



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



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## ABSTRACT

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

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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 polymer 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 ( $M_n$ ) 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  $^{13}\text{C}$  NMR). ORC (Engage 8842), an ethylene-octene random copolymer, is from Dow Chemical Company. The density is 0.857 g/cm<sup>3</sup> and the melt flow rate is 1.0 g/10 min (190 °C, 2.16 kg). HDPE (5200B) with density of 0.960 g/cm<sup>3</sup> and melt flow rate of 0.11 g/10 min (190 °C, 2.16 kg) is from Yanshan. The  $M_n$  is 12.2 kg/mol and the  $M_w$  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<sup>-1</sup>. 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 CuK $\alpha$  radiation ( $\lambda = 0.154$  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  $\times$  2048 pixels with pixel size of 80  $\mu\text{m}$ ) was employed to collect the SAXS patterns. The exposure time was 30 s

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