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Composition dependence of rheological properties of polymer blends

Seung Han[a], Tak Jin Moon[a], Young Chan Bae[b,*], Seungjong Yi[c] and Sang Hwan Lee[c]
[a]*Department of Materials Science, Korea University, Seoul 136-701, Korea*
[b]*Department of Industrial Chemistry, Hanyang University, Seoul 133-791, Korea*
[c]*School of Mechanical Engineering, Hanyang University, Seoul 133-791, Korea*
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A semi-empirical rheological equation of state was developed to describe temperature, shear rate and composition dependence of the steady-state shear viscosity of poly(L-lactic acid)(PLA)/poly(ε-caprolactone)(PCL) systems. The composition dependent rheological equation of state proposed here has a very simple algebraic form with a few adjustable parameters. Its simplicity is a great advantage for practical application and it appears to be suitable for describing the rheological behaviour of PLA/PCL blends. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Conventional plastics are not easily degraded in the environment due to their high molecular weight and hydrophobic character. Disposal of plastics, then, has become a major environmental concern, resulting in plastics being developed that degrade in the environment.

Poly(L-lactic acid) (PLA) is a component of an interesting family of biodegradable polymers. Because of their good biocompatibility, they are useful as versatile materials for many temporary therapeutic uses such as osteosynthesis, bone reconstruction, drug delivery and structure materials[1]. For these applications, it is sometimes desirable to modify the mechanical properties and the degradation behaviour by copolymerization with other monomers, such as ethylene oxide and ε-caprolactone [2,3], or by blending with various polymers, such as poly(D-lactic acid), poly(ethylene-vinyl acetate) (EVA) and poly(ε-caprolactone) (PCL) [4–6].

Although much work has been reported on the biodegradable properties of PLA, PCL, and their blends with other synthetic polymers, the literature has given less attention to fundamental studies of those polymers such as mechanical and rheological properties. In this study, the rheological property which is one of the most important factors in manufacturing processing equipment was examined.

Over the past several decades, many research groups have done a lot of experimental and theoretical work to predict rheological properties of polymeric materials using suitable stress and deformation variables. In our previous studies [7,8], based on the basic thermodynamic principle, a unified simple rheological equation of state for the steady-state shear viscosity as function of shear rate and temperature was proposed and was tested with experimental data. The proposed model was successfully able to predict the viscosity of polymer melts. In this study, we added a composition dependence term to the previously developed rheological equation of state and the model was compared with our experimental results of PLA/PCL blend systems.

THEORETICAL CONSIDERATION

If the steady-state shear viscosity is a state function and the shear rate, temperature and weight per cent of dispersed polymer (w) are independent variables for a given system, η is given by

$$\eta = \eta(\dot{\gamma}, 1/T, w) \qquad (1a)$$

Similarly,

$$\ln \eta = \eta(\ln \dot{\gamma}, 1/T, \ln w) \qquad (1b)$$

Based on the thermodynamic principle, the steady-state shear viscosity can be expressed as a function of temperature, shear rate and weight per cent of dispersed polymer in the polymer mixture, as shown below:

$$\eta = \bar{K}_{\mathrm{matrix}} \dot{\gamma}^{n-1} \bar{w}^{m} \exp\left(\frac{Q_{\mathrm{blend}}}{RT}\right) \qquad (2)$$

where $\bar{K}_{\mathrm{matrix}}$, n, m, and R are the material constant of the polymer matrix, the power law index, a constant, and the universal gas constant, respectively.

In this study, $\bar{w}$ is defined as follows:

$$\bar{w} = w + 1 \qquad (2a)$$

To avoid logarithmic error for calculation of the pure component (i.e. $w = 0\%$), we add 1 to w as a matter of convenience.

$n - 1$ is a function of temperature and weight per cent of dispersed polymer and is given by

$$n - 1 = \Gamma(1/T)E(\ln \bar{w}) = \alpha(1 + \varphi \ln \bar{w}) + \beta(1 + \delta \ln \bar{w})/T \qquad (2b)$$

where α, β, φ and δ are fitting parameters.

Q_{blend} is the activation energy of the blend for the given flow and is expressed as

$$Q_{\mathrm{blend}} = Q_{\mathrm{matrix}} + \phi \ln \bar{w} \qquad (2c)$$

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[*] To whom correspondence should be addressed

where Q_{matrix} is the activation energy of matrix polymer and ϕ is a constant.

Taking the natural logarithm of both sides of equation (2) gives,

$$\ln \eta = \ln \bar{K}_{\mathrm{matrix}} + (n-1)\ln \dot{\gamma} + m \ln \bar{w} + \frac{Q_{\mathrm{blend}}}{RT} \quad (3)$$

Now, we apply the criterion of exactness for a differential expression. From equation (1), the total differential of $\ln \eta$ is defined as

$$\mathrm{d} \ln \eta = \left[\frac{\partial \ln \eta}{\partial(1/T)}\right] \mathrm{d}(1/T) + \left[\frac{\partial \ln \eta}{\partial \ln \dot{\gamma}}\right] \mathrm{d} \ln \dot{\gamma} + \left[\frac{\partial \ln \eta}{\partial \ln \bar{w}}\right] \mathrm{d} \ln \bar{w} = F_1 d(1/T) + F_2 \mathrm{d} \ln \dot{\gamma} + F_3 \mathrm{d} \ln \bar{w} \quad (4)$$

Then, F_1, F_2, and F_3 can be expressed using equation (3) as follows:

$$F_1 = [\partial \ln \eta / \partial(1/T)] = \beta(1 + \delta \ln \bar{w}) \ln \dot{\gamma} + (Q_{\mathrm{matrix}} + \phi \ln \bar{w})/R \quad (5)$$

$$F_2 = [\partial \ln \eta / \partial \ln \dot{\gamma}] = \alpha(1 + \partial \ln \bar{w}) + \beta(1 + \delta \ln \bar{w})/T \quad (6)$$

$$F_3 = [\partial \ln \eta / \partial \ln \bar{w}] = \delta \ln \dot{\gamma}(\alpha + \beta/T) + \phi/RT + m \quad (7)$$

To satisfy equation (3) to be a state function,

$$\mathrm{curl}(\ln \vec{\eta}) = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \partial/\partial \ln \dot{\gamma} & \partial/\partial \ln \bar{w} & \partial/\partial(1/T) \\ F_1 & F_2 & F_3 \end{vmatrix} = \vec{0} \quad (8)$$

And the following relations should be satisfied.

$$J \equiv \frac{\partial^2 \ln \eta}{\partial(1/T)\, \partial \ln \dot{\gamma}} = \frac{\partial^2 \ln \eta}{\partial \ln \dot{\gamma}\, \partial(1/T)} \equiv D \quad (9)$$

$$K \equiv \frac{\partial^2 \ln \eta}{\partial \ln \dot{\gamma}\, \partial \ln \bar{w}} = \frac{\partial^2 \ln \eta}{\partial \ln \bar{w}\, \partial \ln \dot{\gamma}} \equiv E \quad (10)$$

$$L \equiv \frac{\partial^2 \ln \eta}{\partial \ln \bar{w}\, \partial(1/T)} = \frac{\partial^2 \ln \eta}{\partial(1/T)\, \partial \ln \bar{w}} \equiv F \quad (11)$$

We proved that equation (3) is a state function by showing that our experimental results satisfied equations (9)–(11).

EXPERIMENTAL

PLA was supplied by Chronopol Inc. and PCL (Tone P-787) was from Union Carbide. PLA/PCL blends were prepared using the solvent casting method and the weight fractions of PLA were 1, 0.8, and 0.6. Chloroform was used as a solvent in this study. The prepared solutions were dried under vacuum at 50°C for 48 h.

A capillary rheometer (RH14-C, Rosand Co.) was used to measure steady-state shear viscosities of PLA/PCL blends. The test temperatures were 170, 180, 190, and 200°C.

RESULTS AND DISCUSSION

Figure 1 shows that steady-state shear viscosities of PLA/PCL blends increase with PCL content. From equation (5), the F_1 value for various PCL compositions can be determined from the slope of the plot of $\ln\eta$ *versus* $1/T$ ($F_1 = \partial\ln\eta/\partial(1/T)$). *Figure 2* shows a plot of F_1 *versus* $\ln\dot{\gamma}$. The PLA/PCL compositions were 100/0, 80/20, and 60/40. It is obvious that the slope of a plot of F_1 *versus* $\ln\dot{\gamma}$ in *Figure 2* is J ($\partial^2\ln\eta/\partial(1/T)\partial\ln\dot{\gamma}$), in equation (9). The calculated J values for the PLA/PCL compositions of 100/0, 80/20, and 60/40 were −2040, −1776, and −1609, respectively, and the values are listed in *Table 1*.

Again, from equation (6), F_2 for various PCL compositions can be determined from the slope of the plot of $\ln\eta$ *versus* $\ln\dot{\gamma}$ ($F_2 = \partial\ln\eta/\partial\ln\dot{\gamma}$). *Figure 3* shows a plot of F_2 *versus* $1/T$. The PLA/PCL compositions were 100/0, 80/20, and 60/40. Then, the slope of a plot of F_2 *versus* $1/T$ in *Figure 3* is the D value ($\partial^2\ln\eta/\partial\ln\dot{\gamma}\partial(1/T)$), in equation (9). The calculated D values for the PLA/PCL compositions of 100/0, 80/20 and 60/40 were −1949, −1786 and −1535, respectively, and the values are listed in *Table 1*.

Figure 4 shows a plot of F_2 *versus* $\ln\bar{w}$ at various

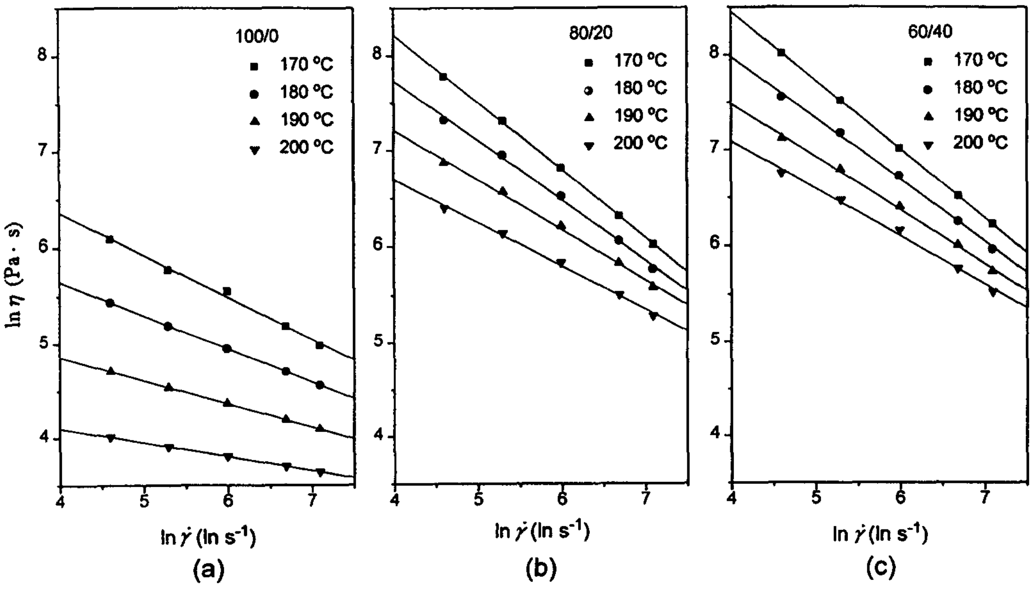

Figure 1 Viscosities of PLA/PCL blends as a function of shear rate at various temperatures for (a) PLA/PCL = 100/0, (b) PLA/PCL = 80/20 and (c) PLA/PCL = 60/40: (■) 170°C; (●) 180°C; (▲) 190°C; (▼) 200°C

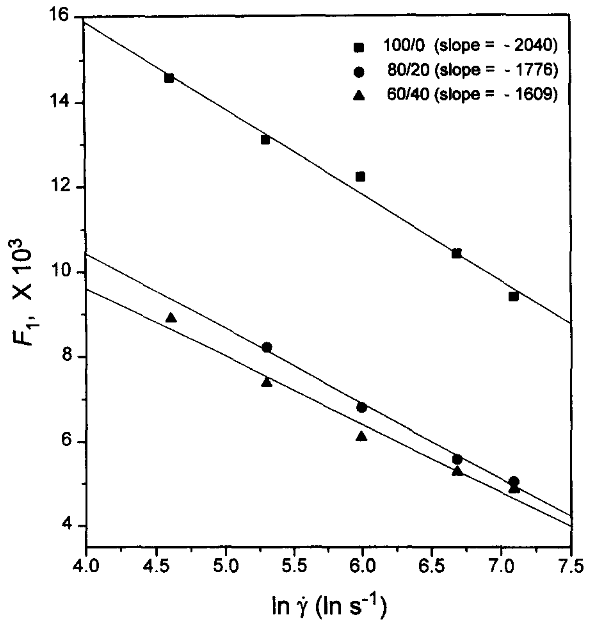

Figure 2 F_1 for various PCL compositions ($[\partial\ln\eta/\partial(1/T)]_{\ln\bar{w}}$) *versus* $\ln\dot\gamma$: (■) PLA/PCL = 100/0; (●) PLA/PCL = 80/20; (▲) PLA/PCL = 60/40

Table 1 Calculated values of *J*, *D*, *K*, *E*, *L*, and *F*

PCL composition (wt.%)	*J*	*D*
0	− 2040	− 1949
20	− 1776	− 1786
40	− 1609	− 1535
Temperature (°C)	*K*	*E*
170	-8.02×10^{-2}	-8.02×10^{-2}
180	-8.23×10^{-2}	-8.23×10^{-2}
190	-8.51×10^{-2}	-8.51×10^{-2}
200	-9.48×10^{-2}	-9.48×10^{-2}
Shear rate (s^{-1})	*L*	*F*
100	− 1492	− 1492
200	− 1494	− 1494
400	− 1612	− 1611
800	− 1383	− 1383
1200	− 1228	− 1228

temperatures ($T = 170$, 180, 190, and 200°C). The slope of the plot is K ($\partial^2\ln\eta/\partial\ln\dot\gamma\partial\ln\bar{w}$), in equation (10). The calculated K values for temperatures of 170, 180, 190, and 200°C were -8.02×10^{-2}, -8.23×10^{-2}, -8.51×10^{-2}, and -9.48×10^{-2}, respectively. Their values are listed in *Table 1*.

The F_3 value at a given temperature can be determined from the slope of the plot of $\ln\eta$ *versus* $\ln\bar{w}$ ($F_3 = \partial\ln\eta/\partial\ln\bar{w}$). *Figure 5* shows a plot of F_3 *versus* $\ln\dot\gamma$ and measured temperatures were 170, 180, 190, and 200°C. The slope of a plot of F_3 *versus* $\ln\dot\gamma$ is E ($\partial^2\ln\eta/\partial\ln\bar{w}\partial\ln\dot\gamma$), in equation (10). As listed in *Table 1*, the calculated E values for temperatures of 170, 180, 190, and 200°C were -8.02×10^{-2}, -8.23×10^{-2}, -8.51×10^{-2}, and -9.48×10^{-2}, respectively.

The F_3 value at various shear rates can be determined from the slope of the plot of $\ln\eta$ *versus* $\ln\bar{w}$. *Figure 6* shows a plot of F_3 *versus* $1/T$. The shear rates were set at 100, 200, 400, 800, and 1200 s^{-1}. Its slope is the value L ($\partial^2\ln\eta/\partial\ln\bar{w}\partial(1/T)$), in equation (11). The calculated L values at various shear rates of 100, 200, 400, 800, and 1200 s^{-1} were −1492, −1494, −1611, −1383, and −1228, respectively. The values are listed in *Table 1*.

Figure 7 shows a plot of F_1 *versus* $\ln\bar{w}$ at various shear rates. The slope of a plot gives the F value ($\partial^2\ln\eta/\partial(1/T)\partial\ln\bar{w}$), in equation (11). As listed in *Table 1*, calculated F values for shear rates of 100, 200, 400, 800, and 1200 s^{-1} were −1492, −1494, −1612, −1383, and −1228, respectively.

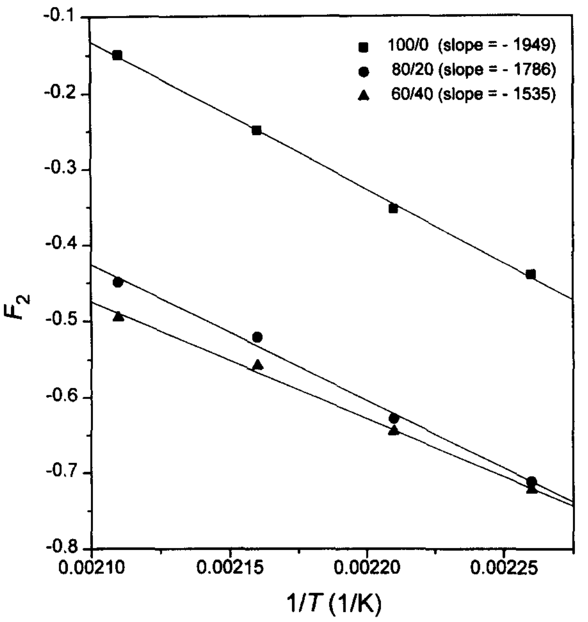

Figure 3 F_2 for various PCL compositions ($[\partial\ln\eta/\partial\ln\dot\gamma]_{\ln\bar{w}}$) *versus* $1/T$: (■) PLA/PCL = 100/0; (●) PLA/PCL = 80/20; (▲) PLA/PCL = 60/40

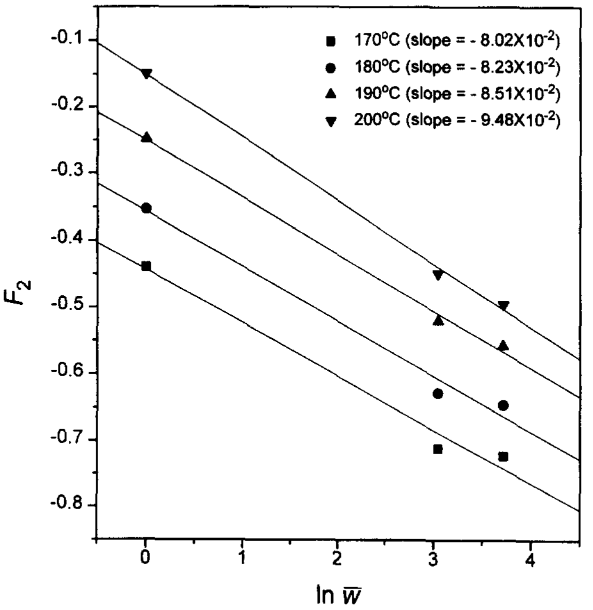

Figure 4 F_2 for various temperatures ($[\partial\ln\eta/\partial\ln\dot\gamma]_{1/T}$) *versus* $\ln\bar{w}$: (■) 170°C; (●) 180°C; (▲) 190°C; (▼) 200°C

We compared two calculated values, J and D, K and E, L and F. As listed in *Table 1*, the difference between these pairs was negligible. Thus, equation (3) satisfies the criterion of exactness for a differential expression as previously discussed in equation (8). Model parameters are obtained using the least-squares method and they are listed in *Table 2*.

Figure 8 shows the comparison of measured viscosities with calculated viscosities using equation (3) at $T = 180$°C. The proposed model in this study agrees very well with experimental data.

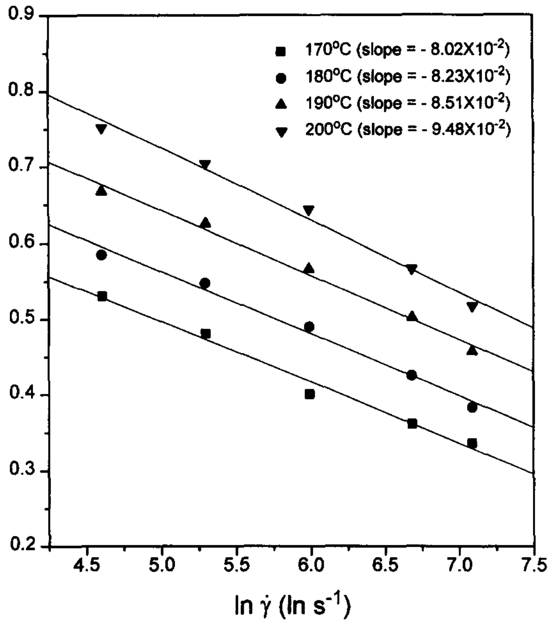

Figure 5 F_3 for various temperatures ($[\partial\ln\eta/\partial\ln\bar{w}]_{1/T}$) *versus* ln$\dot{\gamma}$: (■) 170°C; (●) 180°C; (▲) 190°C; (▼) 200°C

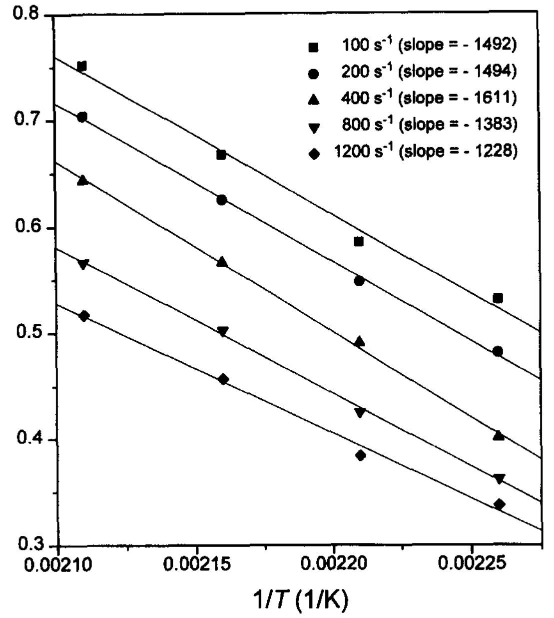

Figure 6 F_3 for various shear rates ($[\partial\ln\eta/\partial\ln\bar{w}]_{\ln\dot{\gamma}}$) *versus* 1/$T$: (■) 100 s^{-1}; (●) 200 s^{-1}; (▲) 400 s^{-1}; (▼) 800 s^{-1}; (◆) 1200 s^{-1}

CONCLUSION

Steady-state shear viscosities of PLA/PCL blends were measured as functions of shear rate, temperature and PCL composition. In this study, the semi-empirical rheological equation of state to predict temperature, shear rate and composition dependence of steady-state shear viscosities for polymer blends was proposed.

The proposed model agreed successfully with our experimental results. The composition dependent rheological equation of state presented here has little theoretical basis: it is essentially empirical, at best semi-empirical. However, its simplicity is a great advantage; a simple algebraic form with a few adjustable parameters appears to be suitable for describing steady-state shear viscosities of PLA/PCL blends.

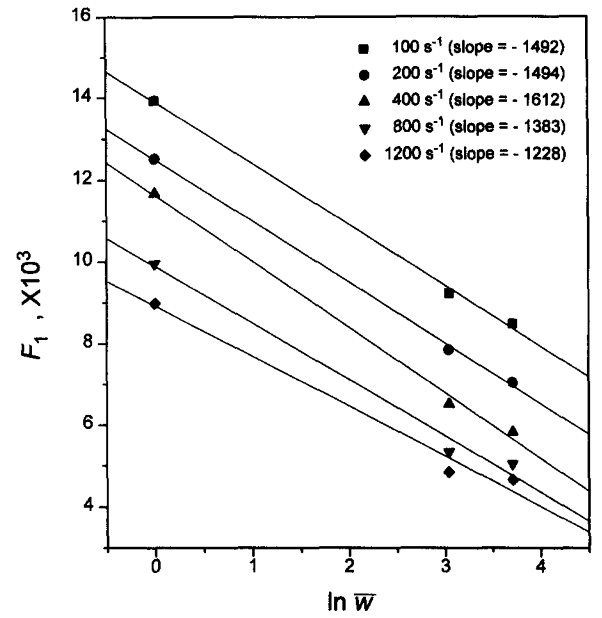

Figure 7 F_1 for various shear rates ($[\partial\ln\eta/\partial(1/T)]_{\ln\dot{\gamma}}$) *versus* ln$\bar{w}$: (■) 100 s^{-1}; (●) 200 s^{-1}; (▲) 400 s^{-1}; (▼) 800 s^{-1}; (◆) 1200 s^{-1}

Table 2 List of model parameters

Model parameter	Value
B	− 1997
δ	4.76 × 10^{-2}
φ	− 0.29
ϕ/R	− 2011
Q_{matrix}/R	23612
α	4.06
m	5.43
$\ln\bar{K}$	− 46.11

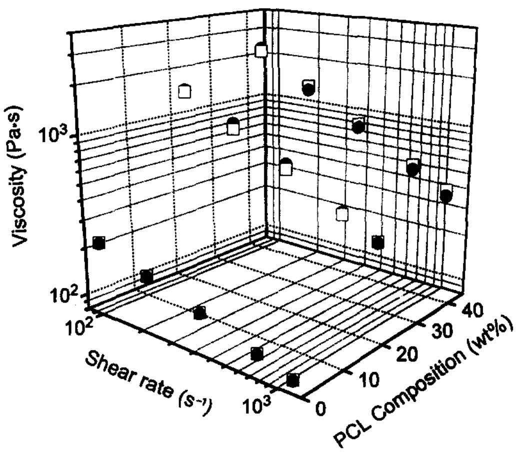

Figure 8 Three-dimensional plot for viscosity at a temperature of 180°C as function of shear rate and PCL composition: (●) measured; (□) calculated from equation (3)

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