

A Modified Rheological Model of Viscosities for BR–SBS Blends

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ABSTRACT: Blends of polybutadiene (BR) and styrene–butadiene–styrene triblock copolymer (SBS) have been prepared by a two-roll mill. The morphologies of extruded samples from a capillary rheometer were observed by scanning electron microscopy (SEM). It is found that PS phase is dispersed in the BR phase. The glass transition temperature (T_g) of the blend has been examined by using differential scanning calorimetry (DSC). From the T_g behavior and the electron microscopy study, it is found that certain degree of miscibility between the polystyrene phase and the BR phase is observed. The rheological behavior of the blend has been investigated by a capillary rheometer. It is found that the viscosity of the blend increases with increased content of PS phase. The behavior is in accord with the expected behavior of filler effect. To predict the filler effect of PS phase on the BR–SBS blend, a modified model of Chen and Cheng is proposed to elucidate the rheological properties of the BR–SBS blends with different compositions. Chen and Cheng's micromechanical model derived in Part I of this series, which relates the macroscopic shear stress to the macroscopic shear rate of a rigid non-Newtonian suspension when the direct contribution of Brownian force is completely neglected. The agreement between the theoretical predictions and the experimental results is satisfactory. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 71: 39–46, 1999

Key words: viscosity model, BR-SBS Blends

INTRODUCTION

The blend of polystyrene (PS) and polybutadiene (BR) shows 2 distinct glass transition temperatures corresponding to a PS phase and the other BR phase, respectively.^{1,2} This indicates that PS and BR are immiscible.³

From our previous results,¹ it is found that the styrene component forms a discrete phase, the butadiene component forms a continuous phase

in BR–SBS blend, and the domain size of styrene phase is rather uniform and small. And the viscosity of BR–SBS blend increases with increased content of styrene phase, although the viscosity of PS at the same shear rate and temperature shows much lower value. It might be attributed to the strong interaction between styrene and butadiene due to chemical bonding, which plays a role like surfactants and will reduce the amount of strain within the discrete domain and the PS domain will behave like rigid particles.⁴ Therefore, the BR–SBS polyblend fluid can be regarded as a suspension fluid with PS domain as fillers and BR phase as a suspending medium.

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Many equations have been proposed to estimate the viscosity of a suspension in which rigid particles are dispersed in a Newtonian fluid. Einstein was the first to develop a theory for predicting the viscosity of a dilute suspension of rigid spheres. The Einstein equation⁵ is valid only for extremely low concentration suspensions with the suspending medium being a Newtonian fluid. Many studies were carried out to extend the Einstein equation. Taylor^{6,7} developed a theoretical expression for a dilute emulsion dispersed in a Newtonian fluid. Jaffery^{8,9} considered the effect of the shape of the particles in the suspension and proposed a rigid ellipsoidal particle model. This model includes a parameter that depends on the geometry of ellipsoidal particles to modify the Einstein equation. At a higher concentration, some models have been proposed, such as the cell model by Simha^{8,10} and the Mooney equations,¹¹ to consider the particle–particle interactions that could influence the blend viscosity. Chen and Cheng¹² adopted Eshelby's eigen-strain¹³ and Mori–Tanaka's mean stress concept¹⁴ to estimate the viscosity of a solid-filled PEEK fluid. The proposed equation is able to describe the non-Newtonian behavior of a suspension.

In this article, we study the rheological properties of BR–SBS blends. The melt viscosities of BR–SBS blends behave as a PS domain filled in the suspending medium of BR melt. To describe the rheological properties of the blends as function of weight fraction of PS phase, the model proposed by Chen and Cheng¹² is modified by replacing the power law model with the modified cross model to predict the rheological behavior of the BR–SBS blend.

THEORETICAL CONSIDERATION

Many equations have been proposed to estimate the viscosity of a suspension in which rigid particles are dispersed in a Newtonian fluid. Einstein was the first to develop a theory for predicting the viscosity of a dilute suspension of rigid spheres.⁵ The Einstein equation is given as

$$\frac{\zeta^S}{\zeta_0} = 1 + 2.5\phi \quad (1)$$

where ζ^S is the viscosity of suspension, ζ_0 is the viscosity of suspending medium, and ϕ is the volume fraction of the filled particles.

In a previous report, Chen and Cheng¹² adopted Eshelby's eigen-strain¹³ and Mori–Tanaka's mean stress concept¹⁴ to develop a model (equation) to estimate the viscosity of a solid-filled PEEK fluid. In the present study, this model is extended to predict the melt viscosity of BR–SBS polyblend. The details are given below.

For a suspension, Chen and Cheng¹² assume that the relationship between shear stress and shear rate can be expressed by the following power law form:

$$\bar{Q} = d\dot{\gamma}^n$$

where \bar{Q} and $\dot{\gamma}$ are the shear stress and shear rate, respectively, d and n are power law constants. The apparent viscosity (ζ^S) of the polymer fluid is defined as

$$\zeta^S = \frac{\bar{Q}}{\dot{\gamma}} = d\dot{\gamma}^{n-1} \quad (2)$$

For heterogeneous polyblends, the discrete phases disperse in the continuous phase. If the discrete phase can be regarded as rigid particles, and the continuous phase as the suspension medium, the viscosity of the continuous phase (ζ_0^S) is expressed as

$$\zeta_0^S = d\dot{\gamma}_m^{n-1} \quad (3)$$

and

$$\dot{\gamma}_m = \frac{\dot{\gamma}}{W_m} \quad (4)$$

where $\dot{\gamma}_m$ is the shear rate of the continuous phase, and W_m is the weight fraction of the continuous phase. The apparent viscosity of the polymer blend (ζ^S) can then be derived as¹²

$$\zeta^S = \frac{\zeta_0^S}{bW_m} \quad (5)$$

For an incompressible fluid suspension, assuming that the density of continuous phase is close to 1.0, and the disperse phase behaves as a rigid sphere; the parameter b can be expressed as¹²

$$b = \frac{1}{1 + 1.5W_f} \quad (6)$$

where W_f is the weight fraction of the dispersed phase. Introducing eqs. (3) and (4) into eq. (5), it is shown that

$$\zeta^S = \frac{d\dot{\gamma}^{n-1}}{bW_m^n} \quad (7)$$

As $W_f = 0$, the viscosity of the continuous phase (ζ_0) at certain shear rate ($\dot{\gamma}$) can be expressed as $d\dot{\gamma}^{n-1}$, so the viscosity ratio of the blend to the pure continuous phase fluid at same shear rate is given as

$$\frac{\zeta^S}{\zeta_0} = \frac{1}{bW_m^n} \quad (8)$$

We refer to eq. (8) as Chen's model.¹² However, it is known that the flow curve of viscosity versus shear rate exhibits Newtonian behavior at low shear rate and follows power law equation only over a limited range of shear rate for polymer fluid. In the present study, a modified pseudo cross equation instead of the power law equation is used to describe the flow curve of polymer fluid; that is, eq. (3) is replaced by eq. (9) as

$$\zeta_0^S = \frac{D}{1 + \Omega\dot{\gamma}_m^a} \quad (9)$$

where D is the zero shear rate viscosity of the blend. Ω and a are material constants. Introducing eq. (5) into eq. (9), we obtain

$$\zeta^S = \frac{D}{1 + \Omega\left(\frac{\dot{\gamma}}{W_m}\right)^a} \times \frac{1}{bW_m} \quad (10)$$

Similarly, the viscosity of the pure continuous phase fluid at shear rate $\dot{\gamma}$ can be expressed as

$$\zeta_0 = \frac{D}{1 + \Omega\dot{\gamma}^a}$$

So the viscosity ratio of the blend to the pure continuous phase fluid is given as

$$\frac{\zeta^S}{\zeta_0} = \frac{\frac{D}{1 + \Omega\left(\frac{\dot{\gamma}}{W_m}\right)^a} \frac{1}{bW_m}}{\frac{D}{1 + \Omega\dot{\gamma}^a}} = \frac{1 + \Omega\dot{\gamma}^a}{1 + \Omega\left(\frac{\dot{\gamma}}{W_m}\right)^a} \frac{1}{bW_m} \quad (11)$$

It is noted that

$$\lim_{\dot{\gamma} \rightarrow 0} \frac{\zeta^S}{\zeta_0} = \frac{1}{bW_m} \quad (12)$$

and

$$\lim_{\dot{\gamma} \rightarrow \infty} \frac{\zeta^S}{\zeta_0} = \frac{1}{bW_m^{1-a}} \quad (13)$$

In comparison of eq. (13) to eq. (8), the constant $1 - a$ is equal to the power law constant n .

Equations (12) and (13) are our modified equations to calculate the viscosity variation of BR-SBS blends at different compositions, which will compare with the Einstein equation [that is, eq. (1)] and Chen's model [that is, eq. (8)] over a wide range of shear rate.

EXPERIMENTAL

Materials

The materials used in this study were as follow: polystyrene (PS), $\bar{M}_w = 260,000$; polybutadiene (BR), $\bar{M}_w = 550,000$; and styrene-butadiene-styrene copolymer (SBS), $\bar{M}_w = 300,000$, with 30 wt % styrene and 70 wt % butadiene.

Preparation of the Blends

Polymer blends with weight ratios of 83/17, 67/33, 58/41, 50/50, 42/58, 33/67, and 17/83 (BR-SBS) were prepared in a 2-roll mill with a surface temperature of 150°C and a mixing time of approximately 15 min. The compositions of the polymer blends were carefully chosen so that when they are expressed in terms of the weight ratio of styrene (ST) to butadiene (BD), the corresponding weight ratios of styrene (ST) to butadiene (BD) for all the above blends become 5/95, 10/90, 12.5/78.5, 15/85, 17.5/82.5, 20/80, and 25/75, respectively.

Measurement of Viscosity

The melt viscosities of PS, BR, and BR-SBS blends at 180, 200, 220°C were measured with a capillary rheometer. The Rabinowitsch correction was employed to obtain the true shear rate.

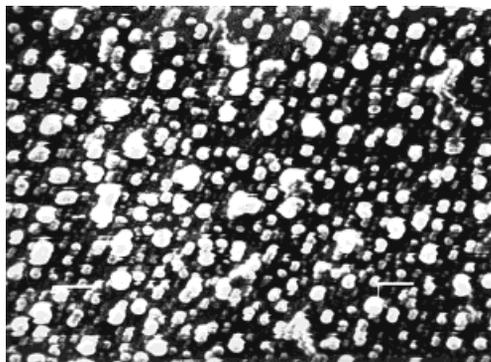


Figure 1 SEM photomicrograph ($\times 5000$) of etched fractured surface for SBS extrudate from the capillary rheometer at 200°C.

Thermal Properties

The glass transition temperatures (T_g) of PS, BR, and BR-SBS blends were determined with a Du Pont 9900 differential scanning calorimeter over the temperature range of -140 to 160°C at a heating rate of $20^\circ\text{C}/\text{min}$.

Morphology

The extrudates from the capillary rheometer were freeze-fractured, and their morphologies were observed with a scanning electron microscope. The sample for scanning electron microscopy (SEM) analysis was etched with a solution that was prepared with 200 mL of H_2SO_4 , 65 mL of H_3PO_4 , 63 mL of H_2O , and 10 g of CrO_3 . Etching was performed with samples being soaked in the solution for 3–10 min. The BR component on the surface of the sample was extracted by the solution. The samples were then rinsed with H_2O and $\text{C}_2\text{H}_5\text{OH}$ and coated with gold before SEM analysis.

RESULTS AND DISCUSSION

SBS is a triblock copolymer with styrene blocks at 2 ends and BR in the middle. There are chemical bondings between the styrene phase and butadiene phase.¹⁵ Figure 1 gives the SEM micrograph of the extrudate of SBS. The discrete phase represents the PS phase, and the continuous one represents the BR phase. The domain size of styrene phase is rather uniform and small. When BR and SBS are blended, BR will mix with the butadiene blocks of SBS. Figure 2 gives the SEM micrograph of the extrudate of the BR-SBS blend with weight ratio of 50/50 (ST to BD is 15/85). It is

also seen in Figure 2 that the styrene component forms the discrete phase, and the butadiene component forms the continuous phase. The domain size of styrene phase is rather uniform and small. From our previous article,¹ it is found that the discrete phase (PS phase) in the BR-SBS blend is much more uniformly dispersed than that in the PS-BR blend, and the droplet size in the BR-SBS blend is much smaller than that in the PS-BR blend. From the study of Wu,¹⁶ it is known that the stronger the interactions between the 2 phases are, the smaller the droplet size is. Hence, the interaction between the PS phase and BR phase in the BR-SBS blend is due mainly to the chemical bonding existing in the SBS.

The measurement of the glass transition temperature (T_g) of a polymer blend is often used as a criterion to differentiate the degree of miscibility.¹⁷ In general, a miscible polymer blend will exhibit a single T_g between the T_g 's of the components. An immiscible polymer blend will exhibit 2 separate transitions that are consistent with the unblended constituents. While for partial miscible polymer systems, the T_g 's will shift toward each other. The glass transition temperature of the BR-SBS blend is determined from differential scanning calorimetry (DSC) analysis. The glass transition temperatures of pure PS and pure BR are 98.7 and -96.8°C , respectively, and the T_g 's of SBS are shifted from the values for PS and BR of 98.7 and -96.8°C to 70.3 and -83.8°C . The T_g -composition relationship of BR-SBS blend is shown in Figure 3, in which the dashed line is drawn to indicate the existence of PS phase, even though its T_g cannot be observed due to the sensitivity of the DSC. It is seen that there

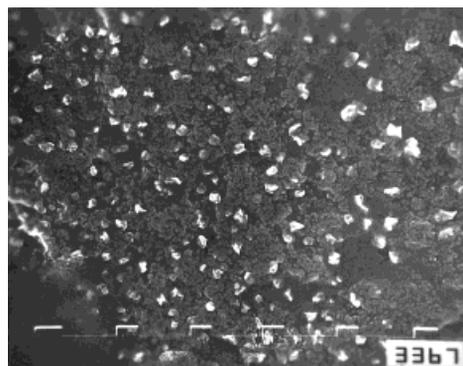


Figure 2 SEM photomicrograph ($\times 5000$) of etched fractured surface for the BR-SBS extrudate from the capillary rheometer with a weight ratio of BR-SBS = 50/50 (or ST/BD = 15/85) at 200°C.

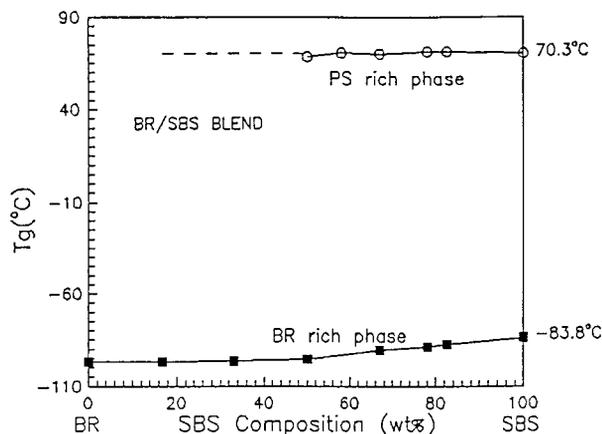


Figure 3 T_g (BR) and T_g (PS) for BR–SBS blends.

are 2 glass transition temperatures for the blend, which indicates the existence of 2 phases in which T_g (BR) is associated with the BR-rich phase and T_g (PS) is associated with the PS-rich phase. The T_g of BR-rich phase is seen to increase with increased content of SBS in the BR–SBS blend, while the T_g of the PS-rich phase is nearly constant at 70°C for all BR–SBS blends. It indicates that the pure BR polymer could mix well with the BR phase in SBS but not significantly disturb the PS phase in SBS.

The viscosity curves for BR–SBS blends and pure PS at 200 and 220°C are shown in Figures 4 and 5, respectively. It can be seen that as shear rate increases, the viscosity decreases, indicating

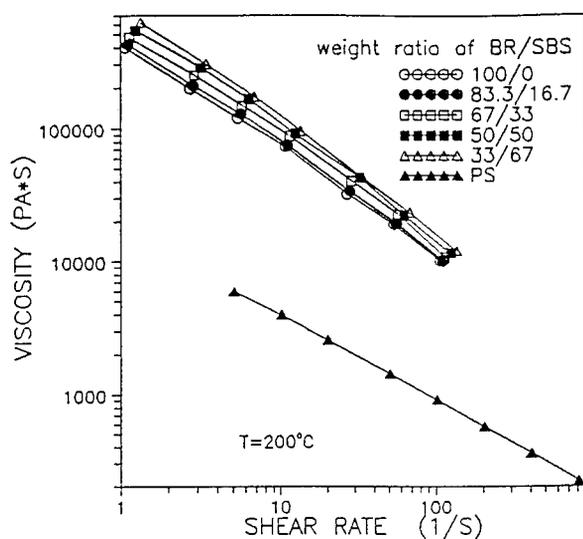


Figure 4 Viscosity versus shear rate for the BR–SBS blends and PS at 200°C.

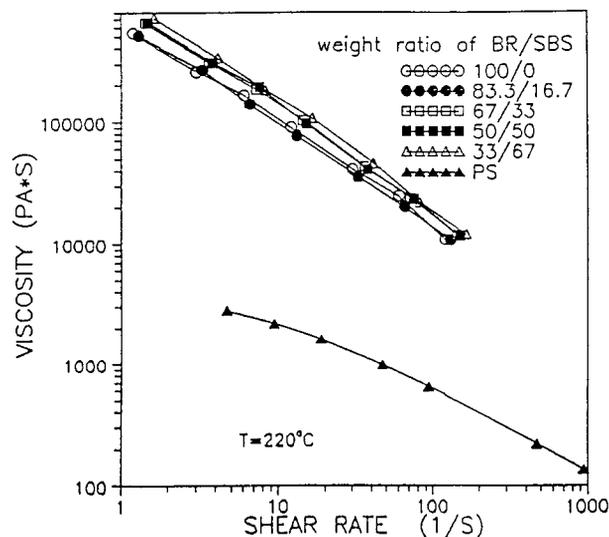


Figure 5 Viscosity versus shear rate for the BR–SBS blends and PS at 220°C.

pseudo plastic flow behavior. We also can see that the viscosity of PS is lower than that of BR–SBS blends, but the viscosity of BR–SBS blend increases with an increase in the content of SBS. In other words, the viscosity of the BR–SBS blend increases with increased content of styrene (or PS), which indicates that PS domains act like rigid fillers in the BR matrix fluid. This might be due to the fact that the domain size of PS is small in the BR–SBS blend, and the interaction coming from the chemical bonding between styrene and butadiene plays a role like surfactants, which will diminish most of the strain to PS domain so that the deformation of PS domain is negligible. Oene⁴ stated that when a suspension of fluid droplets is subjected to flow, the stress arising in the matrix tend to deform the droplet. The stresses are continuous through the interface, thus establishing a system of velocity gradients inside the droplets, which establish streamlines inside and outside the droplets. The phenomena will form an internal circulation. The presence of surfactant may form a solid membrane around the droplets, which will reduce the amount of internal circulation within the droplets, and the droplets will behave as rigid particles.

Figure 6 shows the effect of temperature on the melt viscosities of the BR–SBS blends and PS. It is seen that for BR and all the BR–SBS blends, the viscosity increases slightly with increasing the temperature at a fixed shear rate, while the viscosity of PS decreases with an increase in the temperature at a fixed shear rate. It means that

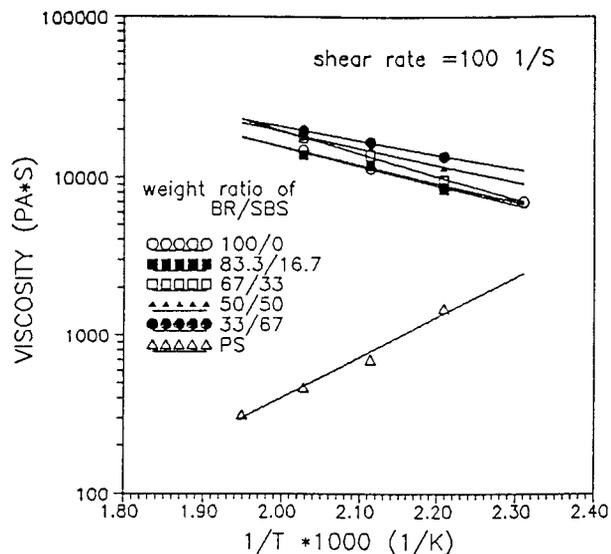


Figure 6 Temperature dependence of viscosity of the BR-SBS blends and PS at shear rate of 100 S^{-1} .

the flow behavior of the BR-SBS blends is dominated by the BR continuous phase, and the PS dispersed phase can be treated as fillers.

In order to observe how the viscosities of the BR-SBS blends vary with the content of styrene phase, the viscosities of a series of BR-SBS blends with different compositions are measured at different shear rate and different temperatures, as shown in Figures 7-12. Meanwhile, the

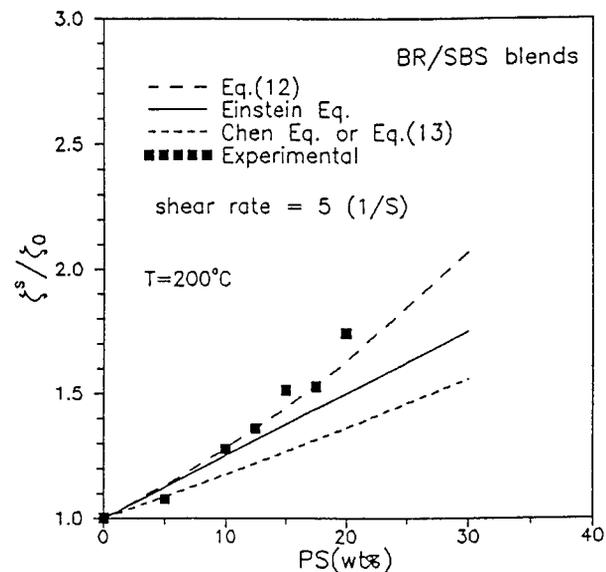


Figure 7 The relative viscosity predicted by eqs. (1), (8), (12), and (13) and experimental values measured at 200°C at shear rate of 5 S^{-1} .

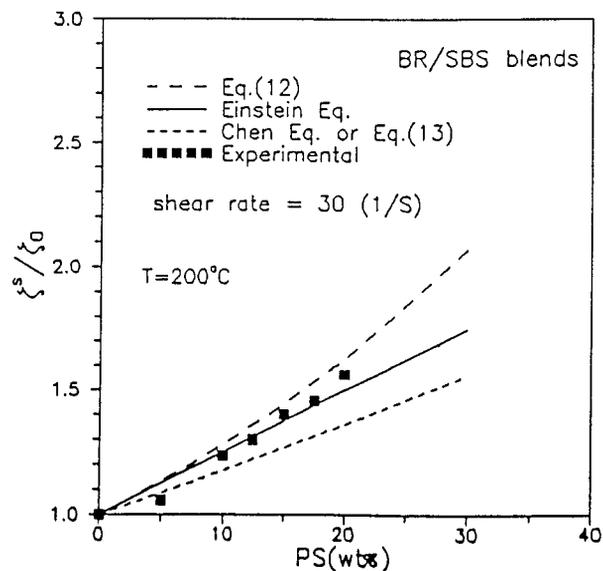


Figure 8 The relative viscosity predicted by eqs. (1), (8), (12), and (13) and experimental values measured at 200°C at shear rate of 30 S^{-1} .

relative viscosity ($\zeta_r = \frac{\zeta^s}{\zeta_0}$) or the viscosity ratio of the blend to the continuous phase fluid (BR) as function of the weight fraction of disperse phase (PS) can be predicted from the equation of Einstein [eq. (1)], the equation of Chen [eq. (8)], and our modified model [eqs. (12) and (13)]. To use eq.

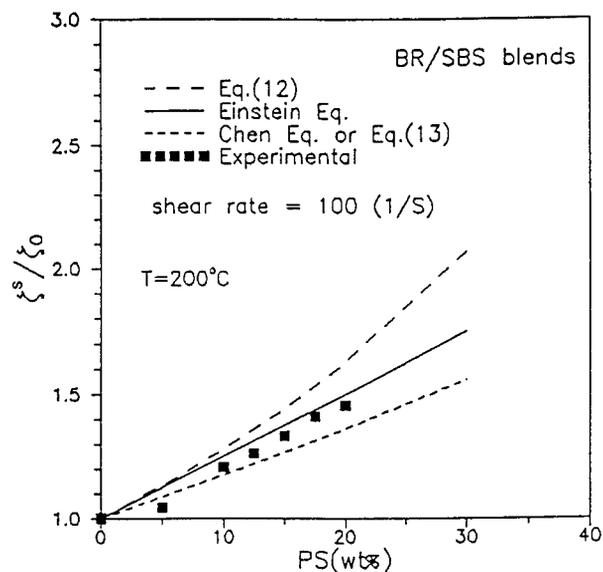


Figure 9 The relative viscosity predicted by eqs. (1), (8), (12), and (13) and experimental values measured at 200°C at shear rate of 100 S^{-1} .

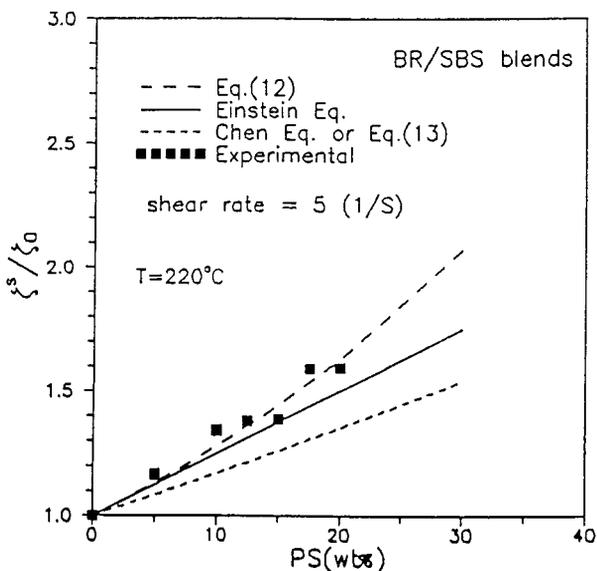


Figure 10 The relative viscosity predicted by eqs. (1), (8), (12), and (13) and experimental values measured at 220°C at shear rate of 5 S⁻¹.

(8), eqs. (12) and (13), we must know the values of a and b . The value of a for pure BR at 200 and 220°C are determined as 0.8306 and 0.7975, respectively, which is equivalent to $1 - n$. The power law constant n can be obtained from curve fitting of the viscosity versus shear rate curve in Figures 4 and 5 into the power law equation [that is, eq. (2)] for pure BR. Also, we assume that the

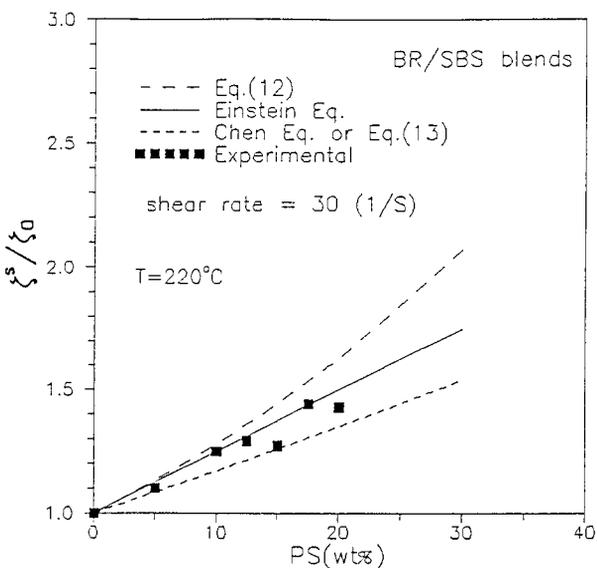


Figure 11 The relative viscosity predicted by eqs. (1), (8), (12), and (13) and experimental values measured at 220°C at shear rate of 30 S⁻¹.

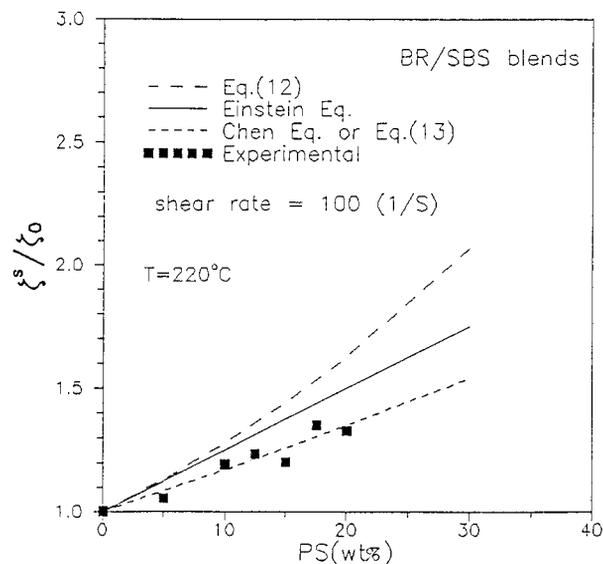


Figure 12 The relative viscosity predicted by eqs. (1), (8), (12), and (13) and experimental values measured at 220°C at shear rate of 100 S⁻¹.

polymer blend fluid is an incompressible fluid suspension. Therefore, the value of b can be obtained from eq. (6).

The predicted relative viscosities together with the experimental values measured at 200°C at shear rate of 5, 30, and 100 S⁻¹ are shown in Figures 7–9, respectively. From these plots, we can find that the relative viscosity predicted by eq. (12) gives the better fit with the experimental

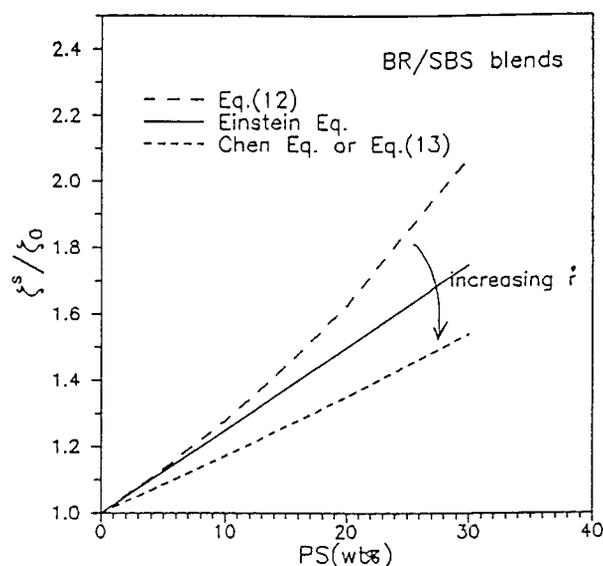


Figure 13 The comparison of theoretical data for eqs. (1), (8), (12), and (13).

values at low shear rate, and eq. (13) [or eq. (8)] gives the better fit with the experimental values at high shear rate. A similar phenomenon can be seen in Figures 10–12 at 220°C.

The comparison of theoretical data for eqs. (1), (8), (12), and (13) are shown in Figure 13. It indicates that Einstein equation is close to our modified model at low $\dot{\gamma}$ [that is, eq. (12)] at a low content of the disperse phase. Chen's model is equivalent to our modified model at large $\dot{\gamma}$ [that is, eq. (13)]. It seems that eqs. (12) and (13) give the upper and lower bounds of the relative viscosity of the BR–SBS blends.

CONCLUSION

In this work, the morphology, T_g , and the viscosities of BR–SBS blends were investigated. From the morphology observation, the styrene component forms the discrete phase, and the butadiene component forms the continuous phase. From the differential scanning calorimetry analysis, it is seen that the presence of 2 glass transition temperatures indicates 2 phases, and the fact that the T_g 's approach each other indicates that the BR–SBS blend is partial miscible. From the viscosity measurement, the viscosity of the BR–SBS blend increases with an increase in the content of PS. The behavior is in accord with the expected behavior of the filler effect. To predict the filler effect of PS phase in the BR–SBS blend, a modified model of Chen's is proposed to calculate the

relative viscosity of the BR–SBS blends with different compositions. The agreement between the theoretical prediction and the experimental results is satisfactory.

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