Melt rheology of compatibilized polystyrene/low density polyethylene blends

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Abstract: Investigations have been made on the melt rheological behaviors of compatibilized blends composed of polystyrene, low density polyethylene and hydrogenated (styrene-butadiene-styrene) triblock copolymer used as a compatibilizer. The experiments were carried out on a capillary rheometer. The effects of shear stress, temperature and blending ratio on the activation energy for viscous flow and melt viscosity of the blends are described. The study shows that the viscosity of the blends exhibits a maximum or minimum value at a certain blending ratio. The activation energy for viscous flow decreases with increasing LDPE content. Furthermore, the concept of equal-viscosity temperature is presented and its role in the processing of the blend is discussed. In addition, the morphology of the extrudate sample of the blends was observed by scanning electron microscopy and the correlation between the morphology and the rheological properties is explored.

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INTRODUCTION

The mechanical properties of multicomponent polymer materials are first determined by the properties of the constituent polymers. However, to a great degree, they are influenced by the blend morphology, which, in turn, depends on the thermodynamic interactions between the two polymers, the rheological behaviour of the constituents and the processing conditions. Rheological studies can give access to information pertaining to the structure, morphology and processing of the material.¹

In the last decade, a tendency for alloying, compounding and morphologically modifying large-volume resins has arisen in consideration of the ever-increasing economic and regulatory pressures.² Polyethylene (PE) and polystyrene (PS) are the most widely used plastics.³ Great efforts have been made to increase the impact strength of polystyrene by blending it with polyethylene.³–⁶ However, it was found that simple blending often led to poor properties, due to a lack of sufficient adhesion between PE and PS phases. In our laboratory, a desired combination of toughness of LDPE and rigidity of PS has been realized by adding a tri-block, hydrogenated copolymer, poly(styrene-butadiene-styrene) (SEBS), as a compatibilizer to strengthen the phase adhesion of the blends. Based on the proper selection of materials and blending conditions, blends with excellent toughness, exceeding the level reported in the literature, were prepared as reported in our previous paper.⁷

So far, the investigations on the PS/PE system reported in the literature dealt mostly with the mechanical properties and morphology of the blends with emphasis on the compatibilizing role of graft or block copolymers. Based on our recent achievements in the in-situ morphological observations in the stretching process by TEM of PS/LDPE blends, the deformation mechanisms of the system have been explored.⁸–¹¹ In the 1970s, Han et al studied the rheology of polystyrene, high density polyethylene(HDPE) and their simple blends.¹²,¹³ However, little has been reported in the literature relative to the rheological properties of the blends with a compatibilizer. Obviously, in order to optimize the processing conditions, to generate the desired morphology and to improve the mechanical properties of the blends, it is necessary to study the melt rheological properties of PS/LDPE blends compatibilized by SEBS.

The present study aims at determining the melt rheological properties of a PS/SEBS/LDPE systems with a view towards understanding the processing behaviour of the blends. First, an attempt was made to study the effect of the blend ratio on various rheological parameters, such as melt viscosity and activation energy for viscous flow. Based on the related rheological data, the concept of equal-viscosity tem-
perature \( (T^*) \) is proposed, and then the role of \( T^* \) on controlling the morphology of the blends is evaluated. Secondly, the morphologies of the extrudate samples of the blends are observed by scanning electron microscopy, and the correlation between the morphology and the rheological properties is investigated.

**EXPERIMENTAL**

**Materials**

Homopolymer PS, LDPE and block copolymer SEBS were used in this study, whose sources and characteristic data were reported in a previous paper.\(^7\)

**Preparation of the blends**

Keeping the content of copolymer SEBS constant (10wt%, in respect to the total weight of the blend), a series of blends covering the whole composition range of PS/LDPE varying in a step of 10wt% were made under the best processing conditions determined in previous paper.\(^7\) For convenience, the blends are designated as weight ratio of PS to LDPE.

**Determination of rheological property**

The rheological behavior of the blend melts was determined by a capillary rheometer (CFT-500, made in Japan). Experiments were carried out at five different temperatures: 160°C, 180°C, 190°C, 200°C and 220°C. A capillary die made of tungsten carbide with an \( L/R \) ratio of 10/1 was used.

**SEM observation**

A section about 2–3mm long was cut out from an extruded sample, and was tailored into a rectangle using a razor blade. After being dipped in liquid nitrogen for 20 minutes, the sample section was broken along the extrusion direction. The morphology of the fracture surface was observed using electron microscopy (HITACH S-510) after being coated with a thin layer of gold. The accelerating voltage was 20kV.

**RESULTS AND DISCUSSION**

In the present rheological measurements, the parameters that could be directly obtained are the applied pressure \( \Delta P \) and the volume flow rate \( Q \). For a Newtonian liquid, the shear stress at wall \( (\tau_W) \) and shear rate \( (\gamma') \) can be calculated from the two parameters according to the following equations:\(^{14}\)

\[
\tau_W' = \frac{\Delta P}{2L/R} \quad (1)
\]

\[
\gamma' = \frac{4Q}{\pi R^3} \quad (2)
\]

where, \( L \) and \( R \) are the length and the radius of the capillary, respectively.

Since the polymers are viscoelastic, the pressure drop at the die entrance is very large, and the Bagley correction\(^{14,15}\) was applied to obtain the true shear stress at wall \( (\tau_W) \) according to the following expression:

\[
\tau_W = \frac{\Delta P}{2(L/R + n_B)} \quad (3)
\]

where, \( n_B \) is the correction coefficient, which can be easily obtained from the flow data recorded with three dies of different \( L/R \).\(^{14}\)

On the other hand, polymers are non-Newton fluids so that the true shear rate \( \gamma_W \) can be obtained from \( \gamma' \) after Rabinowitsch–Mooney correction:\(^{14,16,17}\)

\[
\gamma_W = \frac{3n + 1}{4n} \cdot \gamma' \quad (4)
\]

then the viscosity of the melt can be calculated from:

\[
\eta = \frac{\tau_W}{\gamma_W} \quad (6)
\]

**Flow curves**

The flow curves, ie plots of shear stress versus shear rate for PS/SEBS/LDPE blends covering the whole composition range have been measured over a temperature range from 160°C to 220°C in steps of 10 or 20°C. A typical result for the plot at 200°C is shown in Fig 1. It can be seen that these curves apparently deviate from linear relationship inclining to the axis of shear rate, which means that the homopolymers of PS, LDPE and their blends compatibilized by a block copolymer are pseudoplastic non-Newton fluids,\(^{18}\) similar to most polymeric melts.\(^{14}\)
Melt viscosity
Figure 2(a)–(d) shows plots of the melt viscosity versus shear stress for homopolymers PS, LDPE and the PS/LDPE 80/20, 50/50, 20/80 blends compatibilized by 10 wt% SEBS. It shows that the viscosity of PS, LDPE and the blends decreases with increasing shear stress, showing a typical property of pseudo-plastic non-Newton fluids. However, the dependence of the melt viscosity on shear stress is different as temperature varies. At low temperature (160 °C, 180 °C), the viscosity of PS is much higher than that of LDPE, and the viscosity of the blends decreases with increasing LDPE content over the whole range of shear stress studied, whereas at higher temperature (200 °C, 220 °C) a crossover between the curve of PS and those of the blends occurs. Obviously, this is caused by the drastic decrease of viscosity of PS with shear stress.

In order to observe how the melt viscosity varies with the blending ratio at different temperatures, cross plots of Figs 2(a)–(d) are given in Figs 3(a)–(d). First, we can see that, at a fixed temperature, the variation of melt viscosity with blend composition is different with...
shear stress. For example, it is seen in Fig 2(c) that, at low shear stress \( (\tau_{W} = 50 \text{kPa}) \), the viscosity goes through a minimum at a blending ratio of about 10wt% of LDPE, while there is no minimum at higher shear stress \( (\tau_{W} = 150 \text{kPa}) \). Secondly, at a given shear stress, the dependence of the melt viscosity on the blend composition varies with temperature. As an example, we discuss the case at \( \tau_{W} = 50 \text{kPa} \). Figure 3(a) \( (T=160^\circ \text{C}) \) and 3(b) \( (T=180^\circ \text{C}) \) show that the viscosity of the blends decreases monotonously with LDPE content, whereas at 200°C a viscosity minimum occurs at 10wt% LDPE. When the temperature goes up to 220°C, the viscosity of the blend exhibits both a minimum at 10wt% LDPE and a maximum at 90wt% LDPE. This phenomenon where a certain blending ratio gives rise to a minimum value or maximum value of melt viscosity was also observed by Han in PS/HDPE and PS/PP systems,\(^{13}\) and Gupta in a PP/ABS system.\(^{20}\) Han et al further gave a phenomenological interpretation for the rheological behavior.\(^{18}\)

**Activation energy of flow**

The viscosity variation of the blends with temperature at different shear stress is shown in Figs 4(a)–(c). The viscosity of PS, LDPE and all of the blends decreases with increasing temperature. However, the melt viscosity of PS changes with temperature much more sharply than that of LDPE.

Furthermore, it can be observed that, for a given
shear stress, the viscosity of PS and LDPE may become equal when temperature goes through a certain value. We define the temperature at which PS and LDPE have the same viscosity as the 'equal-viscosity temperature', \( T^* \). The viscosity of PS is higher than that of LDPE when temperature is lower than \( T^* \), whereas PS exhibits lower viscosity than LDPE when \( T \) is larger than \( T^* \). Comparing these three figures, it is found that \( T^* \) decreases with increasing shear stress. \( T^* \) was found to be 220, 200 and 190°C when shear stress was 50, 100 and 150 kPa. Han et al.\(^{18} \) plotted the logarithm of viscosity of PS and HDPE against reciprocal temperature (1/T) and obtained parallel lines, which implies that no \( T^* \) exists between PS and HDPE.

The advantage of the existence of an equal-viscosity temperature for blend constituents is obvious. If mixing is performed at around \( T^* \), high compounding efficiency would be expected because the viscosities of the two components are close. Besides, it is favourable for controlling the morphology of the blend. For example, when blending is carried out at a temperature much lower than \( T^* \), where the viscosity of PS is much higher than that of LDPE, LDPE tends to form a continuous phase even if it is a minor component. On the contrary, mixing at a temperature higher than \( T^* \) favours formation of a PS matrix. On the other hand, if a blend is prepared at \( T^* \), the morphology of the blend is then mainly governed by its composition, i.e., the major and the minor components form the matrix and the dispersed phase respectively. In particular, an interlocked bi-continuous morphology is expected when the amounts of the two components are about the same.

The plots of the logarithmic viscosity of the blends versus 1/T (K\(^{-1}\)) shown in Fig 4 give a group of straight lines, which indicate that the relation between
the viscosity of the blend and temperature follows the Arrhenius equation, ie

$$
\eta = A \cdot \exp^{-E_a/RT}
$$

(7)

where, $E_a$ is the activation energy, $R$ the gas constant, and $A$ a material constant. From the slopes of these lines, the activation energy for viscous flow of the blends and homopolymers can be calculated, and its variation with shear stress is shown in Fig 5. It is clear that the activation energy of PS is much higher than that of LDPE over the entire range of shear stress.

Figure 7. SEM micrographs of extruded PS/LDPE 80/20 blends containing 10wt% SEBS. (a) 160°C, (b) 180°C, (c) 200°C, (d) 220°C.

Figure 8. Schematic diagram of a deformed liquid drop in a flowing field.
studied. In addition, the activation energy of PS increases with increasing shear stress, and that of LDPE is almost independent of shear stress. The variation of the activation energy with shear stress for the blends depends on the content of PS in the blend: the higher the content of PS, the sharper the variation. There is little attention paid to the dependence of the activation energy on shear stress in the literature, and the reason for this dependence is not yet clear.

Cross plots of Fig 4 can give the variation of activation energy with blending ratio, as shown in Fig 6. It can be seen that the activation energy of the blends decreases with increasing content of LDPE in the range of shear stress studied here, which implies that with addition of LDPE, the viscosity of the blends becomes less sensitive to temperature.

**Morphological observation of the blends after extrusion**

Figure 7(a)–(d) shows the morphology of the sections along the flow direction for PS/LDPE 80/20 blends after extrusion from a die at a shear stress of 50 kPa. These figures clearly show that the blends extruded at different temperatures exhibit different morphological...
features and that LDPE phase exhibits large deformation and extension over a temperature range from 180°C to 200°C.

Now we can discuss the relationship between the morphological characteristics and the rheological behaviors of the blends. Figure 8 is a schematic representation showing a liquid drop in a shearing field. Obviously, the deformation of the liquid drop depends on the difference of two shear stresses (τ₁ − τ₂), which is determined by the shear rate of the matrix. However, if the shear stress applied to the drop cannot overcome the internal friction between molecules of the liquid drop, no large deformation will occur. At a given shear stress of τ = 50kPa, when the temperature is lower than 220°C, the viscosity of the continuous PS phase is higher than that of dispersed LDPE (see Fig 3). So it can be inferred that the liquid drops of a dispersed LDPE phase are unstable owing to shearing from the continuous phase, and that they will deform in the flowing process. However, at 160°C, as the viscosity of PS is very high, leading to a low shear rate of the matrix, this results in only a little deformation of LDPE (shown in Fig 7(a)). When the temperature goes up to 180°C, the viscosity of PS decreases sharply, and the shear rate of the matrix clearly increases, therefore the LDPE phase shows large deformation and fibrillation. In addition, these fibres orient along the flow direction (Fig 7(b)). Similar fibrillation can also be observed in Fig 7(c), but the orientation is not regular, which may be caused by the vortex flow, which was observed by Han in a PS/HDPE blend.13 At 220°C, the viscosity of PS becomes lower than that of LDPE, then the shear stress applied on the LDPE particles cannot overcome the internal friction of LDPE molecules, so that there is no obvious particle deformation observed (Fig 7(d)).

Figure 9 shows SEM photographs of sections of an extruded sample along the flow direction for PS/LDPE 20/80 blends with a dispersed phase of PS. The photographs show quite different morphological characteristics from those with LDPE as dispersed phase shown in Fig 7, ie the deformation and orientation of the dispersed PS phase along the flow direction hardly occur at low temperature (160, 180, 200°C). This is understandable because the viscosity of the continuous LDPE phase is much lower than that of the dispersed PS phase. At 220°C, as the viscosity of PS becomes lower than that of LDPE, the dispersed PS phase deforms along the flow direction upon shearing the continuous phase, but the viscosity difference between the two phases is very small, so that the deformation is not very substantial.

We have just tried to interpret qualitatively the morphological characteristics of the blends by taking into account the rheological behaviour obtained experimentally. Although some equations21,22 qualitatively describe the deformation of a drop in a uniaxial shear flowing field, a quantitative discussion of our results using these equations is not realistic because of the lack of data for some parameters of the equations.

CONCLUSIONS

The following conclusions can be drawn from the results of the present research:

1. PS, LDPE and their blends compatibilized by SEBS are pseudoplastic in nature; their viscosity decreases with increasing shear stress, similarly to most polymer melts.
2. The melt viscosity of PS decreases sharply with temperature, whereas the viscosity of LDPE varies slightly only with temperature. For a given blend composition and at a shear stress, there exists a temperature T*, at which PS and LDPE show equal viscosity. The temperature T* decreases with increasing shear stress. The existence of T* is favourable for controlling the morphology of the blends.
3. As shear stress increases, the activation energy for the viscous flow of PS rises, while that of LDPE hardly changes. The activation energy of the blends decreases as the content of LDPE increases.
4. The morphology of an extruded sample is determined by the rheological behaviours of its constituents. The deformation of the dispersed phase along the flow direction is found to be dependent on the viscosities of the two phases and the temperature.

REFERENCES