Material Behaviour

Melt die-swell behavior of polyoxymethylene blended with ethylene-vinyl acetate copolymer and high-density polyethylene

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A B S T R A C T

The influence of extrusion conditions (temperature ranging from 170 to 220 °C, loads varying from 1.2 to 12.5 kg) and high-density polyethylene (HDPE) content on swelling behavior of polyoxymethylene (POM)/ ethylene-vinyl acetate copolymer (EVA)/HDPE blend melts was examined. It was found the melt die-swell ratio of the blends decreased approximately linearly with rise in temperature, while it increased as a quadratic function with increasing shear rate or shear stress. The melt die-swell ratio increased with increasing HDPE weight fraction under constant test temperature, and the effect of temperature on the sensitivity of the melt die-swell ratio to the HDPE weight fraction was insignificant, while the effect of load on the melt die-swell ratio was significant. The correlation between the melt die-swell ratio of the blends and the HDPE weight fraction followed a quadratic relation. The melt extrudate swell behavior mechanisms of the blends during the die extrusion flow are discussed.

1. Introduction

Die swell, also known as the Barus effect, is a common phenomena occurring in polymer melts during extrusion. It is related to the viscoelasticity of polymeric fluid including melt and liquid. Therefore, studies on the melt die-swell behavior and the governing factors are crucial to reveal the die-swell behavior mechanisms and also helpful to navigate product design and processing for polymer materials [1–6]. Since 1998, Liang and co-workers [7,8] have investigated the effects of extrusion conditions on the melt die-swell behavior of polyolefin blends using a capillary rheometer. Polyformaldehyde (POM), an engineering resin, has been extensively used in many fields including transportation, construction, electronic applications, and in general household materials, etc. [9–16], because of its comprehensive properties such as good dimensional stability, excellent corrosion resistance, creep resistance, high strength and stiffness, self-lubricating capability, as well as favorable performance in processing and practical applications. However, the application scope of the POM remains limited due to its shortcomings, such as low notch sensitivity, poor heat resistance and its high cost. Hence, finding novel ways to improve the properties and decrease the price of the POM resin for expanding its applications has been an important research topic during recent decades. As a general purpose resin, high-density polyethylene (HDPE) is generally applied in agriculture and industries such as automobiles, electronic appliances, vessels, tubes and film [17,18] due to its ease of processing and low

price. To prepare a new kind of polymeric blend with good processing and low cost, POM can be blended with HDPE. However, the compatibility between POM and HDPE is poor under general conditions, thus it is necessary to improve the compatibility between them. As ethylene-vinyl acetate copolymer (EVA) includes ethylene monomer and vinyl acetate monomers, and it can be used as a compatibilizer between the POM and HDPE. In addition, EVA has been extensively used for various applications including adhesives, blow molded products, wires and cables, foam and extruded products, and lamination as well as injection molded products, mainly due to its excellent flexibility, impact resistance, optical transparency, adhesion, environmental stress cracking resistance, weather resistance, chemical resistance and sealing ability [19]. Thus, POM/HDPE/EVA blends can have extended applications due to their good combination of mechanical and physical properties.

Some studies on POM blends have been extensively reported in recent decades, including mechanical properties [19,20], morphology [20], friction [21,22], crystallization [23,24], processing [15,16,25] etc. However, there are relatively few reports on the structure-property relationship of POM/HDPE/EVA blends, especially on the rheological behavior of POM blend melts. Chen and his co-workers [26] investigated the rheological behavior of POM polymer melt flowing through micro-channels, the results showed that the rheological behavior of POM resin was different (but not significant) from that of polystyrene (PS) resin on microscopic scale; in addition, wall slip occurred more easily for the PS resin within micro-channels than POM

resin due to the effect of molecular weight. Liang and his colleagues [27,28] studied the melt flow properties and die-swell behavior during extrusion of POM/EVA/HDPE composites filled with nano-sized calcium carbonate under various temperatures and loads. However, there are very few reports related to the melt die-swell behavior of the POM and its blends. The objectives of this study were to investigate the effects of extrusion conditions (e.g. temperature and load) and the HDPE content on the melt die-swell behavior of the POM/EVA/HDPE blends during die extrusion flow, for understanding the melt die-swell mechanisms and for providing useful data for the processing technology and machinery design for POM blends.

2. Experiments

2.1. Materials

The POM (trade mark ZPR) was supplied by the Baotailing Engineering Plastics Co., Ltd. (Nantong city, China); its density (ρ) in the solid state and the melt flow index were 1410 kg/m^3 and 20 g/10min, respectively. The HDPE (trade mark 5000S) was supplied by the Petro China Daqing Petrochemical Company Ltd. (Daqing city, China); its density in the solid state and melt flow index were respectively 954 kg/m^3 and 0.9 g/10 min.

The EVA with VA (vinyl acetate) content of 14% was used as the compatibilizer, produced by the Beijing Dongfang Petrochemical Co., Ltd (Beijing, China). The melt flow index and density in solid state were 2 g/10min and 935 kg/m^3, respectively.

2.2. Preparation

After the POM was mixed with EVA and HDPE (the weight ratio between EVA and HDPE was 1:10), the mixtures were melt blended in a co-rotational twin-screw extruder, model SHJ-SC-58 (Nanjing, China), under conditions of temperature ranging from 170 to 180 °C and screw speed of 100 rpm. The screw diameter and length-diameter ratio were 35 mm and 40, respectively. The POM/EVA/HDPE blend extrudates were then granulated. The weight fraction of the HDPE (ϕ_{HDPE}) were respectively 3, 6, 9, 12 and 15 wt%,. The granulated POM/EVA/HDPE blends were dried at 80 °C for 4 h before the die extrusion experiments.

2.3. Methodology

The rheological tests were performed using a melt flow indexer (XNR-400C, supplied by the Kauth Scientific Technical Services Co. Ltd., Chengde, China) at a temperature ranging from 170 to 220 °C and load varying from 1.2 to 12.5 kg. The die length and the die diameter (d) were, respectively, 8.000 mm and 2.095 mm; the die entry angle was 180°. The extrudate swell degree is usually presented using a die-swell ratio (B) which is defined as a ratio of the extrudate diameter (d_e) to the die diameter:

$$B = \frac{d_e}{d} \tag{1}$$

The fracture surfaces of the extrudate from the experiments were examined using a scanning electron microscope (SEM), model S-3700N supplied by the HITACHI instrument Ltd (Tokyo, Japan), to observe the interface between the components of the blend melts. The extrudate fracture surfaces were coated with gold before the SEM examination.

3. Results and discussion

3.1. Effect of test temperature on die-swell ratio

To investigate the influence of test temperature on the melt extrudate swell of the POM/EVA/HDPE blend under loads of 2.16 and 5 kg, and HDPE weight fraction of 6 wt%, the dependence of the melt
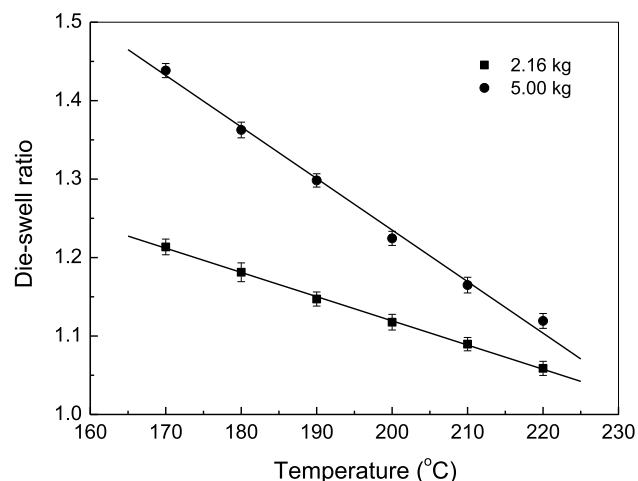

Fig. 1. Dependence of melt die-swell ratio on temperature ($\phi_{HDPE} = 6$ wt%).

die-swell ratio of the POM/EVA/HDPE blend on test temperature (T) is shown in Fig. 1. It can be seen that the melt die-swell ratio (B) decreases with rise of temperature under a constant load, and the relationship between them is approximately linear. That is

$$B = \beta_0 + \beta_1 T \tag{2}$$

where β_0 and β_1 are the coefficients related to the melt elasticity. The parameters β_0 and β_1 can be determined by means of a linear regression analysis method from the experimental data. The values of β_0 and β_1 of the POM blend melt under different loads are summarized in Table 1. Under the test conditions, the values of β_0 and β_1 increase with increasing load, and the linear correlation coefficient (r) is greater than 0.99. It should be noted that β_1 reflects the sensitivity of the melt die-swell to temperature. This indicates that the sensitivity of the melt die-swell to temperature increases with increasing load under experimental conditions.

It is generally believed that the transition ability of polymer macromolecular chains increases with the rise in temperature. In this case, the melt viscosity decreases correspondingly, resulting in shortening the relaxation process. Thus, the viscous dissipation of the deformation energy stored in the melt during extrusion flow increases and the ability of the elastic recovery of the deformation is weakened correspondingly in this case, leading to the reduction of the melt extrudate swell degree of the blends.

3.2. Dependence of die-swell ratio on flow rate

To observe the effect of flow rate on the melt extrudate swell of the POM/EVA/HDPE blend under test temperatures of 180 °C and 220 °C and a HDPE weight fraction of 6 wt%, a plot of the melt die-swell ratio of the POM/EVA/HDPE blend against apparent shear rate is presented in Fig. 2. It can be observed that the melt die-swell ratio increases with increasing apparent shear rate ($\dot{\gamma}_a$) when the test temperature is constant, and the sensitivity of the melt die-swell ratio to apparent shear rate decreases with a rise of temperature. In general, the shear rate increases with an increase of flow rate, and the residence time of polymer melt in the die decreases correspondingly. The relationship between the apparent shear rate and melt volume flow rate (MVR) can be expressed approximately as follows:

Table 1
Values of α_1 and α_2 of the blends under experimental conditions.

F (kg)	α_1	α_2	r
2.16	1.73545	− 0.00308	0.99869
5.00	2.52864	− 0.00646	0.99297