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European Polymer Journal 43 (2007) 599–610

EUROPEAN POLYMER JOURNAL

www.elsevier.com/locate/europolj

Effects of branching characteristics and copolymer composition distribution on non-isothermal crystallization kinetics of metallocene LLDPEs

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Received 30 April 2006; received in revised form 21 October 2006; accepted 22 October 2006
Available online 5 December 2006

Abstract

The effects of branch content (BC) and copolymer composition distribution (CCD) on the non-isothermal crystallization kinetics of metallocene m-LLDPEs were studied using modified Avrami analysis, modulated differential scanning calorimetry (MDSC), and Crystaf. Several m-LLDPEs and an m-HDPE – all having comparable M_w and PDI – were experimented. In addition, a ZN-LLDPE was used for comparison purposes. The branch content, unlike the used cooling rates (2–6 °C/min), significantly affected the crystallization behavior. Crystallization peak temperature, T_c^{peak}, decreased linearly with increasing BC. All the m-LLDPEs showed primary and secondary crystallizations. The secondary crystallization showed to be more pronounced at high BC. The primary crystallization Avrami parameter n for m-HDPE ranged between 3.72 and 4.50, indicating spherulitic crystal growth whereas that for the m-LLDPEs, varied from 2.02 to 5.70. The ZN-LLDPE (having broader composition distribution) offered higher values of T_c^{onset} and T_c^{peak} than the m-LLDPEs with similar BC, M_w, and PDI. It, unlike the m-LLDPEs and m-HDPE, fairly agreed with the crystallization kinetic model proposed by Liu et al. The lamella thickness of the m-LLDPEs, L, calculated as per Gibbs–Thomson equation, showed to be in the range 2–16 nm, depending on BC and it decreased approximately following the relationship: L (nm) = 15.0 $e^{(-0.0498BC)}$.

Keywords: Metallocene LLDPE; Branch content; Copolymer composition distribution (CCD); Non-isothermal crystallization; MDSC

1. Introduction

The relationship between microstructure and properties of polymer requires, among other factors, investigation of melting and crystallization behaviors. The microstructure plays an important role in determining the polymer mechanical, optical, rheological, and thermal properties. The study of polymer crystallization kinetics is significant from theoretical and practical points of view [1–9]. A number of studies have been devoted to explore the crystallization behavior of ethylene/α-olefin copolymers [10–15].

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doi:10.1016/j.eurpolymj.2006.10.019

The influence of molecular weight (M_w), molecular weight distribution (MWD), the branch type, the branch content (BC), and crystallization conditions on the crystallization behavior of ethylene/α-olefin copolymers have been studied for a long time [16–28]. Most of these studies used Ziegler–Natta linear low density polyethylenes (ZN-LLDPEs). Due to the random comonomer composition and sequence distribution, and intermolecular heterogeneity of ZN-LLDPEs, the effects of the individual factors on the crystallization phenomenon is difficult to separate. For example, for a given short chain BC, the super molecular structure becomes more poorly developed with an increase in the content of high M_w species [16]. On the other hand, with the increase in BC, a lamella first becomes shorter, then segmented, and eventually disintegrates into small crystallites [29]. Also, the previous studies used primarily fractions of conventional heterogeneous ZN-LLDPEs [16,18,21,25,30].

Metallocene LLDPEs (m-LLDPEs) generally have homogeneous composition distribution and narrow MWD. The single-site metallocene catalyst prevents the formation of high and low M_w tails in the resulting copolymers; consequently, m-LLDPEs have more controlled structure. Several studies on the thermal properties and molecular structure of m-LLDPEs have been reported by different authors [26,29,31–41]. Most of these studies focused on the influence of short chain branch distribution [26,31–33,37,40,41] on melting and crystallization kinetics, particularly of a single polymer and its fractions using different fractionation techniques [35,36,38–40]. Bensason et al. [29] classified homogeneous ethylene/1-octene copolymers based on comonomer content and reported the melting phenomena and crystal morphology by relating their results to the tensile and dynamic mechanical properties. However, the influence of BC, branch type, and copolymer composition distribution (CCD) on the crystallization kinetics of m-LLDPEs is yet to be studied. This prompted us to undertake the present study. Our objective is to investigate the effects of BC and CCD on the non-isothermal crystallization kinetics of m-LLDPEs (ethylene/1-butene copolymers) using modulated differential scanning calorimetry (MDSC) [34,42–46] and Crystaf [47]. Note that during processing, the molten polymer crystallizes non-isothermally to form the solid end-products; hence, the study of non-isothermal crystallization kinetics is important [38,48,49].

We have used m-LLDPEs having similar M_w and PDI, and BC in the range of 0–42 branches/1000C. A ZN-LLDPE of the same average BC and M_w has been used to highlight the influence of broader composition distribution on the kinetics of non-isothermal crystallization of LLDPEs. A metallocene high density polyethylene m-HDPE (which is a polyethylene homopolymer having linear backbone) with comparable M_w and PDI has been used as a reference.

2. Experimental

2.1. Materials and sample preparation

Four commercial samples of m-LLDPEs, one ZN-LLDPE and one metallocene high density polyethylene m-HDPE were used in this study. Weight average molecular weights (M_w) of all the LLDPEs (both metallocene and ZN) are close to 100 kg/mol and the PDI of the m-LLDPEs is ≅ 2. Table 1 provides molecular characterization data for all of the polyethylene samples. The density and melt index (MI) values were provided by ExxonMobil. The M_w and BC were determined by gel permeation chromatography (GPC) and ^{13}C NMR, respectively. Details about the GPC and NMR characterizations are available in a previous publication [50]. The experimental polymer samples were named according to their branch type and content. For

Table 1
Molecular characterization of the experimental polymer samples

Experimental samples	Density (g/cm^3)	MI (g/10 min)	M_w (kg/mol)	PDI	BC CH$_3$/1000C
m-HDPE	N/A	N/A	122	2.34	–
m-EB15	0.910	1.20	108	1.95	14.50
m-EB19	0.900	1.20	110	1.78	18.50
m-EB37	0.888	2.20	87	2.10	36.62
m-EB42	0.880	0.80	126	1.81	42.00
ZN-EB13	0.918	1.0	118	3.07	13.20