



Melt processing and structural manipulation of highly linear disentangled ultrahigh molecular weight polyethylene

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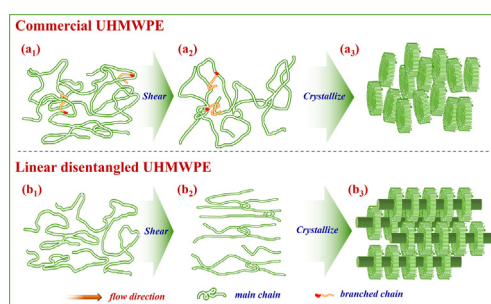
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HIGHLIGHTS

- Nascent UHMWPE with linear structure and low disentanglement was melt processed.
- Large amounts of interlocked shish-kebabs were induced by intense shear flow.
- Mechanical performance was significantly advanced in the structured UHMWPE.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 22 July 2016

Received in revised form 31 December 2016

Accepted 31 December 2016

Available online 3 January 2017

Keywords:

Ultrahigh molecular weight polyethylene

Melt processing

Structural manipulation

Self-reinforcement

Interlocked shish-kebabs

Oriented lamellae

ABSTRACT

Melt processing of commercial ultrahigh molecular weight polyethylene (UHMWPE, $M_w > 10^6$ g/mol) is an insurmountable bottleneck due to the extremely high melt viscosity arising from its numerous chain entanglements. In the current work, we demonstrated that a UHMWPE ($M_w = \sim 3.4 \times 10^6$ g/mol) with a highly linear structure and low entanglements synthesized by a single-active-site Ziegler–Natta catalyst can be melt injection molded without the aid of any additives and, more strikingly, structurally manipulated by means of an intensive shear flow during the packing stage of injection molding. Therewith, large amounts of self-reinforced superstructures, i.e. shish-kebabs and oriented lamellae, were generated in bulk UHMWPE. Appealing interlocked shish-kebabs appeared due to the overstocked shishes that made the epitaxial kebabs penetrate into each other. The self-reinforced superstructures, together with the eliminated structural defects and the increased crystallinity, brought about considerable mechanical enhancement. In particular, the yield strength and ultimate tensile strength of structured linear disentangled UHMWPE were increased by 75% and 71%, from 23.3 ± 0.2 and 40.4 ± 0.6 MPa for compression-molded counterpart to 40.8 ± 1.3 and 69.0 ± 0.8 MPa, respectively. Our current effort makes a pivotal breakthrough in efficient fabrication of high-performance UHMWPE parts, holding a great prospect towards the application in severe conditions and the instructive effects on synthesis in return.

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1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) is a unique polymer with outstanding mechanical properties, high abrasion resistance, good biocompatibility and chemical inertness

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[1–3]. It has been widely used in, but not limited to, engineering applications [4,5], such as automotive and bottling sectors, and biomedical applications [6–9], such as total joint arthroplasty in orthopedic and spine implants. Nonetheless, there poses a substantial dilemma that the improvement in mechanical performance with increasing molar mass comes at the expense of processability. The extremely high molecular weight of UHMWPE (usually exceeding 1 million g/mol) results in a very high viscosity that precludes manufacturing UHMWPE components via thermoplastic processing techniques, such as injection molding and extrusion [10,11]. In this regard, the use of external processing fields, particularly flow fields, to manipulate the hierarchical structure, is far from being practical. Currently, only the low-efficiency quasi-static approaches, i.e., ram extrusion and compression molding are viable to consolidate nascent UHMWPE [2]. These techniques mainly sinter the UHMWPE granules at an elevated temperature and high pressure for a long time [12]. Such long-time exposure at high temperature may increase the risk of molecular chain scission and oxidation, jeopardizing the performance of the final product [13]. Moreover, these processing methods leave undesirable fusion defects or grain boundaries in the final product [6,14], which may serve as initiation sites for cracks and trigger the failure of the material under long-term and reciprocated loadings [15].

It has been firmly established that the extremely high melt viscosity of commercial UHMWPE roots from the considerable number of physical entanglements deriving from the intertwined chains that grow from adjacent active sites on one heterogeneous Ziegler–Natta catalyst upon polymerization [16]. The high entanglement density gravely restrains the mobility of molecular chains. In this context, largely decreasing the number of entanglements per chain is envisaged as a feasible route for the improvement of the processability. At present, the most widely used strategy at present is to dissolve the polymer into a suitable organic solvent below the so-called overlap concentration, usually in excess of 50 times the volume of UHMWPE [17]. The UHMWPE in the disentangled state is allowed to be drawn/spun. In this context, existing commercial routes, such as gel spinning, were successfully introduced to acquire high-modulus, high-strength UHMWPE fibers by controlling the chain orientation [18]; however, the utilization and extraction of massive solvents in the processing is raising concerns due to the environment and health risks. Blending UHMWPE with low-viscosity polymers, such as high density polyethylene (HDPE) [19], polypropylene [20], and polyethylene glycol [21], is also a possible solution to dilute the entanglements. Here arises an obstacle about the effective dispersion of the low-viscosity polymers due to the vast mismatch between the viscosities of the blend components. To circumvent this problem, a solid-state shear pulverization proposed by Diop et al. was demonstrated to effectively mix, in an industrial output, up to 50 wt% UHMWPE with HDPE [22]. Such blends were readily processed by normal extrusion and/or injection molding.

Recently, an advanced approach has been proposed to directly prepare nascent UHMWPE with low entanglements by tailoring the molecular architecture upon polymerization. By utilizing a single-site catalyst, a growing alkyl chain could crystallize into a folded-chain crystal itself when synthesized at low polymerization temperature and at low catalyst concentration. As long as the spatial distance between the growing chains is kept far enough, the monomolecular crystals of a polymer can be formed, giving rise to a lower initial melt viscosity compared to the entangled state [23,24]. Rastogi et al. synthesized this sort of less-entangled powder by using a homogeneous metallocene and post-metallocene single-site catalyst system [23]. Nonetheless, inclusion of a homogeneous catalyst is hampered by reactor fouling, the consumption of high amounts of co-catalyst, and technical obstacles related to the transition from heterogeneous to homogeneous catalytic sys-

tems [25]. In recent studies, Tang et al. ameliorated the heterogeneous catalyst route using a single-active-site Ziegler–Natta catalyst to synthesize a linear disentangled UHMWPE with low entanglements at low temperatures [26,27]. In this catalyst, a coordination group-containing salicylaldehyde or substituted salicylaldehyde derivative is used as the electron donor. The catalyst is prepared by introducing a pre-treated carrier (silica), a metallic compound (TiCl_4) and the electron donor into a magnesium chloride (MgCl_2)/tetrahydrofuran solution and then post-treating the product. Crucially, this technological leap avoids equipment renewal and achieves the steady commercial-scale yield.

Linear UHMWPE with less entanglements has been demonstrated to possess better semisolid-state processability (processability at temperatures below or around its melting point) than commercial UHMWPE in a temperature window of 120–145 °C [10,25]. An intriguing question that arises here is whether melt processing of linear disentangled UHMWPE is even available. This solution would be attractive both academically and commercially since it would offer a compelling opportunity to efficiently fabricate UHMWPE and also to further enhance its mechanical properties via structural manipulation. This is because the properties of a semicrystalline polymer are not only related to the molecular architecture, but also to the crystalline morphology and structure solidified during the processing [28].

In this contribution, we first attempted to evaluate the melt processability of nascent linear disentangled UHMWPE, and encouragingly found that it could be melt injection molded. There-with, significant progress was made towards the achievement of numerous interlocked shish-kebabs and oriented lamellae in neat UHMWPE by exerting an intensive shear flow during the packing stage of injection molding. Mechanical properties of the structured linear disentangled UHMWPE were improved notably. In particular, its yield strength and ultimate tensile strength (UTS) climbed by 75% and 71%, respectively, from 23.3 ± 0.2 and 40.4 ± 0.6 MPa for compression-molded UHMWPE to 40.8 ± 1.3 and 69.0 ± 0.8 MPa.

2. Material and methods

2.1. Material

Linear disentangled UHMWPE with a viscosity-average molecular weight of $\sim 3.4 \times 10^6$ g/mol was synthesized using single-active-site Ziegler–Natta catalyst system [26,27], and was kindly provided by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. The commercial UHMWPE, purchased from Samsung General Chemicals Corporation, Ltd., Korea was used as a control, which has a viscosity-average molecular weight of $\sim 6.1 \times 10^6$ g/mol. The ^{13}C Solid state NMR spectra shows that the linear disentangled UHMWPE has a highly linear chain structure (Fig. S1a) and commercial UHMWPE shows a certain of branching (Fig. S1b). The ultralow molecular weight polyethylene (ULMWPE) was supplied by Petroleum & Chemical Corporation, China, whose weight-average molecular weight was 2.8×10^4 g/mol, and the melt flow rate is 45 g/10 min (0.325 kg, 190 °C).

2.2. Sample preparation

Linear disentangled UHMWPE powders were firstly pelletized by co-rotating twin screw extruder (Nanjing Rubber & Plastics Machinery Plant Co. Ltd., China) in the temperature range of 130–260 °C from hopper to die at a constant screw speed of 130 rpm. The extruded pellets were dried completely and then injection molded by a modified injection molding technique, named oscillation shear injection molding (OSIM). Compared to

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