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Applicability of the rheological equation of state for thermoplastic composites

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A simple experimental method for determining the steady-state shear viscosity of thermoplastic composite melts has been used. Using this method, we have determined the steady-state shear viscosity of an automotive thermoplastic composite system, namely, wollastonite-filled poly(ethylene terephthalate) (WFPET), at various temperatures and shear rates. All the viscosity properties investigated can be successfully described and predicted by a thermodynamically based rheological equation of state. The effects of composition and mixing conditions on the steady-state shear viscosity of all the WFPET investigated were also determined using this rheological equation of state.

1. Introduction

In the last few years, there has been much interest in and need for the use of thermoplastic composites in various automotive applications such as body panels, support panels and components because thermoplastic composites have great versatility and high performance. However, owing to the diversified methods practiced in formulating desirable thermoplastic composites, the processibility and/or process window of thermoplastic composites in such manufacturing processes as injection moulding, blow moulding and extrusion are often very difficult and/or limited. The above processing constraints, in conjunction with increasing sophistication and complexity in automotive styling and design, result in many unexpected technical difficulties and/or problems in manufacturing this class of material. Typical problems are non-uniform ingredient dispersion in the production parts, uncontrollable mould-fill mechanisms, poor surface appearance of the parts, etc. This situation can be drastically improved by different technical approaches. From the viewpoint of materials science and engineering, one of the most cost-effective solutions is to develop thermoplastic composite material with the desired performance requirements and the controllable processing characteristics such that the material processibility in manufacturing and production would be successfully ensured and its product quality, reliability and durability could be economically obtained.

There are two rheological properties that can be used to describe the viscoelastic behaviour of thermoplastic composite melts and thereby to characterize the processibility of these melts. The two properties are the steady-state shear viscosity and the transient shear viscosity [1–7]. Owing to the complicated polymer and filler microstructures in thermoplastic composite systems, both the steady-state and the transient shear viscosities of these composite systems strongly depend on the shear rate and the temperature. Therefore, the overall objective of this research is two fold. Firstly we develop an effective method for determining the rheological (viscous and elastic) properties of thermoplastic composite melts. Secondly we develop useful composition–processing–structure–property relationships for describing and predicting the rheological properties of these melts.

In this study, we shall concentrate on the determination of the steady-state shear viscosities of a potentially useful automotive thermoplastic composite wollastenite-filled poly(ethylene terephthalate) (WFPET) at various temperatures and shear rates. On the basis of these data, we shall develop composition–processing–structure–property relationships for describing and predicting the steady-state shear viscosity of the WFPET melts as a function of the processing variables, namely, the shear rate and the temperature. These relationships will be used in the development of a mathematically based co-injection-moulding technology for automotive applications.

2. Experimental procedure

2.1. Material

The thermoplastic composites used in this investigation were three compositions of WFPET. The wollastonite filler, which was supplied by Nyco, had an aspect ratio of five and an average particle size of 10 μm. The formulation and sample designation of each of the WFPET composites are listed in Table I. The only difference between compositions I and II is

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TABLE I Compositions and sample designations of the WFPET

Constituent	Composition (%) for the following WFPET designations		
	I	II	III
PET	61.6	61.6	61.6
Rubber modifier	21.7	21.7	21.7
Wollastonite	13.0	13.0	13.0
Stabilizer	3.7	3.7	3.7
Carbon black	0.0	3.6	0.0

the small amount of carbon black used in composition II. Compositions I and III were mixed using different processing conditions. (The shear rate applied for mixing composition III was twice that of mixing composition I.)

2.2. Sample preparation

Owing to the chain scission (reverse transesterification) reaction induced by water in WFPET, it is very important to reduce the water content in the WFPET compositions to less than 0.02 wt% before sample moulding. To accomplish this, resin pellets for each of the WFPET composites were dried using a vacuum oven at 60 °C for 2 days prior to sample moulding. In order to measure accurately the steady-state shear viscosity of the WFPET samples, compression-moulded test samples with a disc geometry were prepared for this investigation. The diameter of the each disc sample was 50.8 mm, and the thicknesses were 0.8 and 1.6 mm. The compression moulding conditions for making all the disc samples are summarized as follows: (1) the moulding temperature was 271 °C; (2) the time for melting the resin pellets was 2 min; (3) the time for moulding the resin pellets was 2.5 min; (4) the time for cooling the sample in a cold press was 30 s. All the disc samples were then stored in a vacuum desiccator prior to testing.

2.3. Test procedure

The steady-state shear viscosity for each sample was measured using a Rheometrics mechanical spectrometer (RMS 605). The configuration of the test fixture used in the RMS 605 unit was a set of parallel plates. The diameter of each plate was 50 mm, and the gap distances between the plates used for all the samples were 0.8 and 1.3 mm. The test temperatures used in this investigation were 280, 290 and 300 °C. For each test temperature, the shear rates used were between 1 and 100 s^{-1}, and the heating time periods prior to testing for all the samples were varied from 15 to 30 min. During each test at a fixed temperature, the RMS 605 unit measured the torque imposed upon the upper plate for 30 s at each pre-programmed shear rate. The software program in the RMS 605 unit simultaneously analysed the raw data and calculated the average value of the steady-state viscosity at each shear rate.

3. Theoretical considerations

Based on the thermodynamic principles, a unified rheological equation of state for the steady-state shear viscosity of liquid-like material can be obtained by application of the criterion for exactness of a differential expression. If $\eta = f(T, \dot{\gamma})$, then the total differential of η is defined by

$$\mathrm{d}\eta = \left(\frac{\partial \eta}{\partial T}\right)_{\dot{\gamma}} \mathrm{d}T + \left(\frac{\partial \eta}{\partial \dot{\gamma}}\right)_T \mathrm{d}\dot{\gamma} \qquad (1)$$

or

$$\mathrm{d}\eta = M\,\mathrm{d}T + N\,\mathrm{d}\dot{\gamma} \qquad (2)$$

where $M = (\partial\eta/\partial T)_{\dot{\gamma}}$, $N = (\partial\eta/\partial\dot{\gamma})_T$, η is the steady-state shear viscosity, T is the temperature and $\dot{\gamma}$ is the shear rate.

By further differentiation we obtain

$$\left(\frac{\partial M}{\partial \dot{\gamma}}\right)_T = \frac{\partial^2 \eta}{\partial T\,\partial \dot{\gamma}}, \quad \left(\frac{\partial N}{\partial T}\right)_{\dot{\gamma}} = \frac{\partial^2 \eta}{\partial \gamma\,\partial T} \qquad (3)$$

Since the order of differentiation in mixed second derivatives is immaterial, the two above equations give

$$\left(\frac{\partial M}{\partial \dot{\gamma}}\right)_T = \left(\frac{\partial N}{\partial T}\right)_{\dot{\gamma}} \qquad (4)$$

When the differential expression on the right-hand side of an equation of the form of Equation 2 satisfies Equation 4, it is said to be exact, and η can be expressed as a function of T and $\dot{\gamma}$.

The steady-state viscosity η is given by

$$\eta = \bar{K}\dot{\gamma}^{n-1}\exp\left(\frac{Q}{RT}\right) \qquad (5a)$$

or

$$\begin{aligned}\ln\eta &= \ln\bar{K} + (n-1)\ln\dot{\gamma} + \frac{Q}{R}\frac{1}{T}\\ &= \ln A + (n-1)\ln\dot{\gamma} \qquad (5b)\\ A &= \bar{K}\exp\left(\frac{Q}{RT}\right)\end{aligned}$$

where n is the power-law index (its value being equal to unity for a Newtonian liquid and less than unity for a shear-thinning liquid), Q is the activation enthalpy for flow, and A is the steady-state shear viscosity at the shear rate of 1 s^{-1}. Equation 5b shows that the logarithmic steady-state shear viscosity at the shear rate of 1 s^{-1} equals ln A. Therefore, $\bar{K}$ represents a high-temperature limiting value of the steady-state shear viscosity at the shear rate of 1 s^{-1}.

The derivative of Equation 5b at a fixed shear rate gives

$$M' = \left(\frac{\partial(\ln\eta)}{\partial(1/T)}\right)_{\dot{\gamma}} = \frac{Q}{R} \qquad (6a)$$

The derivative of Equation 5b at a fixed temperature gives

$$N' = \left(\frac{\partial(\ln\eta)}{\partial(\ln\dot{\gamma})}\right)_{1/T} = n - 1 \qquad (6b)$$

Furthermore, if Equation 5b is a thermodynamic equation of state, the following condition should be satisfied:

$$J = \left(\frac{\partial n}{\partial(1/T)}\right)_{\dot{\gamma}}$$

$$\Rightarrow J = D \qquad (7)$$

$$D = \left(\frac{\partial(Q/R)}{\partial(\ln\dot{\gamma})}\right)_{1/T}$$

We prove Equation 7 experimentally for the systems used in this study and the rheological equation of state, Equation 5b is used for describing and predicting the values of the steady-state shear viscosity of all the WFPET compositions.

4. Results and discussion

4.1. Effects of shear rate and temperature

Values for the steady-state shear viscosity of the WFPET composition at various temperatures and shear rates are listed in Tables II–IV. Fig. 1 shows the results of the shear-dependent viscosity for composition I at 290 °C (563 K). The power-law index, n, and the steady-state shear viscosity, A, at the shear rate of $1\ \mathrm{s}^{-1}$ can be determined from the values of the slope of the line and the intercept on the axis of the logarithmic shear viscosity at shear rate of $1\ \mathrm{s}^{-1}$, respectively. The values of n and A for all the WFPET compositions at various temperatures are summarized in Table V. It is noteworthy from Table V that a small amount of carbon black (compositions I and II) does not significantly influence the values of n, but this amount of carbon black does change the value of A especially at a higher temperature (e.g., 573 K). Different mixing conditions (compositions I and III) clearly show significant effects on the values of both n and A.

Equation 5b states that there is a linear relationship between $\ln \eta$ and $1/T$ at a fixed shear rate. The activation energy, Q, for flow can be determined from the

TABLE II Steady-state shear viscosity of composition I

Shear rate (s^{-1})	Steady-state shear viscosity (Pa s) at the following test temperatures		
	553 K	563 K	573 K
1.778	1824	1643	—
3.162	—	1039	—
5.623	9072	697.5	547.6
10.000	6458	506.8	342.4
17.780	—	—	222.6

TABLE III Steady-state shear viscosity of composition II

Shear rate (s^{-1})	Steady-state shear viscosity (Pa s) at the following test temperatures		
	553 K	563 K	573 K
1.000	3257	1825	—
1.778	1644	1091	—
3.162	1141	697.5	528.2
5.623	799.0	498.8	348.7
10.000	572.9	335.1	225.3
17.780	—	219.9	—

TABLE IV Steady-state shear viscosity of composition III

Shear rate (s^{-1})	Steady-state shear viscosity (Pa s) at the following test temperatures		
	553 K	563 K	573 K
1.000	2660	2055	1784
1.585	1750	—	—
1.778	—	1253	856.9
2.512	1362	—	—
3.162	—	937.3	595.9
3.981	1100	—	—
5.623	—	713.6	443.2
6.310	915.1	—	—
10.000	625.6	509.2	318.6
17.780	—	367.1	233.9
31.620	—	—	157.4

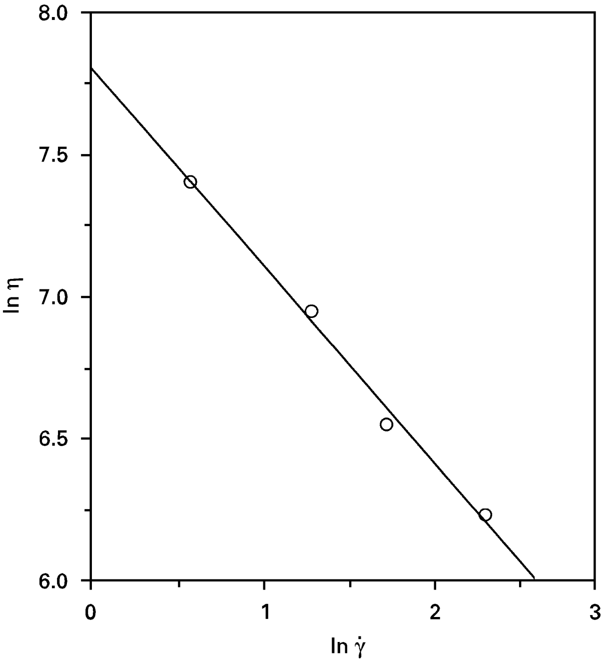

Figure 1 The plot of the shear-dependent viscosity versus shear rate for composition I (see Table I) at 290 °C (563 K).

TABLE V Values of power-law index, n, and steady-state shear viscosity, A, at $1\ \mathrm{s}^{-1}$ of various WFPET compositions

Composition	Temperature (K)	n	A (Pa s)
I	553	0.398	2576
I	563	0.318	2352
I	573	0.236	2006
II	553	0.389	2320
II	563	0.316	1593
II	573	0.260	1243
III	553	0.496	2194
III	563	0.468	1731
III	573	0.440	1162

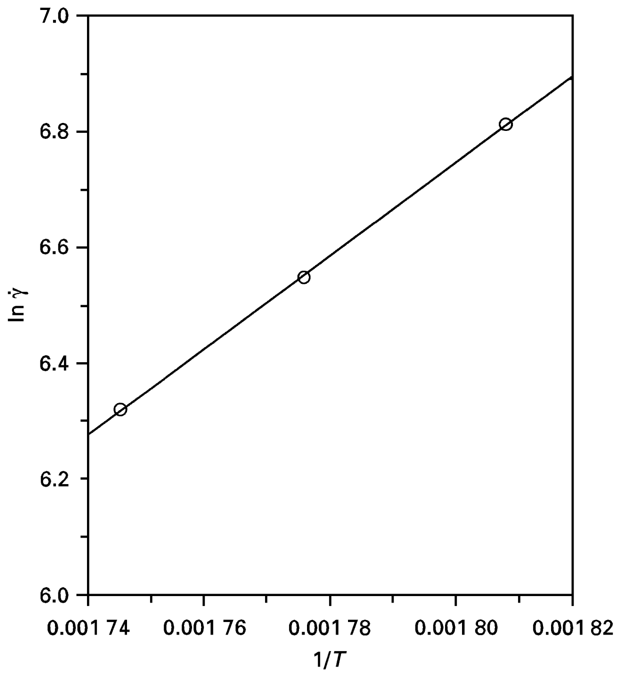

Figure 2 The plot of ln η versus $1/T$ of composition I at the shear rate of $5.623\ \mathrm{s}^{-1}$. (——), line predicted by Equation 5b.

slope of the plot (the value of the slope being equal to Q/R and R, the universal gas constant). Fig. 2 shows the plot of $\ln \eta$ versus $1/T$ of composition I at the shear rate of $5.623\,\mathrm{s}^{-1}$ and the predicted linear relationship using Equation 5b.

Values for the activation energy, Q, for flow at different shear rates are also determined and are summarized in Table VI. The results show that the activation energy for flow can be effectively raised by adding a small amount of carbon black (compositions I and II) and can be greatly changed by using different mixing conditions (compositions I and III).

4.2. Rheological equation of state for the steady-state shear viscosity of wollastonite-filled poly(ethylene terephthalate)

In order to verify that Equation 5b is a thermodynamic equation of state, we also determined the derivatives, J and D, in Equation 3, for all the WFPET compositions. The values of the two derivatives are summarized and shown in Table VII. It is evident that the results in Table VII satisfy the thermodynamic criterion, $J = D$ (see Equation 7). Therefore, we conclude that the steady-state shear viscosity of all the WFPET compositions, regardless of their compositional or processing differences, has the same thermodynamic characteristics and can be readily described by the rheological equation of state expressed in Equation 5b. Fig. 3 shows the experimental data and the theoretical predictions for composition I. The rheological equation of state for composition I can be expressed in Equation 5a and n can be written by

$$n = n_\infty + \left(\frac{\partial n}{\partial(1/T)}\right)_{\dot\gamma}\frac{1}{T} = n_\infty + J(1/T), \qquad (5c)$$

TABLE VI Values of activation energy, Q, for flow of WFPET compositions at various shear rates

Shear rate (s^{-1})	Q ($\mathrm{kcal\ mol}^{-1}$) for the following compositions		
	I	II	III
1.778	10.85	22.27	20.44
3.162	—	24.32	22.74
5.623	15.92	26.17	22.89
10.000	—	29.47	24.14
17.780	22.57	31.43	24.78

TABLE VII Values of slopes, J and D, in Equation 7 for various WFPET compositions investigated

Composition	J	D
I	2564.8	2564.6
II	2050.6	2051.6
III	882.7	883.9

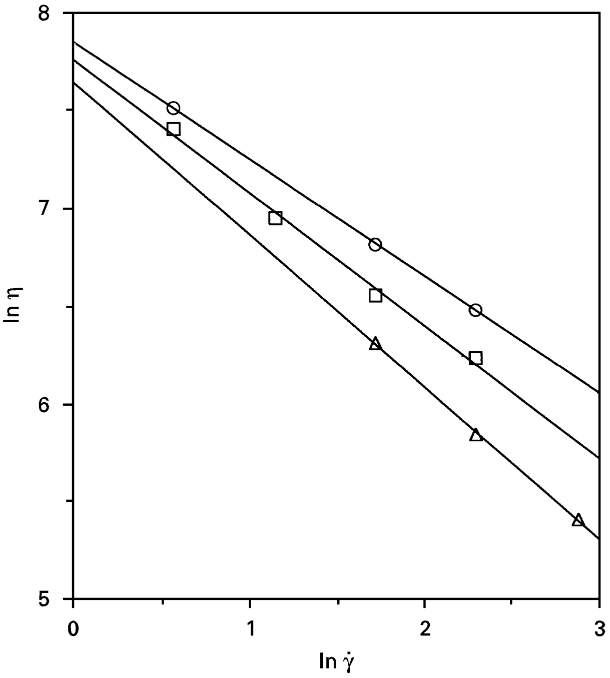

Figure 3 The comparison of the experimental data on ln η with the theoretical predictions for composition I for various temperatures. (○), 553 K; (□), 563 K; (△), 573 K.

The values of the material coefficients in Equations 5a and 5c are as follows:

$\bar{K} = 20.1$ Pa s

$Q = 7.876\,\mathrm{kcal\,mol}^{-1}$

$n_\infty = -4.238$

$J = 2564.8\,\mathrm{K}$

5. Conclusion

The simple rheological equation of state was able to describe and predict the steady-state shear viscosity of thermoplastic composite melts. The proposed equation also successfully describes and predicts the effects of composition and processing on the steady-state shear viscosity of thermoplastic composite melts.

The rheological equation of state presented here has little theoretical basis; it is essentially empirical or, at best, semiempirical. Its advantage follows from its simplicity; a simple algebraic form with a few adjustable parameters appears to be suitable for representing the steady-state shear viscosity of polymeric liquids.

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