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Multisite catalyst mediated polymer nanostructure formation and self-reinforced polyethylene reactor blends with improved toughness/stiffness balance

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The design of supported two- and three-site catalysts for ethylene polymerization and tailoring nanophase-separated polyethylene reactor blends represents the key to the development of advanced all-polyethylene nanocomposite materials exhibiting substantially improved performance and high resource-, eco- and energy efficiency. Two or three different single-site catalysts independently produce high density polyethylene (HDPE), ultrahigh molecular weight polyethylene (UHMWPE) and PE wax on the same catalyst support. Since this catalyst-mediated nanophase separation prevents UHMWPE entanglement, typical for conventional homogeneous reactor blends, much higher UHMWPE content up to 30 wt % is incorporated in the presence of PE wax without impairing injection molding. During melt processing the shear-induced oriented UHMWPE crystallization affords shish-kebab-fiber-like nanostructures. This accounts for effective PE self-reinforcement paralleled by simultaneous improvement of stiffness, strength and toughness. Hence, this strategy holds great promise for converting commodity PE into high performance plastics and single component PE composites, entering the performance range currently claimed by glass fiber reinforced PE.

1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) with molar mass greater than one million exhibits an exceptional combination of high toughness, abrasion resistance and low friction, which is far superior to most other plastics. In particular, this is of great interest for applications in lightweight engineering and medical devices [1]. However, owing to its high melt viscosity resulting from massive chain entanglement, special processing by sintering is required. Alternatively, gel-spinning of dilute UHMWPE solutions perfectly aligns UHMWPE chains and produces ultrastrong fibers surpassing the strength of steel fibers [2]. In sharp contrast, classical PE melt processing by extrusion and injection molding, does not form extended chain PE and exhibits inferior toughness/stiffness/strength balance, making use of merely 1–2% of the theoretical PE stiffness. Today, PE requires reinforcement by alien fibers and fillers with much higher densities. In terms of simultaneously improving PE performance, weight saving, facile recycling and sustainability, it is highly desirable to produce self-reinforced PE as single-component ("all-PE") composites, reinforced with in-situ ultrastrong extended chain PE fiber-like structures, which are formed by shear-induced oriented crystallization during conventional melt processing. Most strategies towards all-polyolefin composites, some of which have led to commercial products, employ special and costly processing technologies such as hot compaction of stretched PE tapes, lamination of fabrics made from drawn PE fibers, solid state extrusion, pressure- and shear-induced 1D- and 2D crystallization [3–7]. Few groups have tackled the challenge of fabricating ultrastrong UHMWPE fibers and all-polyolefin composites directly from a polymerization reactor without requiring costly processing and post-reactor modifications. For example, ultrastrong oriented tapes and fibers were obtained directly from virgin disentangled UHMWPE tailored by catalytic polymerization [8–11]. Aida and others produced

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extended chain PE fibers by ethylene polymerization, termed as extrusion polymerization, on single-site catalysts immobilized in cylindrical pores of mesoporous silica like MCM-41. Here, ethylene polymerization in a confined environment is supposed to reduce entanglement [12–15]. Supporting titanocene on tailored silica supports, prepared by non-hydrolytic sol/gel chemistry, was claimed to produce in-situ UHMWPE fibers [18]. Alternatively, in templating polymerization, catalysts were supported on anisotropic nanomaterials such as carbon nanotubes [16] and electrospun nanofibers [17] in order to create PE nano and micro fibers by mesoscopic shape replication. However, all these intriguing strategies are not yet viable in industrial commodity PE manufacturing, which requires catalyst fragmentation during polymerization to control the growth of micron- and pellet-like PE particles. In fact, PE nanoparticles are highly undesirable, as they would cause severe emission, inhalation and even explosion hazards together with massive reactor fouling. Furthermore, all the above mentioned nanostructured PEs are not processable by classical injection molding. Since more than two decades, it is known that special processing such as melt processing near the polymer melting temperature and the design of special convergent dies and oscillating shear injection produce self-reinforced polyolefins [18–25]. According to model studies on PE/UHMWPE solution blends, the formation of in-situ extended chain UHMWPE shish-kebab fibers is attributed to pressure- and shear-induced oriented PE crystallization [26]. Since UHMWPE has higher chain relaxation time and low crystallization rate, it is elongated during processing in a low viscosity PE melt to form oriented PE shish, which serve as nucleation sites for the lower molecular weight PE with higher crystallization rate, thus producing the PE kebabs.

Tailoring PE molar mass distributions (MWDs) and blending PE together with disentangled, nanophase-separated UHMWPE enables the in-situ UHMWPE shish-kebab-fiber like structure formation during melt processing. Since commercial micron-sized UHMWPE powder does not melt during the short residence time typical for extrusion, classical melt compounding fails to produce PE shish-kebab fiber structures. Moreover, the UHMWPE content (<1 wt %) of commercial PE with bimodal MWD, which are produced in cascade reactors, is insufficient for achieving self-reinforcement. In traditional PE reactor blends, UHMWPE serves as tie molecule, enhancing the fatigue resistance of PE pipes by bonding together PE crystal lamellas [27]. Albeit PE reactor blends with high UHMWPE content are feasible in cascade reactors, they require special processing by compression molding which fails to afford self-reinforcement [28]. In an alternative strategy, multisite catalysts produce PE/UHMWPE reactor blends in a single reactor by combining different catalytically active sites producing PE chains with very different chain lengths. Provided that the sites are independent and do not undergo transmetalation reactions, the PE/UHMWPE weight ratio is exclusively governed by the molar ratio of the different transition metal catalyst precursors. Moreover, owing to the close proximity of the different sites, PE and nanophase-separated UHMWPE are intimately blended together during ethylene polymerization. Unlike much larger micron-sized UHMWPE particles, nanometer-scaled UHMWPE readily melts to form extended PE fibers. This dream of tailoring PE reactor blends in a single reactor by ethylene polymerization on multisite catalysts exists since the 1970's but had been an industrial nightmare at that time. In fact, the complex nature of the early catalyst generations, as evidenced by a multitude of uncontrolled interactions between their catalyst components, accounted for rather ill-defined reactor blend compositions, extremely problematic scale-up and difficult process control. Moreover, most catalysts producing UHMWPE turned out to be highly sensitive to transmetalation, lowering PE molar mass, and also to severe catalyst poisoning by other catalyst components. At the beginning of the 21st century, following the discovery of metallocene single-site catalysts during the 1980's, this multisite catalysis dream has become an industrial reality. Since the individual catalyst components of robust multisite catalysts retain their single-site nature and independently polymerize ethylene, the types and molar ratios of the different transition metal catalyst precursors govern PE molar mass and its MWD [29–31]. Among methylaluminoxane (MAO)-activated single-site catalysts, [1-(8-quinolyl)cyclopentadienyl]CrCl$_2$ (CrQCp) is quite exceptional, as it produces UHMWPE and is unaffected by most other catalyst components. As a consequence, co-supporting CrQCp together with various Zr, Fe and other Cr single-site catalysts on the same support afforded unprecedented precise control of PE's MWD (see Fig. 1). With increasing CrQCp content, the weight fraction of UHMWPE increased without affecting the average molar masses of UHMWPE and the other PE fractions, determined by the choice of the individual single-site catalyst components [32]. Novel PE reactor blends with ultrabroad MWDs, combining UHMWPE with PE wax, became available.

For the first time, this new generation of multisite catalysts enabled tailoring of melt processable PE/UHMWPE reactor blends with high and variable UHMWPE content in a single reactor. Chadwick and Rastogi co-supported [1-(8-quinolyl)indenyl]CrCl$_2$ together with [{(2-chloro-4,6-dimethyphenyl)N=C(Me)}$_2$C$_5$H$_3$N]FeCl$_2$ on MgCl$_2$/AlEt$_n$(OEt)$_{3\text{-}n}$ to produce PE reactor blends with bimodal MWDs and high UHMWPE content, which was varied as a function of the Cr/Fe molar ratio. Only upon drawing of the resulting PE reactor blends in a second process step, following compression molding at a temperature between 137 °C and 142 °C near the PE melting temperature, in-situ extended chain PE shish-kebab fiber structures were detected. Processing by classical injection molding was not reported [33]. In this work we report on designing two- and three-site catalysts producing “all-PE composites” with high UHMWPE content, which previously was thought to be unfeasible in classical injection molding.

2. Experimental section

2.1. Characterization and materials

Differential scanning calorimetry was performed using a DSC 6200 from Seiko Instruments within a temperature range of −70 to 170 °C and a heating/cooling rate of 10 K min^{-1}. Melting points and

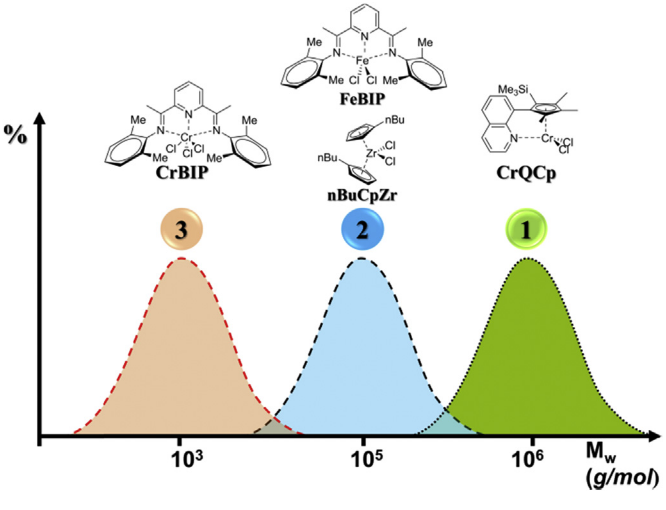

Fig. 1. Tailoring PE with bi- and trimodal MWDs by varying the type and the molar mixing ratio of single site catalysts.