



Phase behavior and alignment transition of ultra high molecular weight polyethylene/polyamide 6 blends under extensional and shear flow



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ABSTRACT

Herein, we have, for the first time, presented detailed comparative studies on complex phase behavior and alignment transition of ultra high molecular weight polyethylene/polyamide 6 (UHMWPE/PA6) blends under unconventional extensional flow and traditional shear flow by combined atomistic and mesoscopic simulation. The Flory-huggins interaction parameter χ , a bridge between atomistic and mesoscopic simulation, was calculated based on atomistic simulation, taking into account the chemical constitution of UHMWPE/PA6 blends. It is found that these blends with differential mass fraction are preferentially aligned into parallel or perpendicular orientations with zero flow. When subjected to extensional (pressure-driven) flow, the aligned aggregates reorient and these elongated aggregates are divided into discrete micelles, leading to the appearance of a thinner layer and a more homogeneous phase at a high pressure. In sharp contrast, when the mesoscopic behaviors were imposed by a shear flow over a series of shear rates, the blend systems preferentially form micelle-like structures at low shear rate, similar to the case under pressure-driven force, and transform to transverse lamella alignment with further increasing shear rate to $\dot{\gamma} = 0.1$, which indicates that the shear flow not only induces the orientation of alignments, but also regulates the ordered distribution of aggregates.

1. Introduction

Ultra high molecular weight polyethylene (UHMWPE) offers superior toughness, high abrasion resistance, low friction coefficient, low moisture uptake and excellent chemical stability, demonstrating a variety of technological applications ranging from bearing components and super tough engineering plastics to medical materials in total joint replacement [1]. One of the fundamental drawbacks of UHMWPE is the extremely high melt viscosity, which does not allow the use of the conventional processing techniques [2,3]. Therefore, its engineering applications are severely constrained to some extent. An effective and convenient route is to reduce the melt viscosity by mixing UHMWPE with normal molecular weight polymer such as high density polyethylene (HDPE) [4], low density polyethylene (LDPE) [5], polypropylene (PP) [6] and polyamide (PA). Some efforts have been made to reduce UHMWPE viscosity while retaining or even enhancing its mechanical properties. For example, Liu et al. [7,8] studied wear performance of UHMWPE/PA blends using pin-on-disc method and investigated the influence of operating parameters such as sliding distance, counter surface roughness, load and sliding speed, on the wear

performance of blends. Yao et al. [9] reported the melt blends of PA6 with UHMWPE, where a significant reduction in domain size and improvements in mechanical properties were obtained by using maleic anhydride grafted HDPE as a compatibilizer. In earlier work by Cheng et al. [10], the microstructure-related properties of recycled UHMWPE/PA6 blends were evaluated using Fourier transform infrared imaging and dynamic mechanical analysis. However, to our knowledge, the detailed information on molecular structure and intermolecular interaction are still been poorly understood.

For the industrial production of UHMWPE, screw extrusion technology has been widely used, which is based on friction-drag conveying mechanism dominated by shear deformation. So far, the dynamic evolution of a wide variety of systems under shear deformation has been well studied, including polymer melts [11–13], polymer layers [14,15], polymer-based composites [16,17], suspensions [18,19] and so on, whether in experiment, in theory or in simulation. Nevertheless, most previous processing technique based on the shear flow usually suffered from severe thermal oxidative degradation and melt fracture. Recently, a novel polymer processing machine known as eccentric rotor extruder is developed where a number of eccentric rotor plasticizing

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and conveying units replace the traditional screw, dominated by extensional deformation. Compared with the conventional screw extruder, this technology evolution has distinct advantage such as efficient positive displacement conveying and distributive mixing [20–22], which avoids UHMWPE decomposition induced by ultra strong mechanical action, reduces the duration of the processing, improves the blending performance and promotes the industrial production of UHMWPE-based materials. Therefore, it is important, both for practical and designing purposes, to analyze the conveying characteristic in this extensional flow field. However, understanding of the conveying characteristic from theoretical aspect is still obscure. Especially, the phase morphology and aggregation structure under extensional fields are still lacking because of the strong dependence on the experimental conditions as well as the absence of effective approaches. Fortunately, computer simulations are applicable to address these problems, such as molecular dynamics (MD) and dissipative particle dynamics (DPD). The DPD method is a mesoscopic simulation technique for complex flows that can study systems over larger length and time scales than classical MD methods, with the molecular weight in the range of thousands of g/mol, but the crucial input parameters in DPD simulation can be obtained from MD methods although UHMWPE was not investigated before at atomistic level due to the extremely long chain.

Phase morphology and interfacial behaviors significantly influence rheological and mechanical properties of materials and two-phase morphology is beneficial to viscosity reduction and mechanical maintenance for UHMWPE-based blends [2,23,24]. Herein, the main contribution of this work is to present complex phase behavior and alignment transition of UHMWPE/PA6 blends with respect to extensional fields by means of a combined MD methods and DPD simulation in contrast to the case induced by shear, given that the extensional fields are encountered in eccentric rotor extrusion technology.

2. Simulation models and protocols

2.1. Molecular dynamics simulation

MD simulations were performed to investigate the atomistic models of UHMWPE/PA6 blends using Materials studio. In the first step, the PE was firstly built with different chain lengths and a cubic simulation box was constructed with the Amorphous Cell program. For each system, the initial density was set as 1.0 g/cm³. Initially energy minimization of each unit cell was accomplished by means of smart minimization method to eliminate the local non-equilibrium. The convergence level was set as 0.001 kcal/mol. The structures were subjected to a 10-circle thermal annealing from 300 to 600 K and then back to 300 K with 5 K interval to further relax local hot-spots and achieve equilibrium. Afterwards, MD simulation was performed at 298 K and 0.0001 GPa for 100 ps, with a time step of 1 fs, using canonical particle number (N), pressure (P) and temperature (T) (NPT) ensemble, followed by 500 ps NVE (V: volume; E: energy) MD simulation at 412 K for UHMWPE and 497 K for PA6. Trajectories were saved every 5 ps and the final 10 ps configurations were used for analysis of binding energy, and radius distribution function. During the whole simulation process, Berendsen method [25] was adopted for maintaining the temperature, pressure and the energy. The condensed-phase optimized molecular potentials for atomistic simulation studies II (COMPASS II) force field was used for computing the interatomic interactions. If the temperature fluctuation in the initial configuration exceeds 24 K at 298 K for simulation in the NPT ensemble, it was discarded and a new one was attempted.

Owing to the computer limitation, MD simulation could not be performed with the actual size of polymer. Thus, a minimum molecular size chosen should be sufficient to represent the real polymer system [26]. To determine an appropriate PE chain length, the density and solubility parameters (δ) of PE were examined as a function of chain lengths. The δ is defined as the root of the cohesive energy density (CED), where the CED is the ratio between the calculated cohesive

energy (E_{coh}) and unit volume (V) of polymer system, as shown in Eq. (1):

$$\delta = \sqrt{CED} = \sqrt{\frac{E_{coh}}{V}} \quad (1)$$

2.2. Mesoscopic simulation

In consideration of variation of PA6 concentration in UHMWPE/PA6 blends, the change in energy during mixing per unit volume is expressed by Eq. (2)[27].

$$\Delta E_{mix} = \phi_A \left(\frac{E_{coh}}{V} \right)_A + \phi_B \left(\frac{E_{coh}}{V} \right)_B - \left(\frac{E_{coh}}{V} \right)_{mix} \quad (2)$$

The terms in parenthesis represent the cohesive energy density of the pure polymer (A and B) and the blend (mix). Φ_A and Φ_B are the volume fraction of bead i and j, namely, $\Phi_A + \Phi_B = 1$.

Thus, the Flory-huggins interaction parameter (χ) of UHMWPE and PA6 pairs can be estimated from the solubility parameter using Eq. (3) [28]

$$\chi = \left(\frac{\Delta E_{mix}}{RT\phi_A\phi_B} \right) V_m \quad (3)$$

where V_m is the average molar volume of the beads.

Then the repulsive parameter α_{ij} between different types of beads is calculated by Eq. (4). When i equals to j, the repulsive parameter α_{ii} between two identical type beads is given by Eq. (5).

$$\alpha_{ij} \approx \alpha_{ii} + 3.27\chi_{ij} \quad (4)$$

$$\alpha_{ii} = \frac{75k_B T}{\rho} \quad (5)$$

where ρ is the bead number-density chosen as 3 and the conservative interaction potential, $k_B T$, is chosen as 1.

In order to further probe the miscibility details of UHMWPE/PA6 blends, Mesocite program was applied to calculate the phase separation dynamics of the blends at the mesoscopic level, which provides the ability to run energy, geometry optimization, dynamics, shear and DPD calculation on mesoscale systems. For UHMWPE and PA6, a PE chain can be described by N_{DPD} , number of beads in DPD simulation. The N_{DPD} is determined by the degree of polymerization and the characteristic ratio (C_n) of the polymer, as shown in Eq. (6).

$$N_{DPD} = \frac{M_p}{M_m C_n} \quad (6)$$

where M_p is the polymer molecular weight, M_m is the monomer weight and C_n is the characteristic ratio.

The DPD simulations were carried out in NVT ensembles, in which the periodic boundary conditions are applied at three directions. The standard way to model shear flow is by applying the Lees-Edwards [29] boundary condition where periodic boundaries are employed in the X and Y directions, as detailed in Fig. 1a. The change of box shape from orthogonal to triclinic induces shear flow $V_y(x)$ in the the Y direction and velocity gradient in the X direction. Δy and L_x represent the displacement in Y direction and the edge length in the X direction, respectively. Based the force analysis on the materials in extensional flow by Qu et al. [30], it is found that a force is exerted on the materials and related pressure is generated, in which the normal pressure is in proportion to the force. In order to establish extensional flow in DPD, a force in the Z direction was imposed on each bead to drive the flow. This body force corresponded to the application of a pressure drop along the length L_z of the simulation box, as depicted in Fig. 1b. The responses of melt pressure to rotor speed and die pressure in real timescales were explored by Yin et al. [22]. Experimental results show that the oscillation amplitude of melt pressure is increase with the increase of rotor speed and slightly influenced by die pressure. In general,

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