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MELT SPINNING OF POLYETHYLENE COMPOSITE FIBERS CONTAINING DISENTANGLED ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE

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ABSTRACT

The commercial entangled ultra-high molecular weight polyethylene (UHMWPE) shows a high degree of entanglement in macromolecular chains, and our research group used the modified Ziegler-Natta catalyst to prepare UHMWPE with a low degree of entanglement to improve its melt processability. The application on plate-like material formed by injection or hot pressing has been explored, and at present we would like to expand the application field to fibers and textiles. The disentangled UHMWPE is added into the high-density polyethylene (HDPE) matrix by using twin screw extrusion for subsequent melt spinning process. The experimental results show that the addition of ultra-high molecular weight polyethylene improves the mechanical properties of fibers, and the effect varies with the addition amount. The addition amount of UHMWPE is optimized as 45 wt.%, which significantly improves the tensile strength of HDPE from 3.7 to 7.7 cN/dtex.

KEYWORDS

Melt spinning, ultra-high molecular weight polyethylene (UHMWPE), disentanglement.

INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) fiber is lightweight and high-strength, with outstanding impact resistance and cutting toughness. It is widely used in defense, aerospace, sports, marine and other fields. The high entanglement density of UHMWPE molecular chains hinders long-range motion, which greatly affects the melt rheology, crystallization behavior, glass transition, and solid-state mechanical behavior of the polymer. Therefore, dissolving polymers in a solvent, e.g. decalin, is the most common disentanglement method, and the polymer chains exhibit different degrees of disentanglement. Gel spinning and dry spinning with the help of semi-dilute solution is currently the main method for industrial production of UHMWPE fibers. However, it is unavoidable to use a large amount of solvent, usually more than 50 times the volume of the polymer, and the subsequent steps require extraction, separation and drying, which is difficult to meet the requirements of environmentally friendly production.

Commercial UHMWPE is generally prepared by a slurry polymerization process under the action of a heterogeneous Ziegler-Natta catalyst supported by $MgCl_2$. The active sites dispersed on the carrier are very close together, and the polyethylene molecular chains growing on the adjacent active sites entangle

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with each other, resulting in an excessively high entanglement density. Our research group has carried out a lot of research on the synthesis of disentangled UHMWPE using a new Ziegler-Natta catalyst [1,2]. From the perspective of heterogeneous catalyst active center separation, the blocking agent polysilsesquioxane (POSS) is loaded on the surface of the traditional Ziegler-Natta heterogeneous catalyst, and the blocking agent isolates the supported active sites, enabling the preparation of disentanglement UHMWPE (dis-UHMWPE) nascent particles at high temperature and high activity. Compared with commercial entangled UHMWPE, dis-UHMWPE has greatly improved molecular chain motion and self-diffusion ability, and macroscopically reduced viscosity, showing differentiated rheological properties, and can better adapt to melt processing.

Topological entanglement is a key factor in controlling polymer melt dynamics, giving an opportunity for melt processing of high molecular weight polyethylene. Since ultra-high molecular weight polyethylene is very easy to restore the entangled state at high temperature, a high fraction of polymers with lower molecular weight are often added to help the polymer to be easily processed in actual production, where UHMWPE plays the role of a reinforcing modifier. In our previous work, disentangled UHMWPE has been incorporated into HDPE and LLDPE [3,4]. The molecular weight and entanglement of high molecular weight polyethylene affect the improvement effect of the matrix. The dis-UHMWPE has a more excellent chain diffusion ability and more extendable during shear flow, promoting the shish-kebab structure leading to better mechanical properties.

We further extend our research work to the field of melt spinning. Past researchers have generally used commercial entangled UHMWPE for melt spinning. Reducing the entanglement density of molecular chains is possible to reduce the apparent viscosity of the melt, enhance the solid-state stretchability of fibers, widen the thermal processing temperature window, and improve the tensile strength and modulus. The adjustment of entanglement state is also the key to improving the structure of fiber aggregates. For example, molecular chains are significantly disentangled in the later stage of thermal stretching, highly oriented along the stretching direction. Herein, we introduce some exploration works related to this research direction.

MATERIALS AND METHODS

Material

HDPE powder was purchased from Sinopec Group with the brand of HDPE-5000S. The melt flow index rate (MFR) is 2.2 g/10 min (190 °C, 10 kg), and its density is 0.95 g/cm^3. A weakly entangled UHMWPE ($M_w=1.5\times10^6$ g/mol) was synthesized based on our previous work [1]. An antioxidant formula was deployed by compounding Irganox 1010 and Irgafos P168 (J&K Chemical Corp).

Sample preparation

HDPE/UHMWPE blends with 0.7 wt% of antioxidant were prepared by melt compounding, and meanwhile a certain amount of flow modifier was incorporated into the matrix. The polymer was melt-blended and granulated in a co-rotating twin-screw extruder at the temperature of 245°C, and the rotation speed was set as 110 rpm. The weight fractions of UHMWPE in the blends are 30, 45, and 60%, where the samples are denoted as 30%UPE, 45%UPE and 60%UPE, respectively. The pellets of neat HDPE and blends were fed and spun in a single screw melt spinning machine in 280°C with the spinning speed of 1 m/min to obtain nascent fibers. The nascent fibers were drawn at the temperature of 120°C to obtain the finished fiber. During the subsequent hot-drawing process, the fibers were drawn 3 times.

Mechanical properties

The mechanical properties of the fibers were tested with a single fiber strength tester (Laizhou YG061FQ). The tensile speed was 200 mm/min and the gauge distance was set as 10 mm. 20 independent tensile tests were carried out and the average values were calculated.

Scanning electron microscopy observation

Scanning electron microscopy (Hitachi S4800) was used to evaluate the surface morphology of the fibers. The fiber surface was rinsed with alcohol and sticked on the sample stage with conductive adhesive. The testing voltage for SEM was set as 5.0 kV.

Differential scanning calorimetry measurement

The melting and crystallization behavior of each blend was determined using differential scanning calorimetry (TA DSC 25). 7.0 mg of samples were encapsulated in aluminum pans and measured under dry nitrogen atmosphere. It was heated at a rate of 10°C /min from 30 to 190°C and held at 190°C for 5 min. Afterwards, it was cooled at a rate of 10°C /min to 30°C.

RESULTS AND DISCUSSION

We adopted different contents of disentangled UHMWPE to optimize the HDPE melt spinning system, and the mechanical performance of the obtained fibers is illustrated in Figure 1. The addition of dis-UHMWPE has a positive effect on the mechanical properties of the HDPE fibers, and the reinforcing effect is different depending on the UHMWPE content. With the addition of 30% UHMWPE, the tensile strength of the fibers is slightly increased over 5 cN/dtex. When 45% UHMWPE is incorporated, the reinforcement effect is the most ideal, and the tensile strength reaches 7.7 cN/dtex. However, with the continuous increase of the addition amount, the mechanical properties of the fibers are gradually deteriorated. In terms of elongation at break, the addition of UHMWPE reduces the ductility of the fibers. It demonstrates that for UHMWPE-enhanced HDPE system, the choice of UHMWPE addition amount is crucial to the mechanical performance of the final product.

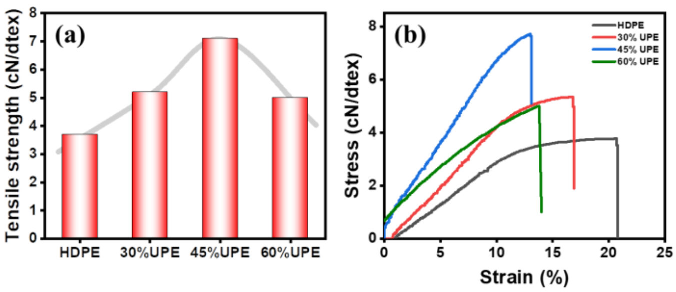

Figure 1. (a) tensile strength of the melt-spun fibers, (b) stress-strain curves of the melt-spun fibers.

We used the scanning electron microscope to observe the surface morphology of the fibers, and the related images are shown in Figure 2.

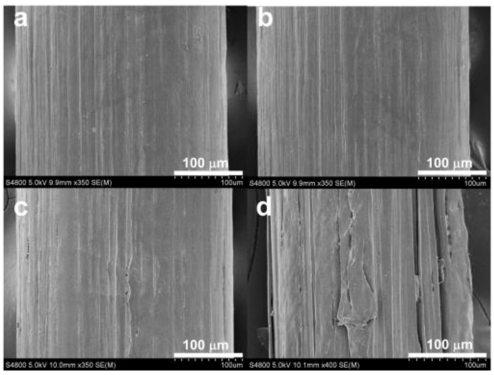

Figure 2. Surface morphology of the melt-spun polyethylene fibers (a: HDPE, b: 30%UPE, c: 45%UPE, d: 60%UPE).

Due to the uniformity of the basic parameter settings of the melt spinning experiment, the diameters of the fibers in each group are similar in the range of around 320 microns, except for the sample with the highest ultra-high molecular weight additions (60%). Different content of ultra-high molecular weight polyethylene has different effects on the surface morphology of fibers. When the content of UHMWPE is lower (30%), the surface morphology of the spun fibers is hardly affected. When the addition amount continues to increase, some defects appear on the surface, such as small cracks and holes, but the effect is still relatively small. When the content is as high as 60%, many obvious defects appear on the surface, and it can be inferred that the fibers have experienced a relatively severe melt fracture phenomenon when the melt exits the spinneret hole. Split parts can even be observed, probably due to poor compatibility between UHMWPE and HDPE. It leads to poorer mechanical properties of the composite fibers.

To extract the parameters of the aggregate structure of the fibers, we used DSC to calculate the crystallinity of the fibers, and the results are demonstrated in Figure 3. It is found that the crystallinity of the masterbatch obtained by twin-screw extrusion remains at the level of about 57%-59%, where the crystallinity of 45%UPE is slightly higher as 58.8%. The thermal drawing process widens the gap in the crystallinity of the fibers with different fractions of UHMWPE. The crystallinity of 45%UPE fibers increases sharply to 78.1%, hinting that some oriented crystalline structures efficiently generate and grow. Fewer defects and better aggregate structure make the 45%UPE fibers perform well in mechanical properties.

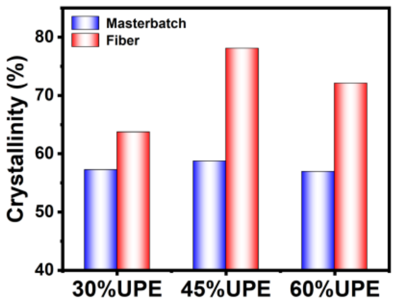

Figure 3. Crystallinity comparison of blended masterbatch and corresponding fibers.

CONCLUSION

We successfully prepare HDPE fibers reinforced by disentangled UHMWPE and find that the tensile strength of the fibers can be greatly improved. Our future work will focus on revealing the relationship between the aggregate structure and mechanical properties of the fibers, and further looking for the characteristics of disentangled UHMWPE in reinforcement of polyethylene fibers.

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