



Blends of ethylene–octene copolymers with different chain architectures – Morphology, thermal and mechanical behavior



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ABSTRACT

Blends of two elastomeric ethylene–octene copolymers with similar octene contents having a random (ORC) and a blocky architecture (OBC) are prepared by melt mixing. The thermal and mechanical properties of ORC, OBC and their blends are investigated by DSC, dynamic mechanical analysis and tensile tests. The morphology of the semi-crystalline samples is studied by AFM and WAXS. Two types of crystals have been observed: (i) Orthorhombic crystals forming lamellae with an estimated thickness of about 13 nm composed mainly of long polyethylene-like sequences of OBC that melt a temperature of about 120 °C and (ii) fringed micellar crystals with a thickness of 2–4 nm formed basically by short polyethylene-like sequences of ORC that have melting temperatures between 30 and 80 °C. The amorphous phase contains a relatively homogeneous mixture of segments of both components indicated by the relatively uniform shape of the loss modulus peaks from dynamic-mechanical measurements for all investigated copolymers and blends. ORC crystallization is hindered in blends as indicated by lower melting enthalpies. This might be related to the high octene content of the amorphous phase at the relevant crystallization temperature as well as geometrical constraints since ORC crystallization occurs in an already semi-crystalline polymer. The results of tensile tests show that the mechanical behavior can be tailored via blend composition and morphology of the semi-crystalline material. The findings clearly indicate that blending is a powerful strategy to optimize the properties of polyolefin-based copolymers.

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1. Introduction

Statistical copolymerization with α -olefins such as hexene or octene is a well known strategy to manipulate the crystallization behavior of polyethylene (PE). This effect is used in case of linear low density polyethylene (LLDPE) to optimize the mechanical and optical properties of these semi-crystalline materials. The influence of α -olefin type and content on these properties has been studied in great detail [1–3]. At crystallinities of 10–20%, which are typical for

ethylene–octene (EO) elastomers, LLDPEs crystallize in form of fringed micelles, often accompanied by the occurrence of a hexagonal crystal structure [3,4]. At higher crystallinities ($X_c \geq 40\%$) orthorhombic crystals forming lamellae and a conventional spherulitic superstructure are observed.

In the past, the production of olefin copolymers on an industrial scale has been basically limited to olefin random copolymers (ORC). Just recently, the new chain shuttling synthesis method of The DOW Chemical Company allowed the production of olefin block copolymers (OBCs) [5]. In this case, EO copolymers are synthesized by using two catalysts with a different octene-selectivity resulting either in (i) chain sequences with a very low octene-content, high crystallinity and high melting temperature ($T_m \approx 120$ °C) or (ii) sequences with a high octene content and almost no crystallinity. A chain shuttling agent allows to change from one catalyst to the other and vice versa during chain growth, leading to a multiblock architecture in one-pot synthesis. Accordingly, the macroscopic properties of olefin block copolymers can be controlled by the chain

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² In memory of Prof. Dr.-Ing. Roland Weidisch, who died in November 2012 at the age of only 47 years. We miss him as mentor, colleague and friend.

shuttling level, the overall octene-content and the hard-soft block ratio [5,6].

At octene contents of about 10 mol%, olefin block copolymers behave like thermoplastic elastomers, whereas crystalline segments act as physical cross-links in the amorphous matrix. Long and flexible chain segments between the crystals, which can stretch easily, lead to higher strain at break and better strain recovery at room temperature compared to random EO copolymers [7]. Hsiao and co-workers found a strong dependence of the chain shuttling level on the tensile properties, especially at elevated temperatures. High chain shuttling levels and more blocks per chain lead to better elastomeric properties, which was attributed to a more efficient molecular bridging between the physical cross-links [8,9].

Blending represents an effective method to tailor the properties of polyolefins such as processability or mechanical behavior. This is related to the fact that mixing or phase separation can occur in the crystalline phase as well as in the amorphous phase of the blend components. What happens is strongly depending on (i) molecular parameters, such as comonomer type and the chain architecture as well as (ii) the processing conditions. Coexistence of crystals with different sizes was commonly found in blends of different random EO copolymers, whereas cocrystallization has been gained by rapid cooling (quenching) [3,10–12]. The situation in the amorphous phase in blends of two different ORC copolymers depends on the comonomer content of both components [13]. Significant differences in their octene contents ($\geq 10\%$) lead to phase separation [10,13,14]. Interestingly, the thermal and mechanical behavior of OBC:ORC blends have not yet been investigated in detail. This is rather surprising since blending offers an easy way to tune the mechanical properties which are of great importance for various applications. Further, synergistic effects can be expected since long (OBC) and short (ORC) flexible blocks are arranged in a non-crystalline matrix like in bimodal networks having advantageous elastomeric properties [15,16].

In this contribution, we report the thermal, mechanical and morphological properties of blends composed of two olefin copolymers with similar comonomer contents but either blocky or random chain architecture. Aim is to study the influence of chain architecture and composition of OBC:ORC blends on mechanical behavior, crystallization and morphology. The results show that application-relevant properties of innovative polyolefin copolymers can be systematically optimized by blending without changing the comonomer content.

2. Experimental

2.1. Materials and processing

Ethylene–octene copolymers with different molecular architectures were provided by The DOW Chemical Company (Horgen, Switzerland). ORC is a random copolymer, in which the octene units are randomly distributed along the polymer chain. OBC is a block copolymer synthesized by chain shuttling polymerization [5] consisting of nearly amorphous blocks with a high octene content and crystallizable blocks with a very low octene content. More detailed information on the ORC and OBC polymers is given in Table 1 and published elsewhere [7].

Blends of OBC and ORC have been compounded by melt mixing for at least 5 min in a minicomponenter (Minilab II, Thermo Scientific) at 190 °C with a screw speed of 100 min⁻¹. The extruded stripes were cut into small pieces with dimensions of 5 × 5 × 1 mm³. Compression molded plates were obtained by (i) melting the blends at 190 °C for 5 min without pressure, (ii) pressing them at the same temperature for 30 s at a pressure of

Table 1
Molecular structure of the used olefin copolymers [7].

| Copolymers | M_w [kg/mol] | PDI | Octene content [%] |
|-------------------------------|----------------|-----|--------------------|
| Olefin block copolymer (OBC) | 124 | 2.1 | 12 |
| Olefin random copolymer (ORC) | 111 | 2.1 | 12 |

30 N/cm² and (iii) subsequent cooling to 40 °C with a rate of 15 K/min while keeping the pressure constant. Before characterization, all samples were stored at room temperature for one week.

2.2. Methods

Calorimetric measurements were performed using a NETZSCH DSC 204 F1 Phoenix at temperatures between –50 and 150 °C with heating and cooling rates of 10 K/min. The crystallinity of the samples is estimated based on the ratio of the measured melting enthalpies to that of perfect PE crystals ($\Delta H_{m,PE} = 290$ J/g) [7]. A DMA Q800 (TA Instruments) was used for dynamic mechanical analysis (DMA) in tension mode between –100 and 50 °C with a heating rate of 2 K/min, a strain amplitude of 0.5% and a measurement frequency of 1 Hz. Tensile tests were performed according to DIN EN ISO 527 on at least five specimens using a Zwick/Roell Z010. The initial gage length was 28 mm and the crosshead speed was held constant at 28 mm/min. For Atomic Force Microscopy (AFM), small areas of the compression molded plates were trimmed with a cryo-ultramicrotome (PT-PC Powertome with CR-X cryo unit, RMC products) at a temperature of –100 °C in order to minimize the irreversible deformation of the blend morphology. AFM images were obtained by a JPK Nanowizard II in tapping mode using super sharp silicon tips with tip radii ≥ 2 nm. Wide-angle X-ray scattering (WAXS) experiments were carried out on a Bruker Nanostar using X-ray radiation with a wavelength of $\lambda = 1.54$ Å and a sample-to-detector distance of 124 mm. A silver behenate standard was used for scattering angle calibration.

3. Results

3.1. Thermal properties

First heating scans from DSC measurements on the olefin random copolymer (ORC), the olefin block copolymer (OBC) and their blends are shown in Fig. 1. Pure OBC exhibits a pronounced

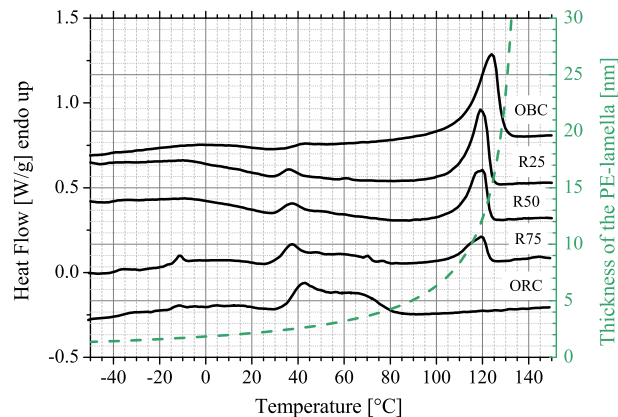


Fig. 1. DSC curves for copolymers and OBC:ORC blends obtained during the first heating. The curves are vertically shifted for better visualization. The dotted line represents the dependence of the crystal thickness on the melting temperature of an orthogonal PE crystal, based on the Broadhurst-equation (1) [17].

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