

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 to 4 nm formed basically by short polyethylene-like sequences of ORC that have melting temperatures between 30 to 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.

Keywords: olefin copolymers thermoplastic elastomer mechanical behavior polymer crystallization morphology

[†]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.

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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, 2, 3] At crystallinities of 10 to 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 spherulithic 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 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] Hsaio 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 polyolefines such as process-

ability 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, 11, 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 has 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]

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

Blends of OBC and ORC have been compounded by melt mixing for at least 5 minutes 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 minutes without pressure, (ii) pressing them at the same temperature for 30 s at a pressure of 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 Figure 1. Pure OBC exhibits a pronounced melting peak at $T_m \approx 124^\circ\text{C}$, which is only 5 to 10 K lower than melting temperatures of classical, orthorhombic PE crystals. The melting enthalpy of OBC is found to be 38 J/g, which corresponds to an overall crystallinity of $X_c = 13.1\%$, estimated based on the measured melting enthalpy of perfect PE crystals ($\Delta H_{m,PE} = 290\text{ J/g}$). The crystalline fraction of the random copolymer ORC is melting between 30 and 80°C . The melting peak has a bimodal shape which could in principle originate either from different thicknesses of the crystalline lamellae (resulting in different melting temperatures according to the Gibbs-Thompson effect [17]) or from the coexistence of different crystalline forms (polymorphs).[18] At low temperatures ($-20 \leq T \leq 20^\circ\text{C}$), ORC shows additional small peaks which may be due to melting of extremely small crystals or structural relaxation phenomena in the (rigid) amorphous phase.

The DSC heating scans for blends exhibit similar features as found for pure OBC and ORC. In particular, all blends show two melting peaks. One melting peak occurs at temperatures between 30 and 80°C (low-temperature peak, LTP) and the other one at about 120°C (high temperature peak, HTP). A detailed analysis of the melting enthalpies (Figure 2) confirms that the melting enthalpy of the high temperature peak, $\Delta H_{m,1}$, is increasing linearly with the OBC content while that of the low temperature peak, $\Delta H_{m,2}$, is decreasing non-linearly. The obtained melting temperatures, $T_{m,1}$ and $T_{m,2}$, the melting enthalpies, $\Delta H_{m,1}$ and $\Delta H_{m,2}$, and the estimated crystallinities, X_1 and X_2 , are given for both melting peaks in Table 2.

In order to approximate the crystal thickness and to estimate the number of methylene units n along the c -axis of the orthorhombic PE-like crystal, we used the Broadhurst equation [17]

$$T_m^n = T_m^\infty \frac{a+n}{b+n} \quad (1)$$

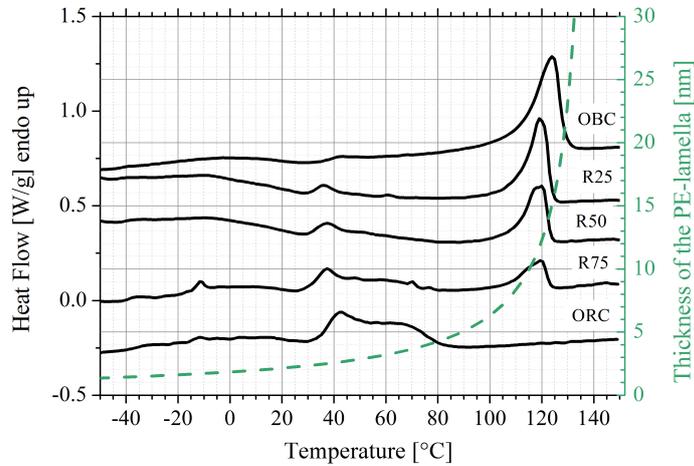


Figure 1: DSC curves of the OBC:ORC blends during the first heating. The curves are vertically shifted for better visualization. The dotted line represents the dependence of the crystal thickness on the melting temperature of an orthogonal PE crystal, based on the Broadhurst-equation (1).[17]

where $T_m^\infty = 140.15$ °C is the melting point of an ideal PE crystal with infinite lamella thickness and $a = 1.5$ and $b = 5.0$ are fit parameters to describe the melting behavior of alkanes and PE crystals.[17] This function is plotted in the DSC diagram (Figure 1) in order to compare the melting temperatures directly with the corresponding crystal thicknesses. Low-temperature peaks at 30 to 80 °C related to ORC indicate crystal thickness between 2 to 4 nm or respectively 15 to 30 methylene units per crystalline stem. These results are in good accordance with the findings by Mauler *et al.*, who found an average number of 16 successive ethylene units (i.e. $n = 32$ methylene units) along the main chain in a similar ORC by ^{13}C -NMR.[2] Hence, one can conclude that the undisturbed PE-like sequences in ORC chains do crystallize partly in a fully stretched conformation which results in a fringed-micellar or bundle-like morphology, as described by Hiltner and co-workers.[3] The high melting temperature of OBC of $T_m \approx 124$ °C corresponds to a crystal thickness of around 13 nm and about 100 methylene units per stem. Considering that the octene units are usually not incorporated in the crystals, one can conclude that the PE-like sequences in the investigated OBC have at least this average length. The coexistence of two distinct melting regions in the DSC heating scans of blends shows that independent crystalline phases exist related

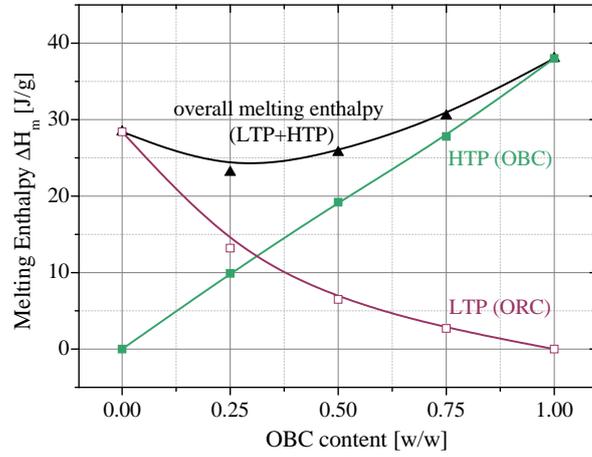


Figure 2: Melting enthalpies of the high temperature OBC-peak (HTP, filled rectangles), the low temperature ORC-peak (LTP, open rectangles) and their sum (triangles) versus the fraction of OBC. The solid lines are guides to the eye and illustrate the overall trend.

Table 2: Parameters taken from DSC scans on olefin copolymer blends

Sample	High temperature peak			Low temperature peak			X_{total} [%]
	$T_{m,1}$ [°C]	$\Delta H_{m,1}$ [J/g]	X_1 [%]	$T_{m,2}$ [°C]	$\Delta H_{m,2}$ [J/g]	X_2 [%]	
OBC	123.9	38.0	13.1	–	–	–	13.1
R25	119.0	27.8	9.6	36.3	2.7	0.9	10.5
R50	120.0	19.2	6.6	37.9	6.5	2.3	8.9
R75	119.3	9.9	3.4	37.3	13.2	4.5	7.9
ORC	–	–	–	43.1	28.4	9.8	9.8

to OBC and ORC. The PE-like blocks of OBC with low octene-contents form obviously really thick crystals (13 nm). Additional melting peaks at temperatures ≤ 20 °C were not found for OBC indicating that the octene-rich OBC-block hardly crystallizes.

The linear increase of the melting enthalpy $\Delta H_{m,1}$ of the high temperature peak (HTP) in the DSC heating scans for blends with increasing OBC content evidences the weak influence of the ORC phase on the crystallization of OBC chains. The simultaneous non-linear decrease of the melting enthalpy $\Delta H_{m,2}$ of the low temperature peak (LTP) with increasing OBC content indicates that the presence of OBC hinders the crystallization of relatively short PE-like sequences in ORC during cooling. This is somehow an expected finding since the crystallization in the random copolymer occurs at lower temperatures than that in the block copolymer. Consequently, crystallization of short PE-like sequences in ORC chains occurs in amorphous domains between already existing crystals formed by parts of the OBC chains. Crystallization under these conditions is surely more complicated than crystallization in pure ORC since the amorphous regions between OBC crystals (i) have nanoscopic dimensions, (ii) contain more entanglements and (iii) a significantly larger amount of octene units which are not incorporated in the OBC crystals. Hence, growth of ORC crystals in blends is kinetically hindered by geometrical constraints as well as the presence of non-crystallizable units. Moreover, nucleation is less efficient due to the limited size of the amorphous regions. These effects together should be responsible for the reduced crystallinity of the ORC chains in blends with OBC keeping all other conditions constant. Note that cocrystallization of PE-like sequences of ORC and OBC obviously does not occur, although they differ only in length.

3.2. Mechanical properties

Dynamic-Mechanical Analysis. Storage modulus E' and loss modulus E'' taken from dynamic-mechanical measurements on OBC, R50 and ORC in the temperature range from -100 to -30 °C are presented in Figure 3. All samples show a distinct relaxation process at temperatures between -60 and -50 °C which is indicated by a significant drop in $E'(T)$ and a corresponding peak in $E''(T)$. The storage modulus decreases from 1 GPa at temperatures significantly below $T_{\alpha}^{1\text{Hz}}$ to $E' \approx 10$ MPa above. This feature reflects the dynamic glass transition (α relaxation) of the amor-

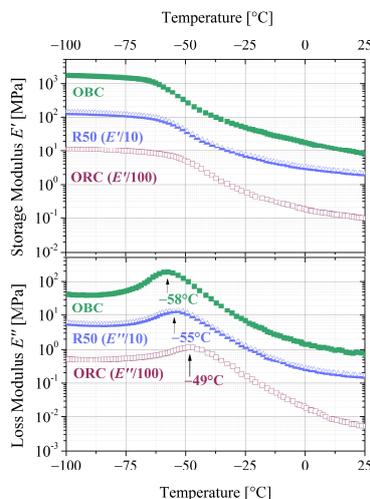


Figure 3: Dynamic mechanical analysis data for OBC, R50 and ORC in the temperature range near the dynamic glass transition temperature $T_{\alpha}^{1\text{Hz}}$. The arrows indicate the increase of $T_{\alpha}^{1\text{Hz}}$ with increasing OBC content.

phous phase occurring in this temperature range at a frequency of 1 Hz. It should be noted that the dynamic glass transition temperature $T_{\alpha}^{1\text{Hz}}$ of the amorphous phase in OBC is lower than that of ORC and that the transition in blends occurs at intermediate temperatures. Moreover, there is no significant difference in the E'' peak width and no clear evidence for the existence of two superimposed E'' peaks in case of blends. This points to a relatively homogeneous mixing of ORC and OBC segments in the amorphous phase. The lower $T_{\alpha}^{1\text{Hz}}$ value for OBC indicates that a larger fraction of octene units in the amorphous domains is leading to a lower softening temperature compared to pure polyethylene ($T_g \approx -36\text{ °C}$ [19]). This may be related to internal plasticization of main chains by alkyl side groups known from many other homologous series [20], probably accompanied by a decrease of the average density of the amorphous domains. Considering the concentration of octene units in the amorphous domains, this interpretation is in line with the discussion about trends in the DSC data.

Tensile Tests. Representative stress-strain curves for the investigated olefin copolymers are depicted in Figure 4. All samples show an elastomeric property profile. While the behavior at small strains ($\leq 100\%$) is only weakly changing, the large strain behavior is significantly depending on blend composition. In particular, the onset of strain hardening and the strain at break are affected.

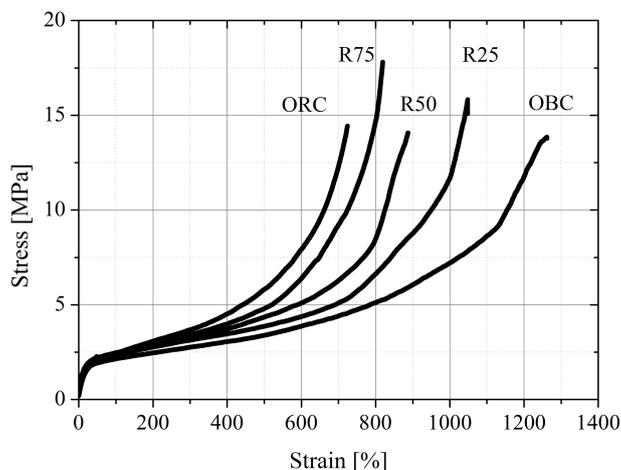


Figure 4: Representative stress-strain curves of OBC, ORC and their blends.

Average values for important mechanical parameters are plotted versus OBC content in Figure 5. Pure ORC samples show the highest values of the 300 % secant modulus but the lowest strain at break. In blends, the strain at break is systematically increasing while the 300 % modulus is decreasing with increasing OBC contents. The tensile strength, however, seems to be only slightly affected by blend composition (Figure 5).

In general, the results show that the mechanical properties can be easily tuned by changing the blend composition. Although the average octene content of all investigated copolymer systems is nearly identical, systematic trends are found in the mechanical behavior depending on the OBC:ORC ratio. This underlines a strong influence of crystallinity and morphology. Considering the dependence of mechanical properties on composition, one can conclude that the stress-strain behavior at large strains ($\geq 100\%$) mainly depends on the average length of (flexible) chain segments between two adjacent crystallites acting as physical cross-links.[21] The blocky molecular architecture of OBC chains results in longer flexible chain segments between the relatively large, but rare crystals. In contrast, ORC contains much shorter non-crystallizable chain sequences where ethylene and octene units are truly randomly arranged. Hence, the flexible chain segments between numerous small ORC crystals (forming fringed micelles[3, 7]) should be also much shorter. This leads to higher repulsive forces due to entropy elasticity and hence to higher stresses compared

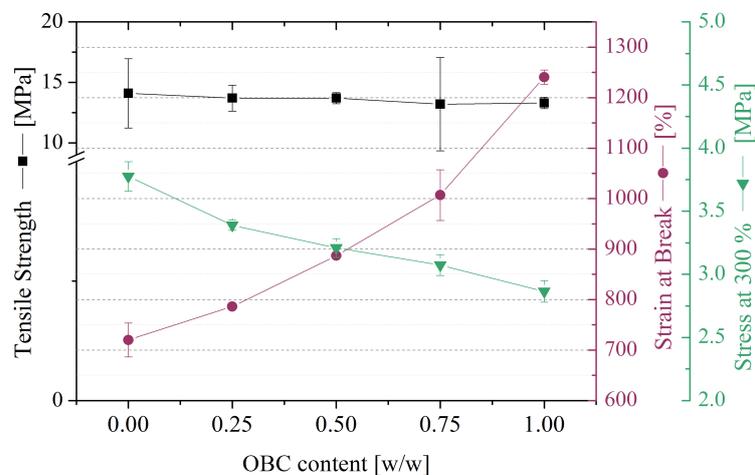


Figure 5: Mechanical properties as a function of the OBC-content. The solid lines are guides to the eye highlighting trends.

to OBC. This picture gives a consistent explanation for the systematic changes regarding 300 % secant modulus and strain at break in OBC:ORC blends.

3.3. Structural properties

Wide Angle X-Ray Scattering (WAXS). WAXS pattern for all investigated olefin copolymer samples are given in Figure 6. Two Bragg peaks are found for OBC at about $2\theta \approx 20.6^\circ$ and 23° which corresponds to spacings of 0.43 and 0.38 nm, respectively. These peaks are attributed to the (110) and (200) reflexes of an orthorhombic lattice, like known for PE. In pure ORC, the first peak is blurred and seems to be slightly shifted to smaller scattering angles while the second reflex is nearly absent. This finding is in agreement with the recent observation that hexagonal and orthorhombic crystals coexist in ORC systems with similar chain architectures.[8] In blends, the intensity of the sharp (110) peak as well as the (200) peak corresponding to orthorhombic OBC crystals are systematically increasing with increasing OBC content.[22] This points to a relatively independent crystallization of PE-like sequences in OBC chains in agreement with the DSC results reported above. Compared to literature, there are obviously no dramatic changes in the crystallization behavior of the individual OBC[7] and ORC[8] chains in blends apart from a reduced crystallinity of the ORC component found by DSC. Hence, two polymorphic forms of polyolefin

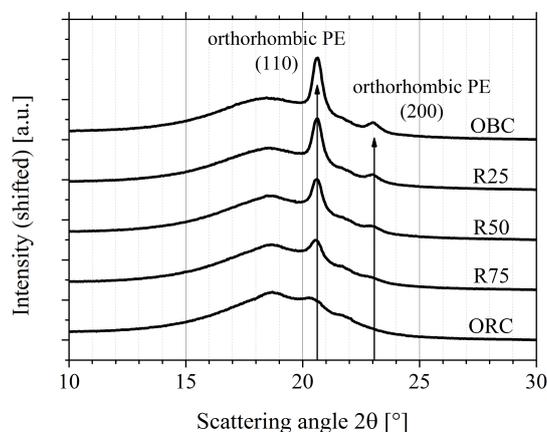


Figure 6: WAXS pattern for the olefin blends. The patterns are vertically shifted for the sake of clarity.

crystals are observed in blends – (i) large orthorhombic crystals originating from long PE-like blocks in OBC and (ii) small crystals mainly formed by short PE-like sequences in ORC, which is supposed to form fringed micelles. Based on the detected scattering pattern, it is hard to decide whether the ORC crystals are mainly orthorhombically or hexagonally packed.

Atomic Force Microscopy. Figure 7 shows AFM phase contrast images of OBC (a), ORC (e) and their blends (b–d). For OBC, the crystals that are formed by the blocks with a very low octene content are seen as needle-like structures. Crystalline and amorphous phases have different hardness and can be detected relatively easily by AFM, in particular in phase contrast images. The average thickness of the crystals, estimated based on measurements of at least 50 representative crystals, are found to be 14 ± 4 nm. In R25, the concentration of large crystals is reduced due to blending with ORC. This trend continues with increasing ORC content until large crystals can not be observed anymore for pure ORC by AFM (Figure 7e). The crystals formed by ORC chains cannot be fully resolved by this method, due to convolution effects of the small crystals (2 to 4 nm) and the AFM tip (radius ≥ 2 nm). What is seen in the images for ORC is only a certain network-like morphology, which indicates the existence of small crystals dispersed homogeneously in the material. In general, the AFM images for the different olefin copolymers and blends confirm that what has been concluded from other methods. The average OBC crystal thickness (14 nm) is in good agreement with the values estimated based on DSC melting temperatures (13 nm, cf. Figure 1). The

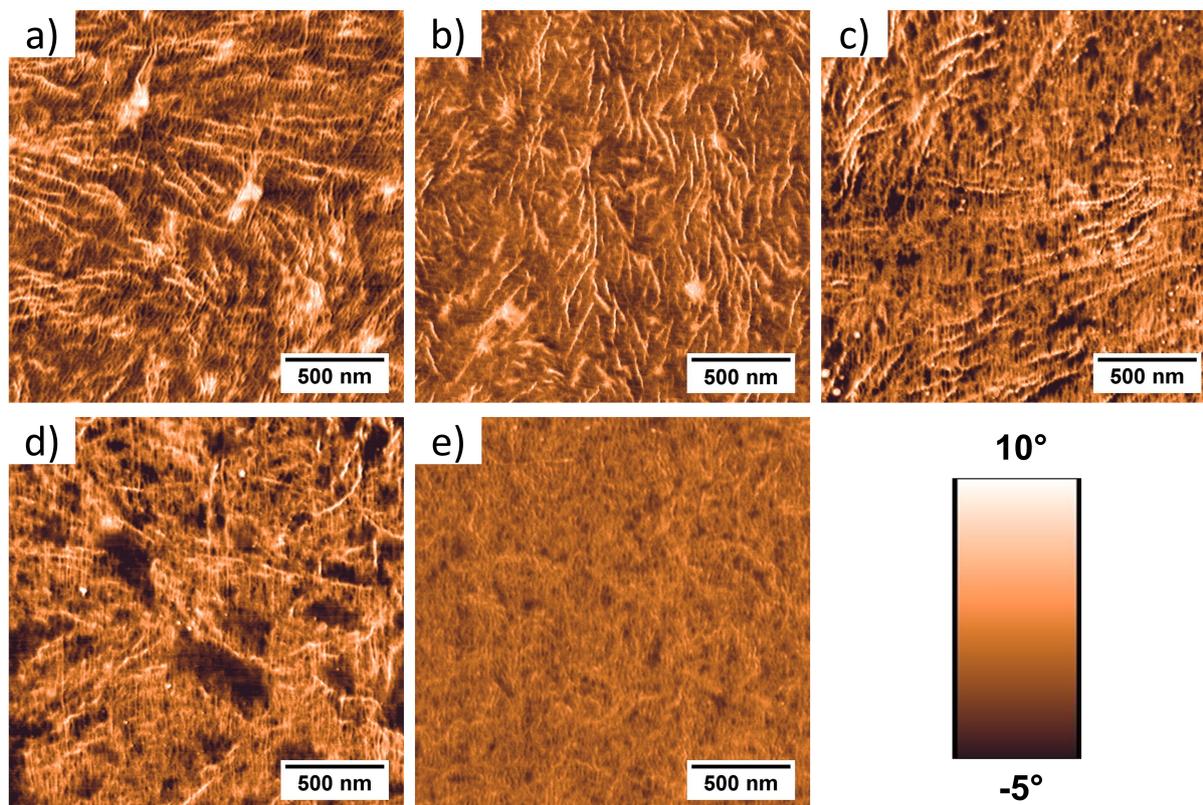


Figure 7: AFM phase images showing $2 \times 2 \mu\text{m}$ scans of (a) OBC, (e) ORC and (b – d) their blends R25, R50 and R75. The color bar is identical for all images and covers the range from -5 to 10° .

AFM images of the blends show big OBC crystals as well as a network-like structure attributed to small ORC crystals. Depending on composition, the features are differently pronounced. This finding is in accordance with the discussion about well distinguishable ORC and OBC crystals based on data from WAXS and DSC.

4. Discussion and Conclusions

Summarizing the results of our calorimetric, mechanical and morphological investigations on melt-mixed and extruded blends of ethylene-octene copolymers with random (ORC) and blocky (OBC) chain architecture one can conclude that these materials show a three phase structure as sketched in Figure 8. The main phases, which have to be distinguished, are:

A **OBC crystals** = orthorhombically packed PE-like crystals with a thickness of 10 to 15 nm

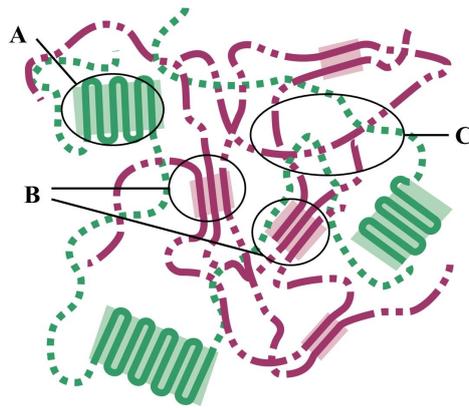


Figure 8: Sketch of the proposed morphology of olefin copolymer blends. OBC and ORC chains are shown as green and red lines, respectively. Chain segments with high octene content are displayed as dotted lines while solid lines represent nearly undisturbed, crystallizable PE segments. **A** - thick OBC crystals arranged as folded lamellae; **B** - thin ORC crystals arranged in form of fringed micelles; **C** - amorphous phase.

along the crystallographic *c*-axis having a melting temperature of about 120 °C. These crystals are obviously formed by long methylene sequences in the OBC block with a very low octene content. The concentration of these crystals is nearly proportional to the OBC content in blends. In accordance with prior results from Hiltner *et al.*, the formation of folded lamellae of OBC is expected.[6]

B ORC crystals = small PE-like crystals with a thickness of about 2 to 4 nm having melting temperatures in the range from 30 to 80 °C. These crystals should originate from the crystallization of short PE-like sequences in ORC chains to fringed micelles or bundles in accordance with literature.[3, 7] Whether these crystals are mainly orthorhombic or hexagonal can not be decided based on the experiments performed here. A mixture of hexagonal and orthorhombic crystals has been reported for similar ORC systems in the literature.[8] There are clear indications that the fraction of crystalline ORC sequences per chain is smaller in case of ORC:OBC blends compared to pure ORC. This might be due to geometrical constraints and an actually higher octene content in the amorphous phase of OBC:ORC blends containing already PE-like OBC crystals at the crystallization temperature of the relevant ORC sequences. This should hinder ORC crystal growth and reduce the nucleation efficiency.

C Amorphous phase = quasi-homogeneous mixture of segments from both components of the

investigated ORC:OBC blends. There is no clear evidence for a separation of chain segments from ORC and OBC in the amorphous phase. Bimodal loss modulus peaks or significant peak broadening which would be expected for well defined domains with typical dimensions larger than a very few nanometer are not observed. The observed relaxation temperatures of -60 to -50 °C are quite similar to those reported for other ethylene-octene copolymers [3, 6] and only 15 to 25 K lower than T_g values reported for fully amorphous PE.[19]

It is interesting to find three phases in binary blends made of two polymeric components which contain two identical monomers. Although the mixed copolymers contain even the same average amount of ethylene and octene, the macroscopic properties of the blends vary strongly and systematically with chain architecture as well as blend composition. The results presented in this paper nicely demonstrate the importance of crystallinity and crystal morphology for the properties of macroscopic samples and show also how a systematic modification of the crystal size distribution can be used to tune the mechanical behavior. Blending of olefin blocky and random copolymers, OBC and ORC, is a obviously a simple but efficient way to manipulate material properties. ORC rich blends have a higher secant modulus (300 %) but lower strain at break and undergo strain hardening at larger strains. OBC rich blends have slightly lower secant moduli but significantly larger values for the strain at break. This underlines not only the large potential of innovative copolymerization techniques and olefin-based copolymers produced using such synthesis routes but shows also that blending can be a powerful strategy to control the morphology of the semi-crystalline polymers and to optimize their properties.

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