Temperature Dependence of the Elongation Behavior of Polyphenylene Sulfide using Melt Spinning Technique

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Abstract. The elongational properties of polyphenylene sulfide (PPS) melt were measured using a melt spinning technique. The relationship between extrusion temperature and melt strength (MS) as well as between elongational viscosity and drawability were investigated with respect to the effects of extrusion temperature and extensional strain rate on the melt extensional stress and elongational viscosity. The results showed that the stretching force for the PPS melt decreased with a rise of extrusion temperature while increased roughly with an increase of extensional rate. The MS decreased with an increase of temperature, and the ln MS was a linear function of 1/T when the extrusion velocity was constant. Both the melt extensional stress and elongational viscosity decreased with the increase of the extrusion temperature. With increase of the extensional strain rate, the extensional stress increased while the melt elongational viscosity first decreases and then increases gradually. A low melt elongational viscosity might be beneficial to improve the melt drawability.

1. Introduction
In polymer processing, melt extensional flow is a common flow pattern, such as entrance converging flow in die extrusion or runner injection of polymer melts from an extruder barrel [1-5], blow molding, blowing film and melt spinning. In general, the flow status of polymeric materials will significantly affect the processing technology and the final properties of products. Therefore, the melt extensional flow behavior of polymeric materials and its mechanisms have been paid attention by rheological researchers and polymer processing engineers [6,7].

The extensional rheological properties of polymeric materials are usually measured using special extensional rheological instruments [8-10]. Handge and Schmidheiny[8], Hachmann and Meissner[9] as well as Wagner et al.[10] introduced the testing instruments and methods for elongation properties of polymer melts. However, these special rheometers are expensive. Melt spinning measurement process is similar to isothermal uniaxial tension, and the elongation rheology parameters such as
elongational viscosity may be obtained. Hence, one may comprehensively study the extensional rheological properties of polymer melts. Muke et al.[11] studied the extensional rheology of two polypropylene melts from uniaxial stretching after extrusion (Rheotens test), and found that the viscosity determined from the Rheotens test can be used to estimate transient elongational viscosity. Baldi et al.[12] compared different experimental techniques and researched the determination of the elongational viscosity of two high-density polyethylene melts by melt spinning experiments. The results showed that for high strain and strain rate levels, the melt spinning experiments provide elongational viscosity data quite close to the transient elongational viscosity values obtained from the melt tensile tests.

Polyphenylene sulfide (PPS) fiber is a kind of engineering thermoplastic fiber. The resin has an excellent high-temperature thermal stability, and possesses a very good performance of denial in dry and wet environments. Its chemicals resistance is also excellent, it can maintain a stable acid-resistance, alkali, organic solvent resistance. Thus, PPS is very suitable as high temperature filter material, especially the pocket filter material[13,14]. The melt flow status of PPS has a significant impact on the physical properties of PPS fiber. However, to the best of our knowledge, the study of the elongational behavior of PPS melt is rarely involved. The objectives of this article are to measure the extensional rheological properties of PPS using melt spinning technique, to investigate the effects of extrusion temperature and extensional strain rate on the melt extensional stress and elongational viscosity, as well as to study the relationship between the melt elongational viscosity, the melt strength and the melt drawability.

2. Experimental

2.1. Materials
The resin used in this study was a polyphenylene sulfide (PPS, DHPPS-YD-I) with density 1.32 g/cm³ and melt flow index (MFI) 165 g/10min. The PPS was supplied by Dunhuang Western Region Special New Material Co., Ltd., Jiuquan city, China.

2.2. Instruments and methodology
The melt elongation rheological measurements were carried out by means of a capillary rheometer (CEAST SR50) supplied by Instron Corporation, which was equipped with a specific stretching unit.

The polymer melt was stretched in uniaxial extension according to the melt spinning principle to measure the rheological properties. For each measurement, the resin was heated to a given temperature and then the melt was extruded at a constant flow rate through a capillary die. Subsequently, the melt was drawn by a set of pinching rotating wheels positioning at some distance downstream. At the beginning, the take-up speed of the wheels was adjusted to the extrusion velocity of the polymer melt. Then, the speed was increased with a constant acceleration rate to stretch the melt until it broke. During the test, the draw-down force measured was plotted as a function of velocity of the rotating wheels. For each temperature, the tests were repeated at least 3 times, the one with the highest draw ratio at break being used to calculate the elongational viscosity. For all the measurements, the length of the spinline was 200 mm, the diameter of extrusion die was 1 mm, the ratio of length to diameter was 30:1; the entrance angle was 90°, the extrusion velocity was 16.875 mm/s and the acceleration rate was 5 mm/s². The melt temperatures of the PPS were from 300 to 320 ºC.

According to the expression derived by Wagner et al.[10], the extensional strain rate, extensional stress and melt elongational viscosity may be determined from the extension flow curves, and the calculation equation is given by

$$\eta_{el} = \frac{\sigma}{\dot{\varepsilon}} = \frac{F \cdot L}{Q \cdot \ln(\lambda)}$$

(1)
where $\lambda$ is the extension ratio, $\dot{\varepsilon}$ is the extensional strain rate, in $s^{-1}$; $\sigma$ is the extensional stress, in Pa; $L$ is the distance between the die exit and the traction wheel, in m; $F$ is the stretching force, in N; $Q$ is the volume flow rate, in $m^3/s$.

3. Results and discussion

3.1. Extension flow curves

Fig. 1 shows the relationship between the stretching force ($F$) and the extension rates for the PPS melt under test conditions of extrusion temperature range from 300 to 320 °C and extrusion velocity of 16.875 mm/s. It can be seen that $F$ increases roughly with the increase of extension rate ($\dot{\varepsilon}$), and the tendency becomes more obvious with a rise of extrusion temperature. Furthermore, the macromolecular chain of PPS is a rigid chain because of the benzene ring. In general, a melt with rigid chain needs more extension force to form macromolecular chain orientation and produce elongational flow than a melt with flexible chain such as HDPE and LLDPE at a constant temperature. Consequently, the extension force of the PPS is much higher than that of the LLDPE and HDPE\[15\]. It may also be observed that $F$ decreases with a rise of extrusion temperature because the movement ability of the macromolecular chain of PPS will be enhanced with the increase of temperature, and the force needed for its orientation reduces. Hence, the stretching force of the PPS melt decreased with a rise of temperature during elongational flow.

3.2. Dependence of melt strength on extrusion temperature

In general, the cross section of the melt thread is difficult to determine under test conditions, hence the melt stretching force at break is usually defined as the melt strength ($MS$)[6]. Fig. 2 displays the dependence of the $MS$ of the PPS melt on the extrusion temperature. It can be seen that the $MS$ of the PPS melt decreases with a rise of temperature, and the slope of the curve of the melt strength versus temperature of the PPS melt is much greater than that of the polyethylene melts, as shown in Liang’s work\[15\]. This indicates that the dependence of the $MS$ of the PPS resin on extrusion temperature is significant.

To further investigate the influence of extrusion temperature on the $MS$ of the PPS resin, we plot the curve of In $MS$ against the reciprocal of temperature ($T^{-1}$) when the extrusion velocity is 16.875 mm/s. The result is shown in Fig. 3. It may be observed that the relationship between the In $MS$ and $T^{-1}$ is a linear function. This indicates that the dependence of the $MS$ for the PPS on the extrusion temperature obeys the Arrhenius expression, that is

$$MS = A\exp\left(\frac{E_{\text{act}}}{RT}\right)$$

(2)
where $A$ is a constant, $R$ is the Molar gas constant, 8.314 J/(mol·K), $T$ is the absolute temperature in K, $E_{MS}$ is the melt strength activation energy, in kJ/mol.

The parameter $E_{MS}$ reflects the sensitivity of the melt strength to temperature. The value of $E_{MS}$ of polymer melts can be calculated from the slope of the curves of the melt strength versus temperature. On the basis of Eq. 2 and Fig. 3, the $E_{MS}$ of PPS is 86.88 kJ/mol, which is much larger than that of the polyethylene melts (20 kJ/mol for LLDPE, 19.1 kJ/mol for HDPE) [15]. As stated above, the macromolecular chain of PPS is a rigid chain with benzene ring. It is generally believed that the motion ability of the molecular chains of polymer melt will be enhanced with a rise of temperature. In this case, the rigid chain of the PPS melt will be oriented easily and the melt strength will be reduced obviously during elongational flow with a rise of temperature. For flexible chain structure resin, such as HDPE and LLDPE, the factor affecting the molecular chain orientation is mainly strain rate, while the influence of temperature is relatively weak. Therefore, the sensitivity of the $MS$ of the PPS to temperature is more significant than that of the polyethylene.

![Figure 2. Relationship between melt strength and extrusion temperature](image1)

![Figure 3. Dependence of melt strength on extrusion temperature at extrusion velocity of 16.875 mm/s.](image2)

3.3. Effects of extensional strain rate and extrusion temperature on melt extensional stress and elongational viscosity

Melt extensional stress is also an important characterization of melt strength of polymeric materials. Fig. 4 illustrates the dependence of the melt extensional stress ($\sigma_e$) of the PPS on extensional strain rate ($\dot{\varepsilon}$) under different extrusion temperatures when the extrusion velocity is 16.875 mm/s. When the
extrusion temperature is fixed, \( \ln \sigma_e \) increases nonlinearly with the increase of \( \ln \dot{\varepsilon} \), while \( \ln \sigma_e \) decreases with a rise of temperature with \( \dot{\varepsilon} \) constant. In general, the storage and dissipation of deformation energy are coexistent during polymer melt flow. The stored energy usually increases with increasing extensional strain rate, while it decreases with a rise of extrusion temperature during melt flow. Consequently, the melt extensional stress increases with an increase of extensional strain rate, whereas it reduces with a rise of temperature during the elongational flow of the PPS melt[6].

Melt elongational viscosity is a basic parameter for presenting the elongational flow property of polymeric materials, it is very important for melt spinning, foaming and blowing technology. Fig. 5 displays the relationship between the elongational viscosity \( (\eta_e) \) and extensional strain rate \( (\dot{\varepsilon}) \) of the PPS melt at different extrusion temperatures when the extrusion velocity is also 16.875 mm/s. It can be seen that the ln\( \eta_e \) of the PPS melt first decreases and then increases gradually with increasing extensional strain rate. The reason for this can be illustrated as follows: the increase of the extensional strain rate might be beneficial to the disentanglement of the macromolecular chains of the PPS melt, resulting in decreased melt elongational viscosity. On the other hand, the orientation degree of the macromolecular chains along the extension direction will increase, leading to the increase of the melt elongational viscosity[15]. Therefore, the change of the elongational viscosity with the extensional strain rate depends on the competition between the disentanglement and the orientation degree of the macromolecular chains of the PPS melt. In the beginning stage, the disentanglement of the macromolecular chains plays a dominant role, and the melt elongational viscosity decreases slightly. When the extensional strain rate reaches a certain level, the orientation effect of the macromolecular chain is enhanced gradually and plays a major role, so the melt elongation viscosity begins to increase. As mentioned previously, the macromolecular chain of PPS is a rigid chain with benzene ring, and the melt extension hardening effect is significant during elongational flow. It may also be observed that the elongational viscosity decreases with a rise of temperature, resulting in increased fluctuations in the elongational viscosity. It is known comparing Figs. 1 and 5 that the melt strength is low as the melt elongational viscosity is low. However, the melt drawability is good, because a low melt elongational viscosity may be beneficial in this respect.

Figure 4. Extensional stress versus strain rate at extrusion velocity of 16.875 mm/s.
Figure 5. Elongational viscosity versus strain rate at extrusion velocity of 16.875 mm/s.

4. Conclusion
The effects of extrusion temperature and extensional strain rate on the melt extensional stress and elongational viscosity of PPS resin were significant. The stretching force for the PPS melt decreased with a rise of extrusion temperature while increased roughly with increase of the extensional rate. The melt strength decreased with an increase of extrusion temperature, and the ln MS was a linear function of 1/T when the extrusion velocity was constant. The melt strength activation energy could be determined based on the curves of the ln MS versus 1/T.

With increase of the extensional strain rate, the extensional stress increased while the melt elongational viscosity first decreased and then increased gradually under the action of both the disentanglement and the flow-induced orientation of the macromolecular chains of the PPS melt. Both the melt extensional stress and elongational viscosity dropped with a rise of extrusion temperature. A low melt elongational viscosity might be beneficial to improve the melt drawability.

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