

Rheological properties of hollow sphere loaded polymer melts

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A simple and semiempirical rheological equation of state was developed to describe and predict the steady-state shear viscosities of hollow sphere loaded polymer melts as functions of temperature, shear rate, and composition of hollow sphere. High density polyethylene (HDPE) was used as a matrix polymer and steady-state shear viscosities of various compositions of HDPE/hollow sphere polymeric composites were measured at various temperatures. The destruction of hollow spheres was observed during viscosity measurement. The proposed model successfully predicted the rheological behaviour of HDPE/hollow sphere systems. It is a simplified algebraic form with a few parameters and gives a great advantage for practical application. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

One of the most prominent peculiarities of polymers is the possibility to change the inherent physical and mechanical properties by chemical or physical modifications. The simplest way of physical modifications of common polymers is their compounding with particulate fillers¹. Mineral fillers (e.g. mica, wollastonite, carbon black, and glass beads) are widely used in formulating cost-effective plastic compositions with desired properties, such as high modulus, tensile or tear strength, abrasion resistance, and fatigue strength^{2,3}. Interest has been shown in the use of hollow microspheres as fillers for polymeric composites due to their unusual and useful characteristics, including low density, high stiffness compared to solid microspheres, low thermal conductivity, and interesting dielectric properties^{1,4}.

Many researchers have proposed to develop relationships to predict mechanical and rheological properties of particulate-filled materials in terms of properties and concentration of the polymeric and filler components. Nielsen⁵ and Palumbo *et al.*¹ proposed the model to predict the elastic modulus of polymeric composites in case of adhesion and non-adhesion between polymer and fillers. Droste *et al.*⁶ studied the effect of the glass transition temperature of filled polymer on their physical properties. Gahleitner⁷ proposed correlations between rheological and mechanical properties of mineral filled polypropylene. However, very little work has been reported on the physical properties of hollow sphere-filled polymers.

In our previous studies^{8,9} based on the thermodynamic principle in case of polymer blends, a unified simple rheological equation of state for the steady-state shear viscosity as functions of shear rate, temperature and composition was proposed and compared with the experimental data.

In this study, we considered the effect of the hollow sphere on the steady-state shear viscosity of polymeric composites. We developed a rheological equation of state to describe and predict the steady-state shear viscosity of various compositions of HDPE/hollow sphere composite melts.

THEORETICAL CONSIDERATION

The steady-state shear viscosity of polymeric composites are affected by shear rate, temperature and particulate fillers¹⁰. If the steady-state viscosity is a state function and shear rate, temperature, and a volume fraction of filler (ϕ_2) are independent variables for a given systems, η is given by,

$$\eta = \eta(1/T, \dot{\gamma}, \phi_2) \quad (1)$$

Similarly,

$$\ln \eta = \eta(1/T, \ln \dot{\gamma}, \ln \tilde{\phi}_2) \quad (2)$$

In this study, we propose that the steady-state shear viscosity can be expressed as functions of temperature, shear rate, and a volume fraction of fillers as follows:

$$\eta = \bar{K}_m \exp\left(\frac{Q_{com}}{RT}\right) \dot{\gamma}^{n-1} (1 + k_E \phi_2)^{-\alpha} \quad (3)$$

where \bar{K}_m , Q_{com} , α , and ϕ_2 are the material constant of the matrix polymer, the activation energy of the polymeric composites for the given flow, a constant, and a volume fraction of fillers, respectively. In the composition-dependent term, we modified Einstein's equation for a Newtonian fluid. We developed the power law concept to the composition-dependent term. In other word, α takes into account non-Newtonian fluid behaviour. k_E is 2.5 for our application because hollow spheres used in this study are fairly spherical, as shown in Figure 8.

$\tilde{\phi}_2$ is defined by

$$\tilde{\phi}_2 = 1 + k_E \phi_2 \quad (4)$$

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$n-1$ is functions of temperature and a volume fraction of fillers and is given by,

$$n - 1 = A(1/T)B(\ln \tilde{\phi}_2) = a(1 + p \ln \phi_2) + b(1 + q \ln \phi_2)/T \quad (5)$$

where $a, b, p,$ and q are adjustable model parameters.

Q_{com} is the activation energy of the polymeric composites for the given flow and is expressed as

$$Q_{com} = Q_{mat} + \delta \ln \tilde{\phi}_2 \quad (6)$$

where Q_{mat} is the activation energy of matrix polymer and δ is a constant. Taking the natural logarithm of both sides of equation (3) gives

$$\ln \eta = \ln \bar{K}_m + (n - 1) \ln \dot{\gamma} - \alpha \ln \phi_2 + \frac{Q_{com}}{RT} \quad (7)$$

We applied the criterion of exactness for a differential expression. From equation (2), the total differential of $\ln \eta$ is defined as

$$\begin{aligned} d \ln \eta &= \left[\frac{\partial \ln \eta}{\partial (1/T)} \right] d(1/T) + \left[\frac{\partial \ln \eta}{\partial \ln \dot{\gamma}} \right] d \ln \dot{\gamma} \\ &+ \left[\frac{\partial \ln \eta}{\partial \ln \tilde{\phi}_2} \right] d \ln \tilde{\phi}_2 = F_1 d(1/T) \\ &+ F_2 d \ln \dot{\gamma} + F_3 d \ln \tilde{\phi}_2 \end{aligned} \quad (8)$$

$F_1, F_2,$ and F_3 can be determined by using equation (7).

$$F_1 = \left[\frac{\partial \ln \eta}{\partial (1/T)} \right] = b(1 + q \ln \tilde{\phi}_2) \ln \dot{\gamma} + \frac{Q_{com}}{R} \quad (9)$$

$$F_2 = \left[\frac{\partial \ln \eta}{\partial \ln \dot{\gamma}} \right] = a(1 + p \ln \tilde{\phi}_2) + b(1 + q \ln \phi_2)/T \quad (10)$$

$$F_3 = \left[\frac{\partial \ln \eta}{\partial \ln \tilde{\phi}_2} \right] = (ap + bq/T) \ln \dot{\gamma} - \alpha + \frac{\delta}{RT} \quad (11)$$

To satisfy equation (7) to be a state function,

$$\begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{\partial}{\partial (1/T)} & \frac{\partial}{\partial \ln \dot{\gamma}} & \frac{\partial}{\partial \ln \tilde{\phi}_2} \\ F_1 & F_2 & F_3 \end{vmatrix} = \vec{0} \quad (12)$$

And following relations should be satisfied.

$$A \equiv \frac{\partial F_1}{\partial \ln \dot{\gamma}} = \frac{\partial^2 \ln \eta}{\partial (1/T) \partial \ln \dot{\gamma}} = \frac{\partial^2 \ln \eta}{\partial \ln \dot{\gamma} \partial (1/T)} = \frac{\partial F_2}{\partial (1/T)} \equiv D \quad (13)$$

$$B \equiv \frac{\partial F_1}{\partial \ln \tilde{\phi}_2} = \frac{\partial^2 \ln \eta}{\partial (1/T) \partial \ln \tilde{\phi}_2} = \frac{\partial^2 \ln \eta}{\partial \ln \tilde{\phi}_2 \partial (1/T)} = \frac{\partial F_3}{\partial (1/T)} \equiv E \quad (14)$$

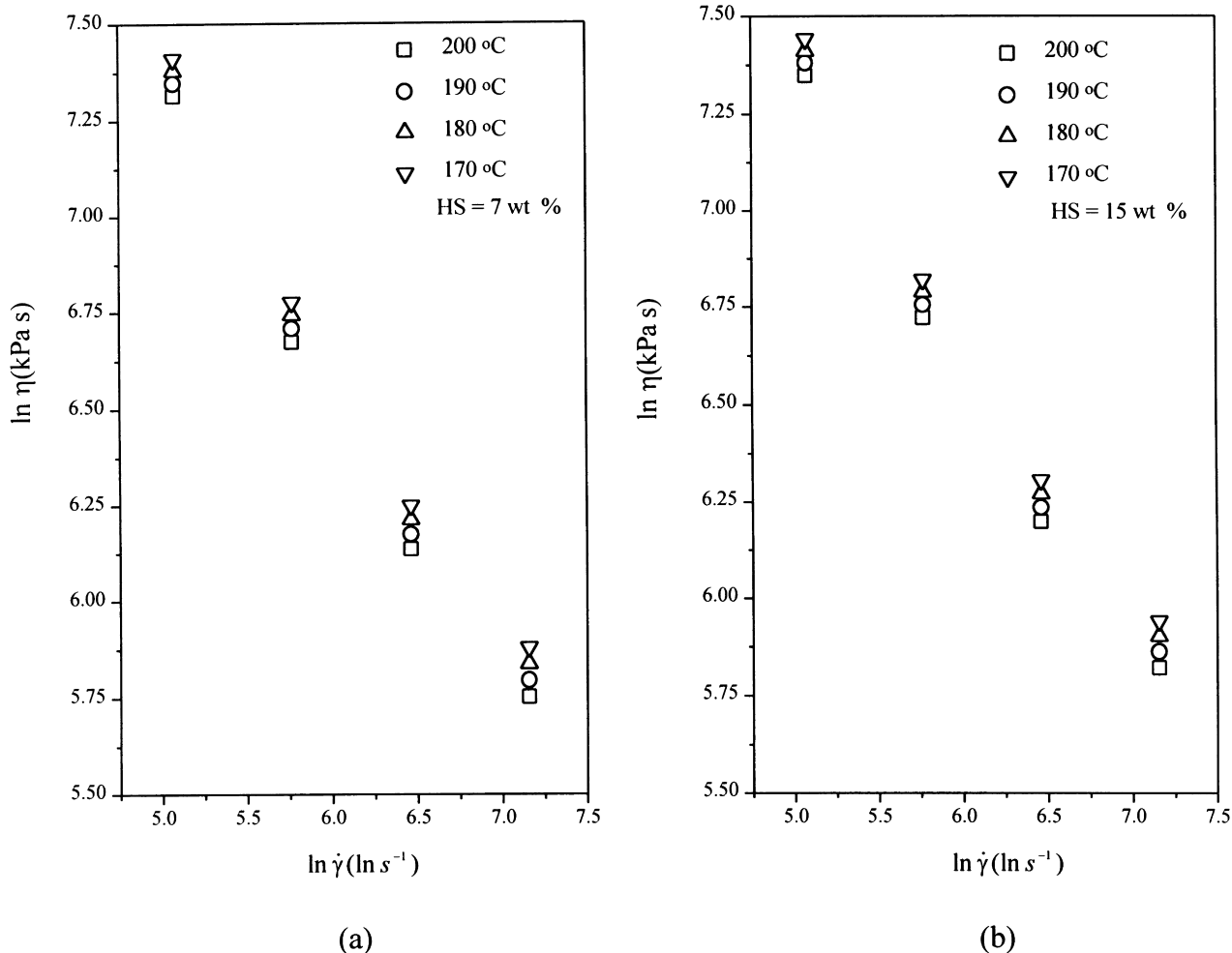


Figure 1 Viscosities of HDPE/hollow sphere composites as a function of shear rate at various temperatures for (a) HS = 7 wt%, (b) HS = 15 wt%: (□) 200°C; (○) 190°C; (Δ) 180°C; (▽) 170°C. HS: hollow sphere

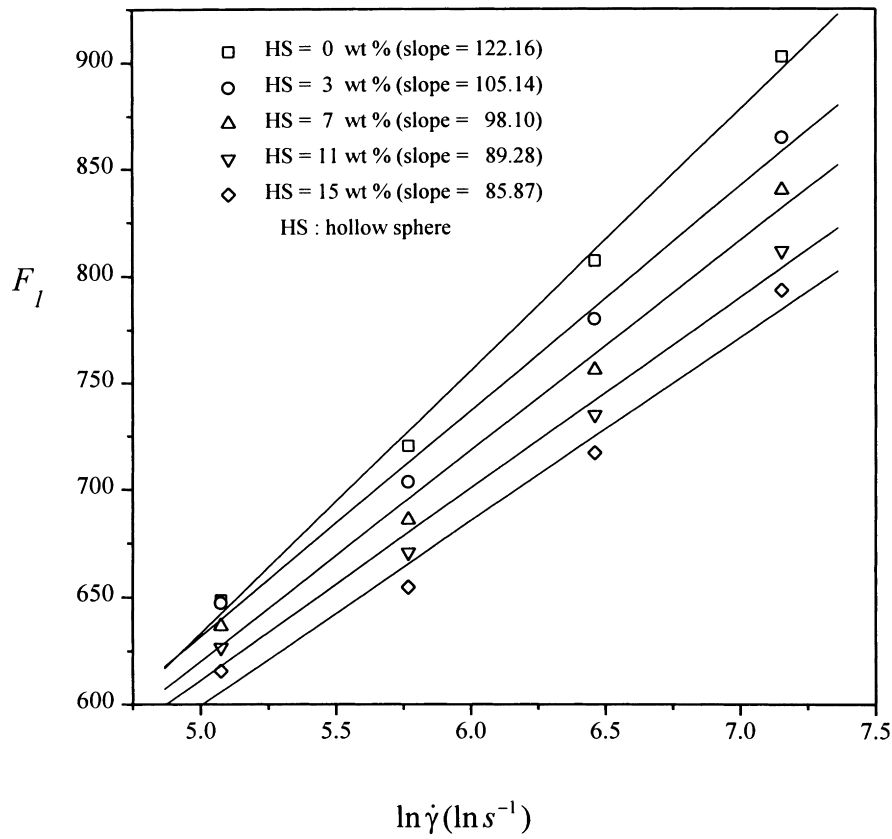


Figure 2 F_1 for various hollow sphere content versus $\ln \dot{\gamma}$: (\square) HS = 0 wt%; (\circ) HS = 3 wt%; (Δ) HS = 7 wt%; (∇) HS = 11 wt%; (\diamond) HS = 15 wt%. HS: hollow sphere

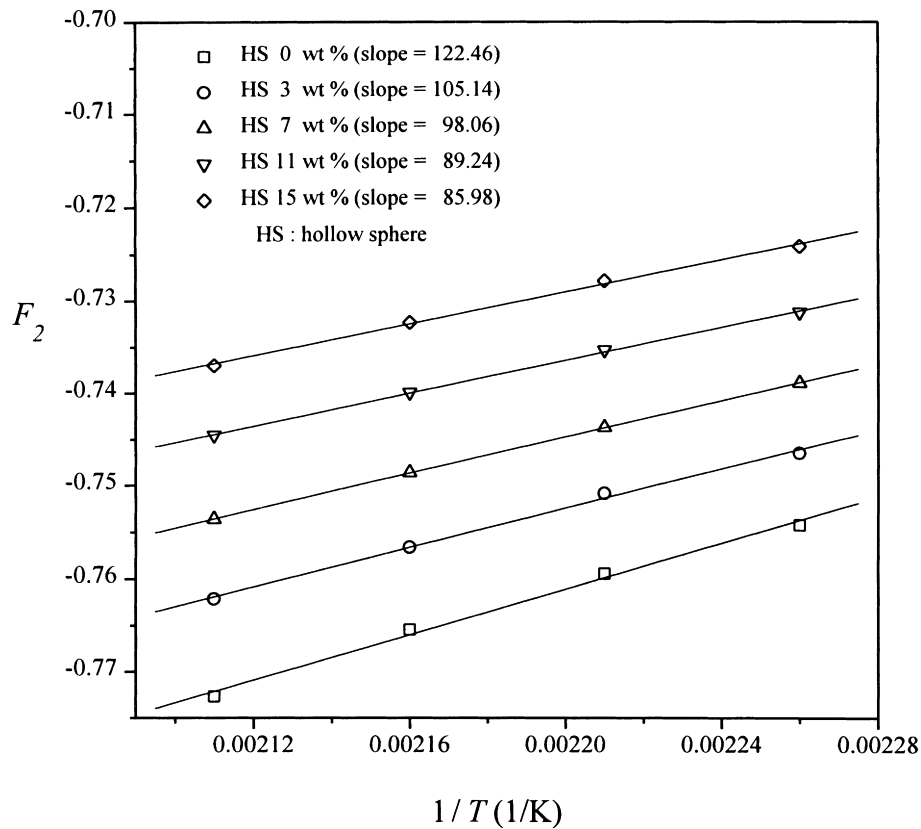


Figure 3 F_2 for various hollow sphere content versus $1/T$: (\square) HS = 0 wt%; (\circ) HS = 3 wt%; (Δ) HS = 7 wt%; (∇) HS = 11 wt%; (\diamond) HS = 15 wt%. HS: hollow sphere

$$C \equiv \frac{\partial F_2}{\partial \ln \tilde{\phi}_2} = \frac{\partial^2 \ln \eta}{\partial \ln \dot{\gamma} \partial \ln \tilde{\phi}_2} = \frac{\partial^2 \ln \eta}{\partial \ln \tilde{\phi}_2 \partial \ln \dot{\gamma}} = \frac{\partial F_3}{\partial \ln \dot{\gamma}} \equiv F \quad (15)$$

We verified that equation (7) is a state function by showing that experimental results and equations (13)–(15) were in good agreement.

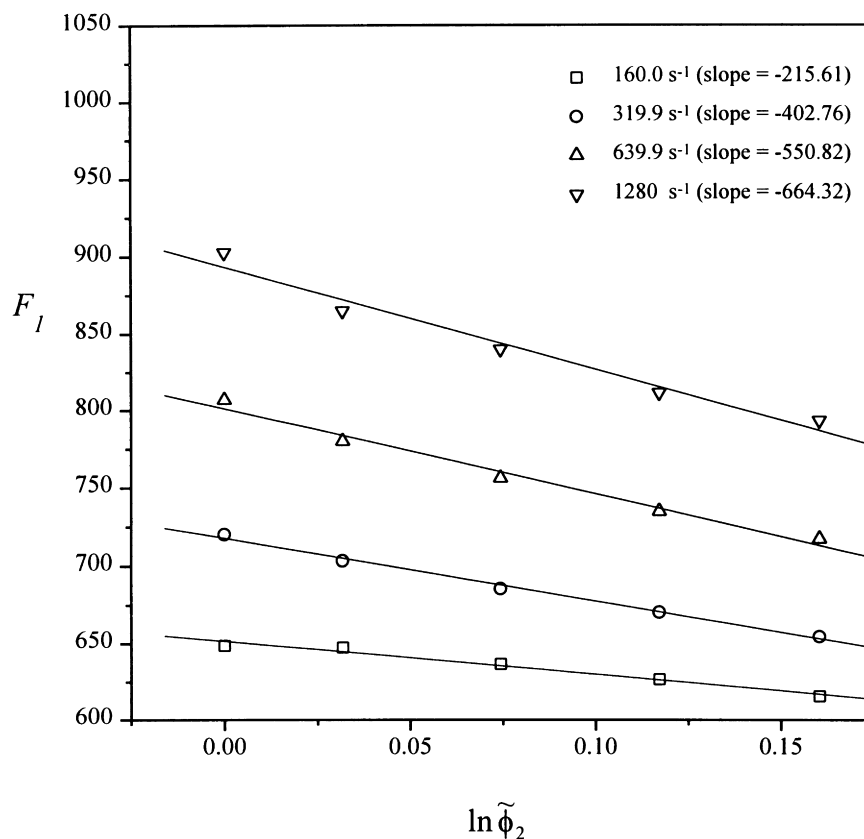


Figure 4 F_1 for various shear rates versus $\ln \tilde{\phi}_2$: (□) 160 s⁻¹; (○) 319.9 s⁻¹; (Δ) 639.9 s⁻¹; (▽) 1280 s⁻¹

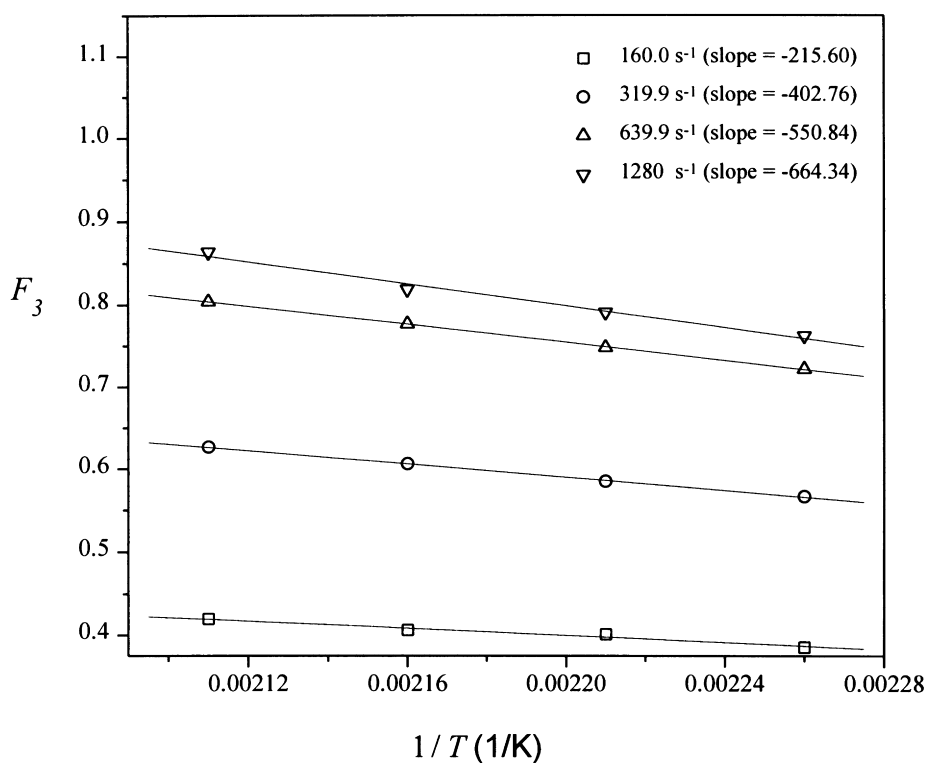


Figure 5 F_3 for various shear rates versus $1/T$: (□) 160 s⁻¹; (○) 319.9 s⁻¹; (Δ) 639.9 s⁻¹; (▽) 1280 s⁻¹

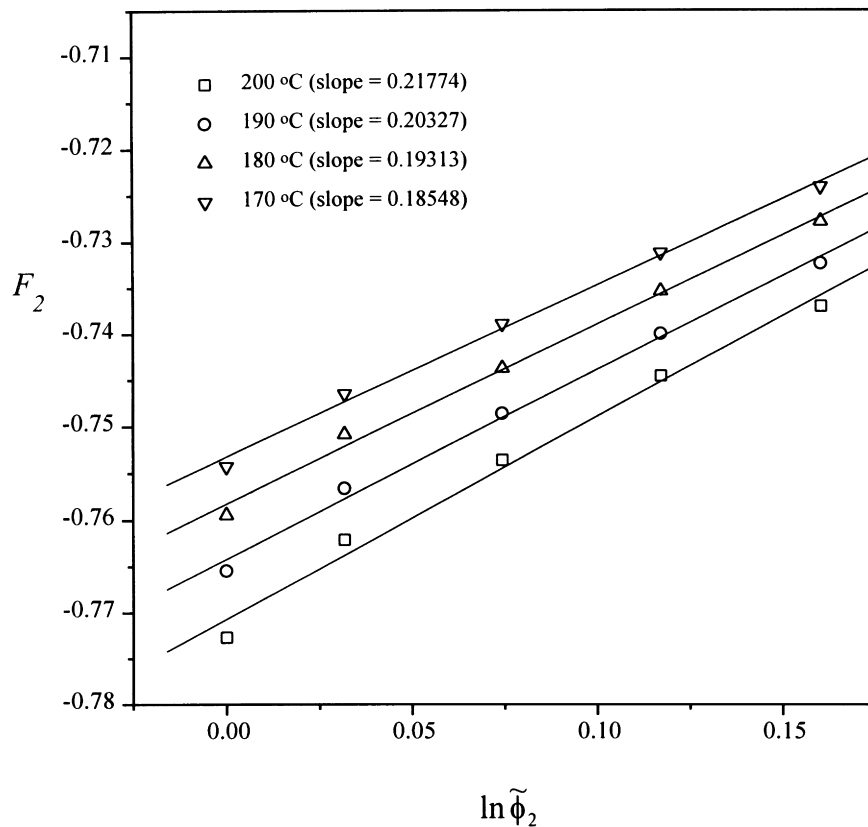


Figure 6 F_2 for various temperatures versus $\ln \tilde{\phi}_2$: (□) 200°C; (○) 190°C; (Δ) 180°C; (▽) 170°C

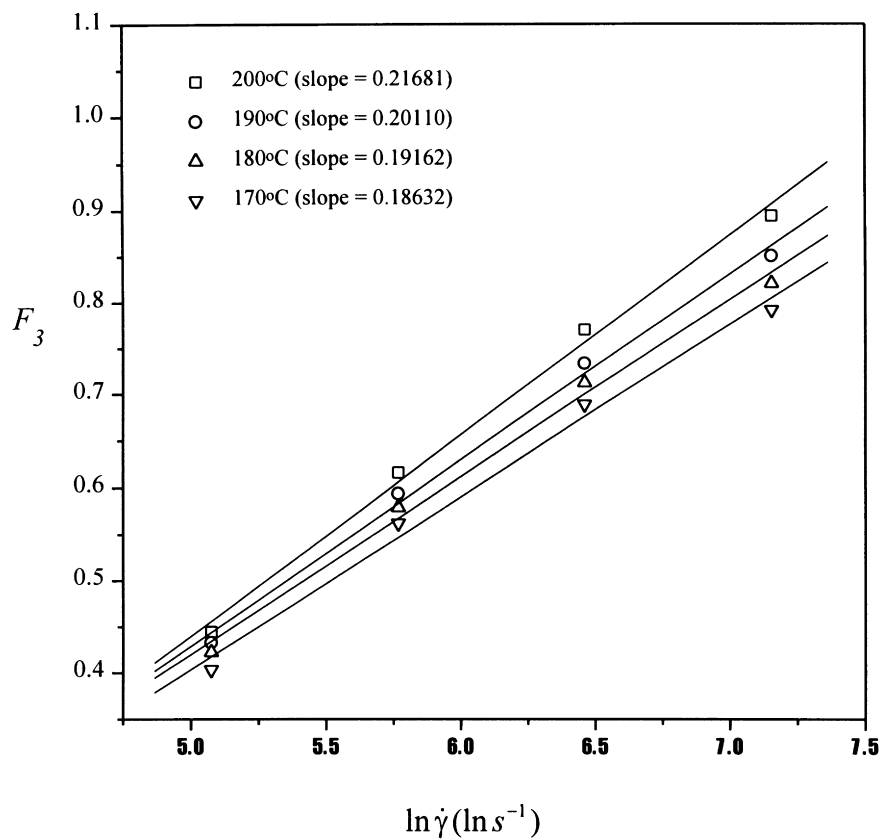


Figure 7 F_3 for various temperatures versus $\ln \dot{\gamma}$: (□) 200°C; (○) 190°C; (Δ) 180°C; (▽) 170°C

EXPERIMENTAL

Materials

High density polyethylene (HDPE 7000F: $\sigma = 0.956 \text{ g/cm}^3$) was provided from Honam Petrochemical Co. and hollow spheres (MICROCELL SL 200: $\sigma_{\text{bulk}} = 0.405 \text{ g}$, $d = 100\text{--}125 \mu\text{m}$) were kindly supplied by Dong Bang Trading Co.

Sample preparation

HDPE/hollow sphere polymeric composites were prepared by using a two-roll mill for 30 min at 160°C . Compositions of hollow spheres were 0, 3, 7, 11 and 15 wt%.

Measurement of steady-state shear viscosity

Steady-state shear viscosities of HDPE/hollow sphere composite melts were measured by using capillary rheometer (RH14-C, Rosand Co.). The length and diameter of the capillary are 10 and 1 mm, respectively. Test shear rates were 160.0, 319.9, 639.9 and 1280 s^{-1} and test temperatures were 170, 180, 190 and 200°C .

RESULTS AND DISCUSSION

As shown in *Figure 1*, steady-state shear viscosities of the HDPE/hollow sphere composites for 7 wt% and 15 wt% were plotted against $\ln \dot{\gamma}$ at various temperatures and compositions. Steady-state shear viscosities of the composites increase with hollow sphere content and decrease with temperature. From equation (9), the F_1 value for various hollow sphere contents can be determined from the slope of a plot of $\ln \eta$ versus $1/T$.

The values of F_1 at various $\ln \dot{\gamma}$ were determined and plotted against $\ln \dot{\gamma}$ in *Figure 2*. The weight percent of the hollow sphere were 0, 3, 7, 11 and 15. From equation (13), values of $A(= \partial^2 \ln \eta / \partial (1/T) \partial \ln \dot{\gamma})$ are slopes of a plot F_1 versus $\ln \dot{\gamma}$. The calculated A values at various compositions of 0, 3, 7, 11 and 15 wt% were 122.46, 105.14, 98.10, 89.28 and 85.87, respectively.

From equation (10), the F_2 value for various hollow sphere contents can be determined from the slope of a plot of the steady-state viscosities versus $\ln \dot{\gamma}$. *Figure 3* shows a plot of F_2 versus $1/T$. The hollow sphere contents were 0, 3, 7, 11 and 15 wt%. From equation (13), values of $D(= \partial^2 \ln \eta / \partial \ln \dot{\gamma} \partial (1/T))$ can be determined from the slope of a plot of F_2 versus $1/T$. The calculated D values at various compositions of 0, 3, 7, 11 and 15 wt% were 122.46, 105.14, 98.06, 89.24 and 85.98, respectively.

Figure 4 shows a plot of F_1 versus $\ln \dot{\phi}_2$ at various shear rates. The slope of a plot of F_1 versus $\ln \dot{\phi}_2$ gives the value of $B(= \partial^2 \ln \eta / \partial (1/T) \partial \ln \dot{\phi}_2)$ in equation (14). The calculated B values at various shear rates of 160.0, 319.9, 639.9 and 1280 s^{-1} were -215.61 , -402.76 , -550.82 and -664.32 , respectively.

The F_3 value at various shear rates can be determined from the slope of a plot of the steady-state shear viscosities versus $\ln \dot{\phi}_2$. *Figure 5* shows a plot of F_3 versus $1/T$. The shear rates were fixed at 160.0, 319.9, 639.9 and 1280 s^{-1} . The slope of a plot of F_3 versus $1/T$ is the value of $E(= \partial^2 \ln \eta / \partial \ln \dot{\phi}_2 \partial (1/T))$ in equation (14). The calculated E values at various shear rates of 160.0, 319.9, 639.9 and 1280 s^{-1} were -215.60 , -402.76 , -550.84 and -664.32 , respectively.

Figure 6 shows a plot of F_2 versus $\ln \dot{\phi}_2$ at various temperatures. The slope of a plot of F_2 versus $\ln \dot{\phi}_2$ is the value of $C(= \partial^2 \ln \eta / \partial \ln \dot{\gamma} \partial \ln \dot{\phi}_2)$ in equation (15). The calculated C values at different temperatures of 170, 180,

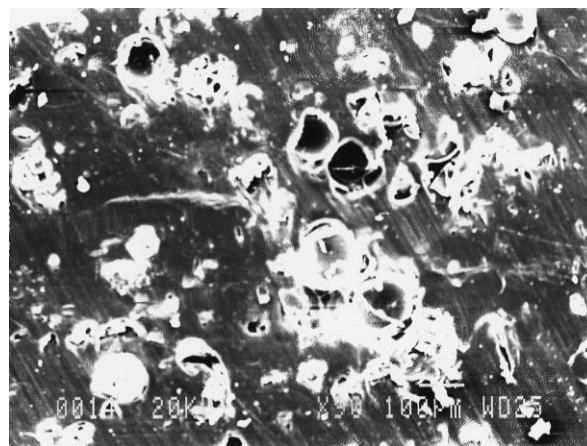
190 and 200°C were 0.18548, 0.19313, 0.20327 and 0.21744, respectively.

The value of $F(\partial^2 \ln \eta / \partial \ln \dot{\phi}_2 \partial \ln \dot{\gamma})$ is the slope of a plot of F_3 versus $\ln \dot{\gamma}$ in equation (15), as shown in *Figure 7*. The calculated F values at various temperatures of 170, 180, 190 and 200°C were 0.18632, 0.19162, 0.20110 and 0.21681, respectively.

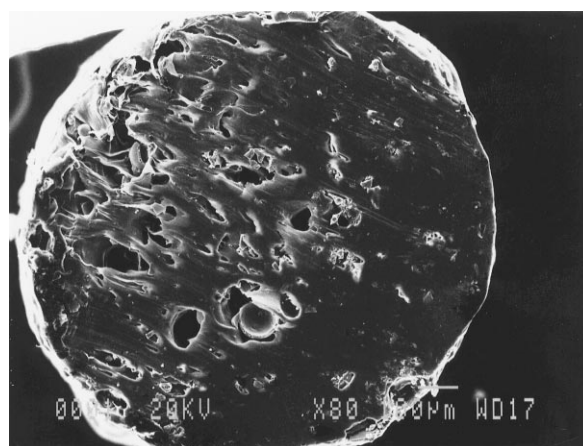
The difference between the three pairs of the calculated values, A and D , B and E , and C and F is negligible. Therefore, equation (7) satisfies the criterion of exactness for a differential expression as previously discussed in equation (12). Adjustable parameters are determined by using the least-squares method, and they are listed in *Table 1*.

Table 1 Adjustable model parameters

Adjustable parameter	value
a	-1.0175
p	-0.6654
b	116.71
q	-1.8456
α	2.45
Q_{mat}/R	52.30
δ/R	856.65
$\ln \bar{K}_m$	11.0167



(a)



(b)

Figure 8 The scanning electron microscope of the HDPE/hollow sphere composites (15 wt% of hollow sphere) before (a) and after viscosity measurement (b)

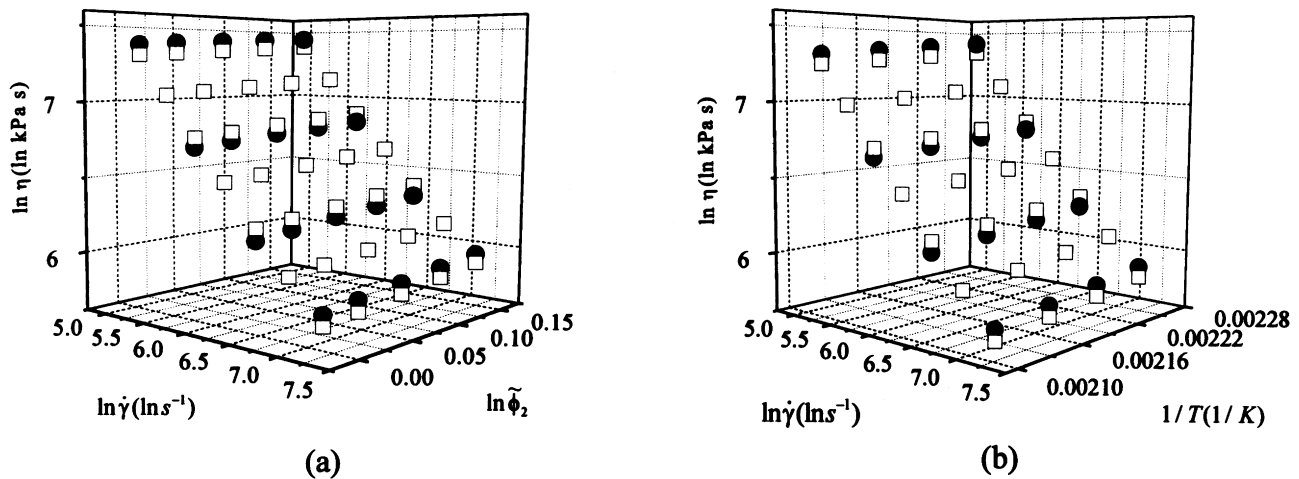


Figure 9 The comparison of measured viscosities with calculated viscosities using equation (7): (a) $T = 170^\circ\text{C}$, and (b) 7 wt% of hollow sphere: (□) calculated values; (●) measured values

As shown in *Figure 8a*, it is clearly seen that not many hollow spheres are destroyed. However, *Figure 8b* shows that slight destructions of particles during the measurement of steady-state viscosities occurred.

Figure 9 shows the comparison of measured viscosities with calculated viscosities using equation (7) in a three-dimensional plot. *Figure 9a* represents the viscosity-shear rate-composition plot at a fixed temperature of 170°C . *Figure 9b* shows viscosity-shear rate-a reciprocal temperature plot at fixed composition of $\ln \tilde{\phi}_2 = 0.07442$. As shown in those figures, our proposed model describes and predicts very well the steady-state shear viscosities of HDPE/hollow spheres composites. A slight deviation might be from the destruction of hollow spheres during the measurement.

CONCLUSION

The steady-state shear viscosities of HDPE/hollow sphere polymeric composites were measured as functions of temperature, shear rate and hollow sphere content. The semi-empirical rheological equation of state to predict steady-state shear viscosities of polymeric composites was proposed in this study. Our proposed model was consistent with the experimental data. The proposed model is semi-empirical. A simple algebraic form with a few adjustable model parameters appears to be suitable for describing

steady-state shear viscosities of HDPE/hollow spheres systems. It gives a great advantage for practical applications. The destruction of hollow spheres during measurements of viscosities was observed through the picture of a scanning electron microscope. A slight deviation between measured viscosities and calculated values might be from the destruction of hollow spheres during the experiment.

REFERENCES

1. Palumbo, M., Donzella, G., Temesti, E. and Ferruti, P., *J. Appl. Polym. Sci.*, 1996, **60**, 47–53.
2. Lee, C. H. and Tensa, S., *J. Adhesion Sci. Technol.*, 1989, **3**(4), 291–303.
3. Fried, J. R., *Polymer Science and Technology* Prentice-Hall, Inc., New York, 1995, p. 257.
4. Liu, J. G. and Wilcox, D. L., *J. Appl. Phys.*, 1995, **77**(12), 6456–6460.
5. Nielsen, L. E., *J. Appl. Polym. Sci.*, 1966, **10**, 97–103.
6. Droste, D. H. and Dibeneffo, A. T., *J. Appl. Polym. Sci.*, 1969, **13**, 2149–2168.
7. Gahleitner, M., Bernreitner, K. and Neissl, W., *J. Appl. Polym. Sci.*, 1994, **53**, 283–289.
8. Han, S., Moon, T. J., Suh, K. D., Noh, S. T. and Bae, Y. C., *J. Appl. Polym. Sci.*, 1996, **61**, 1985–1989.
9. Han, S., Moon, T. J., Yi, S. J., Lee, S. H. and Bae, Y. C., *Polymer*, 1998, **39**, 1113–1117.
10. Nielsen, L. E., *Polymer Rheology*. Marcel Dekker, Inc., New York, 1977, pp. 31, 48, 133.