References