Regulation of crystalline morphologies and mechanical properties of olefin multiblock copolymers by blending polymer with similar architecture of constituent blocks

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In this work, the crystalline morphologies and mechanical properties of olefin multiblock copolymer (OBC) were regulated by blending with polymers possessing architecture similar to the constituent blocks. In order to understand the influence of multiblock architecture on the interaction between OBC and blended substances, ethylene-octene random copolymer (ORC) with similar crystallinity was blended with corresponding substances for comparison. We found that polyethylene (PE) chains, which possessed architecture resembling hard blocks, were inclined to cocrystallize with OBC and form remarkable lamellar structure in their blends. On the contrary, they aggregated together in ORC matrix and developed crystals similar to pure PE. The distinct crystalline properties were closely correlated to their state in the melt as revealed by Time–Temperature superposition examinations. The results of tensile tests exhibited that the strength of OBC samples could be improved without great depression of tenacity when appropriate amount of PE was blended. This might be ascribed to the good compatibility between added PE and OBC hard blocks considering their similar chain architecture. The findings contribute to understanding the relationship between morphologies and apparent properties of multiblock copolymer-based blends, which can be significant to achieve target mechanical properties for multiblock copolymers by a simply blending approach.

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1. Introduction

Block copolymers, consisting of covalently bonded chemically dissimilar sequences, exhibit highly periodic microphase separated structures according to their molecular architecture [1–5]. While for semi-crystalline block copolymers, the ultimate mechanical properties do not depend on their molecular architecture directly but rather on crystalline morphologies, which is in turn determined by molecular architecture and sample history in a quite complicated way. Compared with traditional diblock or triblock semi-crystalline copolymers, semi-crystalline multiblock copolymers have attracted great interest recently due to the unique structure. Owing to the larger number of chemical restrictions imposed on the domains of multiblock copolymer, the shape and size of domains are less stable [6], and the crystalline morphologies can be diversiform. Consequently, the mechanical properties are quite distinct compared to conventional polymers with simple architectures, generating an expanding range of practical applications such as elastomers [7,8], compatibilizers for blends of immiscible homopolymers [9,10], as well as pressure-sensitive adhesives [11,12].

Tailoring the morphology for desired processing and mechanical properties is a topic of fundamental importance with innumerable industrial applications for block copolymers. This is usually achieved by changing the length or relative volume fraction of each component during the synthesizing [13–16]. However, it is comparatively difficult and uneconomical to change the process of synthesizing, especially for copolymers with sophisticated architecture such as multiblock copolymers. As for multiblock copolymers, changing the block number, block length or volume...
fraction may have enormous influence on the synthesizing method, and impurities as well as side reactions are not negligible with increasing block numbers [17]. An elegant approach to regulate the properties of block copolymers lies in blending with polymers possessing architecture similar to one of the constituent blocks [15,18–22]. This allows targeting a multitude of bulk morphologies based on one single block copolymer by simply adjusting the overall blend composition, leading to optimized end-use properties. Actually, new materials with tailored features are also possible to be created through blending with elaborate design. Hashimoto et al. [20,23] reported that when an A-homopolymer was blended with AB diblock copolymers, the distribution of the homopolymer in the A-microdomain was closely correlated to the ratio between the homopolymer with A-block in diblock copolymer, and had obvious impacts on the final block copolymer morphologies. Nojima et al. [21] found that when the homopolymer was uniformly mixed with the constitute blocks of a double crystalline diblock copolymer, they simultaneously formed a mixed crystal; while separate crystals of homopolymer might form with nonuniform localization, leading to distinct crystalline morphologies. In order to design a membrane layers with nanometer-sized pores, Schacher et al. [22] achieved tetragonally perforated lamellae bulk morphology by blending a triblock terpolymer with polymers comprising the same composition of certain block. The pore diameter can be quite regular and pore permeability can respond to pH and temperature. These pioneering works manifest that control of morphology and regulation of end-use properties can be achieved for diblock or triblock copolymers with simple blending approach. However, up to now, little investigations have paid attention to the application of blending approach to multiblock copolymers, which may be attributed to the complex influence factors of morphology as well as properties for multiblock copolymers. Considering the complexity of synthesizing for multiblock copolymers [13,14,17,24], it is quite essential to understand the interactions between multiblock matrix and blended polymers and regulate the apparent properties without changing the synthesizing process.

In this work, we attempt to explore the possibility of regulating the crystalline morphologies and apparent properties of olefin multiblock copolymer (OBC) by simply blending approach. OBC comprises crystallizable hard blocks with low octene content, alternating with amorphous soft block containing high octene concentration. It is synthesized by the Dow Chemical Company via chain shuttling technology, in which two catalysts with different octene-selectivity and chain shuttling agent allowing for changing between the two catalysts are indispensable [25–30]. Although the hard and soft blocks of OBC are distinct in comonomer content, they are comparatively short and can be partially miscible in the melt. On the other hand, the hard blocks are long enough to form chain-folded lamellar crystals with a relatively high melting temperature [29,31]. The lamellae can be arranged into space-filling spherulites even when the crystallinity is as low as 7%, and the impinged spherulites show straight boundaries, which indicates that OBC experiences heterogeneous nucleation with nuclei of similar activity [29,31,32]. This morphology resembles crystallization from a miscible melt, and the phenomenon is distinct from that of traditional block copolymers. During crystallization, the aggregation of hard blocks forces segregation of the noncrystallizable soft blocks into the interlamellar regions. Investigations have found that the block length, octene content as well as the ratio between hard and soft blocks is closely correlated to the apparent properties of this promising elastomer [33–40]. In consideration of the difficulty of altering block architecture during synthesizing, we aim to adjust the apparent properties by blending with PE, which possesses architecture similar to hard blocks of OBC. Based on our exploration, we found that PE chains were inclined to cocrystallize with OBC, which made it possible to increase strength without great depression of tenacity. We believe this work sheds light on comprehending the interaction between multiblock copolymers and blended polymers, and it also demonstrates the feasibility of regulating the physical properties of multiblock copolymers by a blending approach.

2. Experimental

2.1. Materials

OBC material synthesized via chain-shuttling technology is a commercial grade product produced by Dow Chemical Company. It has a number-average molecular weight (Mn) of 76 kg/mol, the hard block content is approximately 18 wt% while the octene content is 2.1 mol% in hard blocks and 19.5 mol% in soft blocks (determined from 13C NMR). ORC (Engage 8842), an ethylene-octene random copolymer, is from Dow Chemical Company. The density is 0.857 g/cm3 and the melt flow rate is 1.0 g/10 min (190 °C, 2.16 kg), HDPE (5200B) with density of 0.960 g/cm3 and melt flow rate of 0.11 g/10 min (190 °C, 2.16 kg) is from Yanshan. The Mn is 12.2 kg/mol and the Mw is 194.8 kg/mol. In order to avoid the nonuniformity brought by melt blending, we selected the method of solution blending to prepare the mixture of OBC or ORC and PE. The detailed procedure was as follows: first, the OBC/ORC and PE were stirred in hot xylene (140 °C) for 2 h to yield a homogeneous solution. Secondly, the powders of OBC/ORC–PE composites were precipitated by excess cold methanol. After filtration, the powders obtained were dried in vacuum for 24 h to remove the residue xylene. The composites containing 10, 20, and 50 wt% of PE were denoted as OBC/ORC–PE10, OBC/ORC–PE20, OBC/ORC–PE50, respectively. In order for comparison, neat OBC and ORC underwent the same process as well. Then all the samples were compression molded to film with thickness of 0.4 mm at 180 °C for subsequent characterizations.

2.2. Characterizations

A Mettler DSC-821e apparatus (Mettler Toledo, Switzerland) was used to evaluate the thermal properties of samples. Each sample with weight of about 5–8 mg was sealed in aluminum pan and all the experiments were carried out in nitrogen atmosphere. The heating rate was always 10 °C/min, while the cooling rate was selected as 2, 5, 10 and 20 °C/min. The tensile testing of dumbbell shaped samples was conducted on a SANS CMT-6503 universal testing machine (Shenzhen, China) with crosshead speed of 50 mm/min at about 20 °C. The capacity of the load cell is 50 N in axial load. A HAAKE MARS III Rotary Rheometer (Thermofisher, Massachusetts) with parallel plate was used to investigate the rheological behavior of OBC/ORC–PE composites. Samples for rheological measurement were prepared by compression-molding to 25-mm disks with powders. Dynamic frequency sweeps were performed over frequency ranging from 0.01 to 100 s⁻¹. The single shear strain of 1.0% and a gap height of 0.35 mm were applied for all measurements.

Wide angle X-ray diffraction (WAXD) measurements were performed using a PANalytical X’pert diffractometer (PANalytical, Netherlands) in a reflection mode with Ni-filtered CuKα radiation (λ = 0.154 nm) under a voltage of 40 kV and a current of 40 mA. Small angle X-ray scattering (SAXS) measurements were performed at the beamline BL16B of the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength was 0.124 nm and a Mar165 CCD detector (2048 × 2048 pixels with pixel size of 80 μm) was employed to collect the SAXS patterns. The exposure time was 30 s
with an additional 5 s for reading and cleaning. The SAXS patterns were integrated as a function of:

\[ q = 4\pi \sin \theta / \lambda \]

where \( q \) is the module of the scattering vector, \( 2\theta \) the scattering angle and \( \lambda \) the wavelength of X-ray.

The morphologies of the samples were observed by Multimode 8 atom force microscope (AFM, Bruker, German) with peak force quantitative nanomechanical property mapping (QNM) mode. Under this mode, the formation of images is based on difference of modulus. Therefore, images with high resolution can be obtained when observing the morphologies of crystallites. The AFM samples were prepared as follows: a piece of molded film was pressed between two silicon slices and heated to melt. Then the film was cooled to 80 °C at 10 °C/min and the crystallization process was accomplished. The film between the two silicon slices was taken out and used for AFM observation. The surface of the film is kept smooth due to the intimate contact with smooth silicon slices.

3. Results and discussion

The heating and cooling thermograms of OBC(ORC)-PE samples with rate of 10 °C/min are shown in Fig. 1, the crystallization and melting temperatures of all the samples are summarized in Table 1. Although the crystallinity of OBC and ORC is quite similar, 5.8% and 5.2% respectively as derived from DSC, they exhibit quite different thermal behaviors when PE is added. As for ORC-PE samples, they exhibit two distinct exothermic and endothermic peaks. The peaks located above 100 °C can be attributed to PE, while the peaks at lower temperatures are ascribed to ORC. It is shown in Table 1 that the crystallization temperatures of ORC decreases slightly with increase of PE content, which demonstrates that the blended PE cannot accelerate the crystallization of ORC. Meanwhile, we also notice that the melting temperatures of pure PE and PE in mixture are quite close, indicating that the thickness of PE lamellae formed in mixture may be similar to that of pure substance. Actually, the melting behaviors of ORC in ORC-PE blend are also similar to that in pure ORC (Fig. 1). Based on the above results, it can be inferred that both ORC and PE have little impact on the other’s thermal behaviors, suggesting limited interaction between them.

With regards to OBC-PE samples, the thermal behaviors can be quite distinct. All the samples exhibit a single exothermic peak, and the crystallization temperatures display a composition-dependent behavior. When 10 wt% PE is added, \( T_c \) increases by nearly 8 °C compared with pure OBC, and the value is further elevated with more PE content. This phenomenon indicates that the blended PE promotes the crystallization of OBC and they tend to crystallize synchronously. It can be seen from Fig. 1(b) that OBC-PE10 also corroborates one endothermic peak, indicating that OBC and PE undergo cocrystallization process and form crystal together during cooling. The cocrystallization in polymers is difficult, and only limited pairs have been reported to cocrystallize [41–45]. In general, there are three requirements for this process: structural similarity, similar potential energies, and almost same crystallization kinetics [46]. As OBC hard blocks and PE possess similar chain architectures in nature and they undergo similar crystallization process, it is reasonable to conjecture that OBC and PE are possible to cocrystallize. With rise of PE content, it is interesting that the endothermic peaks become bimodal, with one peak approaching the melting point of OBC-PE10 and the other close to that of pure PE. The peak at lower temperature is attributed to the cocrystallization formed by OBC and PE, while the other peak may be ascribed to the crystallization of PE aggregates. Extra PE chains cannot fully cocrystallize with OBC; they assemble together and form crystal similar to pure PE. By comparison between OBC-PE and ORC-PE samples, we conclude that although the crystallinity of OBC and ORC is similar, their interactions with OBC are quite distinct, which can be attributed to their different chain architecture.

![Fig. 1. DSC (a) cooling curves and (b) heating curves of OBC-PE samples as well as (c) cooling curves and (d) heating curves of ORC-PE samples.](image-url)
In order to further investigate the crystalline structures of OBC-PE samples, the melting processes after nonisothermally crystallizing at four different cooling rates were characterized. As shown in Fig. 2(a) and (b), only one major endothermic peak can be observed for OBC and OBC-PE10, indicating that PE chains are always inclined to cocrystallize with OBC hard blocks at selected crystallization circumstances. Meanwhile, we notice that the melting peak of OBC-PE10 is sharper and more symmetrical. This can be attributed to that the lamellae formed during cocrystallization of OBC and PE is more regular than that of pure OBC. With regards to OBC-PE20 (Fig. 2(c)) and PE50 (Fig. 2(d)), the bimodal endothermic peaks are clearly visible. It can be figured out that the peak originating from cocrystallization strengthens gradually with decrease of cooling rate. When crystallizing at lower cooling rate, the samples begin crystallizing at higher temperatures and the duration becomes longer. Therefore, the mobility and mixing of chains are more sufficient in this condition. Combined with the variation of peak intensity, it can be concluded that it is beneficial for the occurrence of cocrystallization with enhanced molecular motion.

WAXD patterns of OBC(ORC)-PE samples are given in Fig. 3. As shown in Fig. 3(a), OBC exhibits three diffraction peaks. The strong diffraction peak located at 21.6° corresponds to (110) reflection and the weak diffraction peak located at approximately 24.1 and 29.0° can be attributed to (200) and (210) reflections of polyethylene crystal, respectively [35,36,47,48]. As for PE, the peaks corresponding to (110) and (200) can also be observed, while the intensity of (200) peak is obviously stronger than that in OBC. When OBC and PE are blended, the three diffraction peaks can always be found, and the intensity of (200) peaks increases constantly with PE content. The similar crystalline structures further demonstrate the possibility of cocrystallization and strong interaction between OBC and PE. For comparison, the crystalline structure of ORC and PE are completely distinct. The diffraction peaks of ORC located at 9.8 and 29.0°. In addition, all the peaks of ORC and PE can be distinguished in ORC-PE blends at almost the same locations, indicating that ORC and PE crystallize separately with little interaction.

The morphologies were observed by AFM in peak force QNM mode. This mode maps and distinguishes according to nanomechanical properties, including modulus and adhesion, while simultaneously imaging sample topography at high resolution [49–51]. As the modulus of crystalline and amorphous phase is completely different, the contour profiles of lamellae can be observed clearly. Meanwhile, the probe touches the sample intermittently and the forces applied to the sample can be precisely controlled for this mode. In this way, the damage to samples is

<table>
<thead>
<tr>
<th>Sample</th>
<th>OBC</th>
<th>PE</th>
<th>OBC-PE10</th>
<th>OBC-PE20</th>
<th>OBC-PE50</th>
<th>ORC</th>
<th>ORC-PE10</th>
<th>ORC-PE20</th>
<th>ORC-PE50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc/°C</td>
<td>106.0</td>
<td>116.9</td>
<td>113.9</td>
<td>114.1</td>
<td>116.0</td>
<td>16.7</td>
<td>16.5</td>
<td>14.5</td>
<td>13.3</td>
</tr>
<tr>
<td>Tm/°C</td>
<td>123.0</td>
<td>135.5</td>
<td>126.5</td>
<td>127.8(132.2)</td>
<td>128.5(134.0)</td>
<td>45.2</td>
<td>45.2</td>
<td>43.5</td>
<td>41.5</td>
</tr>
<tr>
<td>Tc(ORC)/°C</td>
<td>108.6</td>
<td>113.0</td>
<td>116.0</td>
<td>131.4</td>
<td>132.5</td>
<td>134.0</td>
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<tr>
<td>Tm(ORC)/°C</td>
<td>108.6</td>
<td>113.0</td>
<td>116.0</td>
<td>131.4</td>
<td>132.5</td>
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Fig. 2: DSC heating curves for OBC-PE samples after crystallizing at four different cooling rates.
chains cannot be fully resolved in Fig. 4(b) due to convolution effects of the small crystallites (2–4 nm) and the AFM tip (radius ≈ 2 nm) [52]. Only a certain network-like morphology can be seen, indicating the existence of small crystallites dispersed homogeneously in the matrix. When 10 or 20 wt% PE is blended, the morphologies can be quite distinct. As for OBC matrix, the lamellae become thicker and much longer. This phenomenon may be correlated to the cocrystallization of OBC and PE, promoting the lamellar growth in OBC. Some large clumpy crystallites can also be found in Fig. 4(e), which may be ascribed to crystallites formed by PE aggregates as revealed by DSC. With regards to ORC matrix, the crystallites are mainly found as clumpy congeries with small amount of lamellae structure, and the size of crystalline congeries in Fig. 4(d) is obviously larger than that in Fig. 4(b). The results reveal that the blended PE has little interaction with ORC matrix; the growth of lamellae is largely confined by ORC matrix and they tend to assemble into crystalline aggregates. With PE content elevated to 50 wt%, the lamellae interlude into continuous networks in OBC matrix. While for ORC matrix, although lamellae structure can be easily found due to the increased quantity of PE, the crystallites are still inclined to aggregate and form dispersed crystalline region. The observation is in accordance with the discussion on different interactions between OBC-PE and ORC-PE samples based on results of WAXD and DSC.

SAXS was performed to examine the arrangement of ordered structures. After Lorentz correction, the scattering peak from the lamellar structure can be clearly seen, as exhibited in Fig. 5. The q value at the scattering peak is utilized to calculate the long period between the adjacent lamellar layers (L).

\[ L = \frac{2\pi}{q} \]

Based on the correlation, the long period of pure OBC and PE is approximately 48.3 nm (q \( \approx \) 0.130 nm\(^{-1}\)) and 31.2 nm (q \( \approx \) 0.201 nm\(^{-1}\)), respectively. It can be figured out that the long period decreases constantly from 48.3 nm of pure OBC to 32.9 nm (q \( \approx \) 0.191 nm\(^{-1}\)) of OBC-PE50 with elevated PE content. Considering the thicker lamellae as revealed by DSC, the amorphous layer decreases obviously when PE is blended, indicating that the added PE tends to aggregate with OBC hard block and forms denser cocry stallites. As for ORC, the peak representing long period is rather broad due to the irregular crystallites. When PE is blended, the broad peak resulting from ORC is partially covered by the peak of PE and becomes difficult to distinguish as a result of its low intensity. The long periods of PE crystallites in the blends are 33.1 (q = 0.190 nm\(^{-1}\)), 33.3 (q = 0.189 nm\(^{-1}\)) and 33.7 (q = 0.186 nm\(^{-1}\)) for ORC-PE10, ORC-PE20 and ORC-PE50, respectively. We notice that the long period in composites is nearly independent of PE content and approaches the value of pure substance. The result indicates that PE chains in ORC-PE samples are inclined to aggregate together, forming domains similar to the state of pure PE.

The large-strain tensile testing results are illustrated in Fig. 6. Both OBC and ORC display typical elastomeric characteristic with no distinctive yield point. The elongation at break of OBC exceeds 1800%, which is larger than that of ORC and demonstrates excellent tenacity and deformation ability. When incorporated with PE, the mechanical properties of the samples change dramatically. As for ORC-PE samples, the tensile strength increases while the elongation at break decrease constantly as the content of PE rises. When the PE content is elevated to 50 wt%, the elongation at break drops below 650%, which is lower than both ORC and PE (beyond 700%). This may be attributed to that the blended PE aggregates together in ORC matrix, inducing defects in their boundary and thus depressing the tenacity. With regards to OBC-PE samples, it can be seen that the tensile strength can be effectively regulated by blending with PE. It is found that OBC-PE10 and OBC-PE20 exhibit similar elongation at break, which is beyond 1600%. According to the above results, it can be concluded that OBC tends to cocrystallize with comparatively small quantity of PE, developing longer and more perfect lamellae. Therefore, the physical network of OBC formed by crystallites persists to a great extent and the tenacity exhibits little variation with 10 or 20 wt% PE. While we also notice that the stress of OBC-PE10 is similar to that of pure OBC at corresponding strains. This phenomenon can be attributed to the fully cocrystallization between PE and OBC hard blocks in OBC-PE10. In this way, the PE chains act as hard blocks rather than reinforcing fillers. As PE chains are not covalently linked to the soft blocks of OBC, they may be exposed to little force during deformation and induce limited change of stress. When 50 wt% PE is blended, the tensile modulus increases dramatically and elongation at break exhibits obvious decrease, while still beyond 1000%. The tensile property of OBC-PE50 may also be correlated to its morphologies. As revealed by AFM, the integral lamellar network develops after blending with 50 wt% PE, leading to elevated strength. Meanwhile, the crystalline network does not exhibits obvious defects owing to the good compatibility between OBC hard blocks and PE. Therefore, the elongation at break of OBC-PE50 still holds a comparatively high value.

The rheological behaviors of samples were explored by dynamic frequency sweeps and temperature sweeps. The strain was
The dynamic temperature sweeps of OBC-PE samples are shown in Fig. 8. The changing tendency of viscosity and storage modulus for OBC-PE samples is quite similar. It can be seen that both the viscosity and storage modulus of OBC-PE10 are lower than that of pure OBC before crystallization, while when 20 or 50 wt% PE is blended, both values increase obviously. This phenomenon is in consistent with the results of dynamic frequency sweeps. The abrupt increase of viscosity and storage modulus indicates the beginning of crystallization. We notice that the crystallization starts at lower temperatures and needs shorter durations after PE is blended, which manifests that PE accelerates the crystallization of OBC to a great extent (Fig. 8).

In this blend system, the starting state of blend melts is indeed of vital importance to the subsequent crystallization. In this work, we try to explore the melting state of the samples through rheological tests [53]. Dynamic frequency sweep tests at different temperatures were conducted and the Time–Temperature superposition (TTS) was examined. It is widely accepted that the rheological response of a material originates from different components or phases in multiple components or multiphase system. Thus, the success of TTS implies that the contributions to the stress from different units are similar or the contributions exhibit weak temperature dependence. Compared to other methods like microscopy measurement [54], rheological measurements usually correspond to longer relaxation (or larger heterogeneity). Therefore, although the success of TTS cannot guarantee the homogeneity of materials, its failure can indicate the appearance of inhomogeneity. In this work, we checked TTS to understand whether the melt of OBC and the melt of OBC (or ORC)/PE blend are homogeneous.

The dynamic modulus of OBC and OBC/PE blend under different temperatures are shown in Fig. 9. All the data have been shifted to the reference temperature $T_{ref} = 135 ^\circ C$, which is higher than crystallization temperatures. The vertical shift factor varies little over the temperature range and can be neglected, and the horizontal shift is determined by superposing the storage modulus at high frequencies to obtain the master curve. The TTS principle works successfully in the experimental temperature range for OBC. The terminal slope of storage modulus is 1.85 in the log–log plot, which is close to that of typical viscoelastic fluid. Both the appearance of typical terminal behavior and the success of TTS imply that mesophase separation is unlikely to happen or extremely weak in pure OBC in the time scale of frequency sweep. The homogenous melt of OBC in this work may be attributed to its low molecular weight as the molecular weight should exceed a threshold molecular weight to induce microphase separation in block copolymers [3,55]. Meanwhile, the low fraction of hard blocks requires much higher molecular weight to initiate evident phase separation based on the classical phase diagram of diblock copolymers. With regards to OBC-PE10, the typical terminal behavior is still seen and no distinct failure of TTS for storage modulus can be distinguished. However, we notice that the curves do not superpose perfectly at extreme low frequencies. This indicates that OBC-PE10 may exhibit weak phase separation. As the content of PE increases, evident failure of TTS is seen below 175 °C for OBC-PE20 and OBC-PE50. Meanwhile, OBC-PE50 exhibits obvious deviation from slope 2 in terminal regime of storage modulus. The failure of TTS via increasing the fraction of PE is reminiscent of the similar effects in microphase separation of diblock or triblock copolymer, which implies that the obvious phase separation occurs in OBC-PE20 and OBC-PE50. As for blend of ORC and PE, it can be seen in Fig. S2 that the curves do not superpose successfully at low frequencies and the TTS for ORC-PE10 fails obviously. Compared with the results of OBC-PE10, we conjecture that phase separation is easier to occur in ORC/PE blend than OBC/PE blend with similar PE fraction.

sufficiently small to insure in the linear viscoelastic regime. The dynamic frequency sweeps of the samples at 180 °C are shown in Fig. 7. The rheological behaviors of ORC and PE at 180 °C are quite similar, and the addition of PE does not change the behaviors of ORC-PE samples obviously. While for OBC, the changes of rheological behaviors are quite interesting. It can be seen that both the viscosity and storage modulus of OBC-PE10 are lower than that of pure OBC, while they increase constantly as the PE content rises. As we know, the viscosity reflects the entanglement of molecules. Therefore, it can be conjectured that the entanglement of OBC-PE10 is weaker than that of pure OBC although PE with higher viscosity is blended. With rise of PE content, more and more PE chains cannot cocrystallize with OBC and viscosity as well as storage modulus increase constantly.

![AFM micrographs of (a) OBC, (b) ORC, (c) OBC-PE10, (d) ORC-PE10, (e) OBC-PE20, (f) ORC-PE20, (g) OBC-PE50, (h) ORC-PE50.](image-url)
We believe the change of viscosity and the formation of cocrystallization are closely correlated to the phase state in the melt. In OBC-PE10, most PE chains are dissolved in OBC matrix. Although the architecture of PE chains is quite similar to OBC hard blocks, they are not chemically linked to OBC soft blocks. Thus the entanglement between PE chains and OBC soft blocks can be relatively weak compared with that between hard blocks and soft blocks, leading to lowing viscosity. With regards to OBC-PE20 and OBC-PE50, strong phase separation occurs in the melts and PE-rich domains form consequently. In this way, the rheological properties of PE can be partially exhibited, which accounts for the rise of viscosity. With regards to the formation of cocrystallization, it has been revealed by the results of DSC that the PE chains tend to form cocrystallites with OBC hard blocks in OBC-PE10, while some PE chains crystallize separately, forming crystallites with similar thickness as pure PE in OBC-PE20 and PE-50. We have known that OBC-PE10 is weakly phase separated in the melt. Most PE chains are dissolved in OBC and can get in contact with OBC hard blocks easily. Considering their similar chain architectures, they are able to form cocrystallites during cooling. However, strong phase separation occurs in OBC-PE20 and OBC-PE50. Large quantities of PE chains aggregate together and form PE-rich domains. In this way, these PE chains are unable to contact OBC hard blocks and thus do not form cocrystallites with OBC.

The above experiments demonstrate that the chains of PE and OBC hard blocks are inclined to cocrystallize, which results in change of morphologies and enhancement of tensile strength without depressing tenacity greatly. Based on our results, the interaction between PE and OBC is schematically depicted in Scheme 1. With regards to OBC, the crystals are formed by hard blocks, which are long ethylene sequences with very low octene content in nature. Short lamellar structure develops as shown in Fig. 4(a). When small quantity of PE is blended, PE chains are inclined to cocrystallize with OBC hard blocks, leading to thicker lamellae and smaller long period. As shown in Fig. 4(c) and (e), much longer lamellae form in OBC-PE blends. While when large quantity of PE is blended, many PE chains may aggregate into PE-rich domains and develop lamellae similar to that of pure PE. The cocrystalline and PE lamellae interlude into continuous network in OBC matrix. We believe the regulation of corresponding mechanical properties is closely correlated to the change of morphologies induced by blending with PE.

4. Conclusions

The crystalline morphologies and mechanical properties of OBC were regulated by blending with PE, which possesses architecture similar to hard blocks. Compared with ORC, in which PE molecules aggregated together in ORC and exhibited little interaction with the matrix, we found that OBC hard blocks were inclined to cocrystallize with blended PE due to the multiblock architecture, generating longer and more perfect lamellae as revealed by AFM. In this condition, the physical network of OBC formed by crystallites
Fig. 7. Frequency dependence of (a) viscosity and (b) storage modulus of OBC-PE samples and (c) viscosity and (d) storage modulus of ORC-PE at 180 °C.

Fig. 8. Temperature dependence of (a) viscosity and (b) storage modulus of OBC-PE samples.

Fig. 9. Shifted storage modulus for (a) OBC, (b) OBC-PE10, (c) OBC-PE20, (d) OBC-PE50.
persistent to a great extent, and thus the elongation at break could hold a comparatively high value with obvious increase of tensile strength. This work explores the interaction between blended polymers and multiblock copolymers, and may be significant to apply the blending approach to regulate the properties of other multiblock copolymers. Furthermore, the blending approach can be effective to design synthesizing process for target mechanical properties as well.

Supporting information available

DSC melting curves of (a) ORC-PE10 and (b) ORC-PE samples at temperature range from 0 and 80°C; Shifted storage modulus for /C14/.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.07.034.

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