

Poly(methyl methacrylate) Toughened by Core–Shell Impact Modifier: Applicability of Rheological Equation of State

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SYNOPSIS

A simple rheological equation of state was developed to describe the steady-state shear viscosity of poly(methyl methacrylate) (PMMA) toughened by core–shell impact modifier. The suggested equation was successfully able to describe and predict viscosity of toughened PMMA as a function of shear rate ($\dot{\gamma}$) and temperature. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is a widely used engineering thermoplastic and has a variety of outstanding properties.¹ One of the outstanding properties of PMMA is its optical clarity. Coupled with its excellent outdoor weatherability, its optical properties make it highly useful in many applications. However, its impact resistance is relatively low compared with those of polycarbonate or other engineering thermoplastics.²

In the past several decades, many efforts have been made to improve its impact resistance. Recently, a staged emulsion polymerization technique was developed to prepare the core–shell type impact modifier that consists of the rubbery material in the core and material compatible with matrix polymer in the outer shell.^{3,4}

In our previous study,⁵ poly(butyl acrylate) (PBA) was used as a core material and PMMA was used as an outer–shell material so that PBA particles could be dispersed uniformly through the PMMA matrix. We reported the mechanical properties of PMMA toughened by PBA–PMMA core–shell particles with respect to the size, concentration, and degree of crosslinking of the impact modifier.

Rheological property is one of the most important factors in manufacturing of processing equipment. Thus, the experimental and theoretical studies for the behavior of polymer melts have been done by many research groups for several decades. The theoretician seeks to express the behavior of polymeric materials rheologically through suitable stress and deformation variables. The rheological equation of state is the equation relating suitably defined stress and deformation variable and is used to predict viscosities of polymer melts.⁶ In this study, based on the basic thermodynamic principle, a unified simple rheological equation of state for the steady-state shear viscosity is compared with experimental data.

THEORETICAL CONSIDERATION

If the steady-state shear viscosity (η) is a state function and shear rate ($\dot{\gamma}$) and temperature ($1/T$) are the chosen independent variables for a chosen system of fixed composition, η is given by

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

Based on the thermodynamic principle, the steady-state shear viscosity using the rheological equation of state can be expressed as functions of temperature and shear rate, as shown below:

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$$\eta = \bar{K}\dot{\gamma}^{n-1}\exp\left(\frac{Q}{RT}\right) \quad (2)$$

where \bar{K} is material constant, n is the power-law index, Q is the activation energy for the given flow, R is a gas constant.

$n - 1$ is a function of temperature and is given by

$$n - 1 = \alpha + \frac{\beta}{T} \quad (2a)$$

where α and β are constants.

Substituting eq. (2a) into eq. (2) and taking the natural log of both sides of eq. (2) gives

$$\ln \eta = \ln \bar{K} + \left(\alpha + \frac{\beta}{T}\right) \ln \dot{\gamma} + \frac{Q}{RT} \quad (3)$$

The derivative $[\partial \ln \eta / \partial (1/T)]_{\dot{\gamma}}$ at a fixed shear rate can be derived using eq. (3) and has the form

$$\left(\frac{\partial \ln \eta}{\partial (1/T)}\right)_{\dot{\gamma}} = \frac{Q}{R} + \beta \ln \dot{\gamma} \quad (4)$$

The derivative $[\partial \ln \eta / \partial \ln \dot{\gamma}]_{1/T}$ at a fixed temperature can also be obtained from eq. (3). The result is

$$\left(\frac{\partial \ln \eta}{\partial \ln \dot{\gamma}}\right)_{1/T} = n - 1 = \alpha + \beta/T \quad (5)$$

Furthermore, because eq. (3) is a thermodynamic equation of state, it follows from eqs. (4) and (5) that the thermodynamic criterion shown below is true:

$$\frac{\partial^2 \ln \eta}{\partial (1/T) \partial \ln \dot{\gamma}} = \frac{\partial^2 \ln \eta}{\partial \ln \dot{\gamma} \partial (1/T)} = \beta \quad (6)$$

To prove eq. (3) is a state function experimentally, one needs to show the relationship in eq. (6) from experimental data. To verify that eq. (3) is a thermodynamic equation of state, we determined J and D derivative for modified PMMA:

$$J \equiv \frac{\partial^2 \ln \eta}{\partial (1/T) \partial \ln \dot{\gamma}} \quad (7)$$

$$D \equiv \frac{\partial^2 \ln \eta}{\partial \ln \dot{\gamma} \partial (1/T)} \quad (8)$$

EXPERIMENTAL

Starting Materials

Methyl methacrylate (MMA, Aldrich Chemical Co.) and *n*-butyl acrylate (BA, Aldrich Chemical Co.) were purified by reduced pressure distillation and were stored in a refrigerator. Triethylene glycol dimethacrylate (TEGDMA, Aldrich Chemical Co.), sodium styrene sulfonate (NaSS, Junsei Chemical Co.), and potassium persulfate (KPS, Junsei Chemical Co.) were used as received. Distilled-deionized water was used for all polymerizations.

Preparation of the Core-Shell Latex

Core-shell latex was prepared by sequential soap-free emulsion polymerization.^{7,8} Here, PBA was used as a core material and PMMA was used as an outer-shell material. In the preparation of the core, BA was polymerized with crosslinker (TEGDMA) in the semicontinuous process at 75°C. NaSS and KPS were used as an anionic comonomer and initiator, respectively. For the outer shell, MMA was polymerized with crosslinker (TEGDMA) in the presence of core latex at 65°C. The composition of core-shell latex is listed in Table I.

Preparation of the PMMA/Core-Shell Particles Blend

The core-shell latexes were deemulsified and then dried in the vacuum oven at 50°C for 7 days. The prepared core-shell particles were blended with PMMA in mass-suspension blending.⁹ Core-shell particles were mixed in the MMA monomer. The composition of core-shell particle to MMA was 10% by weight. Then, this was poured into the glass frame sealed with silicone rubber. This frame was immersed in the water bath, and then MMA in the

Table I Sequential Core-Shell Latex Synthesis

	Ingredient	Weight (g)
Stage 1	BA	97.5
	TEGDMA	2.0
	Water	400.0
	NaSS	0.5
	KPS	0.5
Stage 2	PBA latex	200.0
	Water	100.0
	MMA	19.8
	TEGDMA	0.2

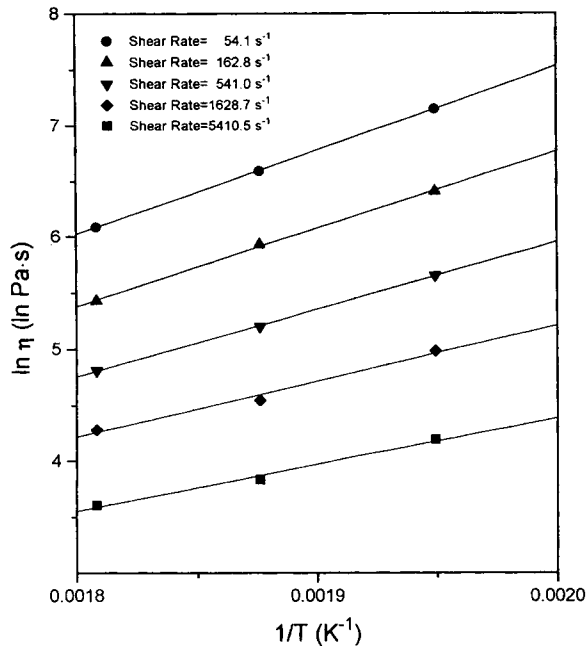


Figure 1 Variation of melt viscosity with temperature at fixed shear rate: (●) 54.1 s^{-1} ; (▲) 162.8 s^{-1} ; (▼) 541.0 s^{-1} ; (◆) 1628.7 s^{-1} ; (■) 5410.5 s^{-1} .

frame was polymerized at 60°C for 12 h to prepare toughened PMMA.

Measurement of Apparent Viscosity

Steady-state shear viscosities of molten polymer were measured using capillary rheometer (Instron Model 3211). Measuring temperatures were 240, 260, and 280°C and cross head speeds of rheometer were 0.2, 0.6, 2.0, 6.0, and 20.0 cm/min .

RESULTS AND DISCUSSION

As shown in Figure 1, steady-state shear viscosities of the modified PMMA were plotted against temperature at various shear rates. As predicted in eq. (3), there exists a linear relationship between the shear viscosity and $1/T$ at a fixed shear rate. Then, the value of $Q/R + \beta \ln \dot{\gamma}$ can be determined from the slopes of the plot in Figure 1 (the value of the slope in Figure 1 being equal to $Q/R + \beta \ln \dot{\gamma}$). The values of $Q/R + \beta \ln \dot{\gamma}$ at various logarithmic shear rates were determined and plotted against $\ln \dot{\gamma}$ in Figure 2. From eq. (7), the value of J for the modified PMMA can be determined from the slope of the plot in Figure 2 and calculated value was -761 .

Figure 3 shows that the steady-state shear viscosity was plotted against logarithmic shear rate at

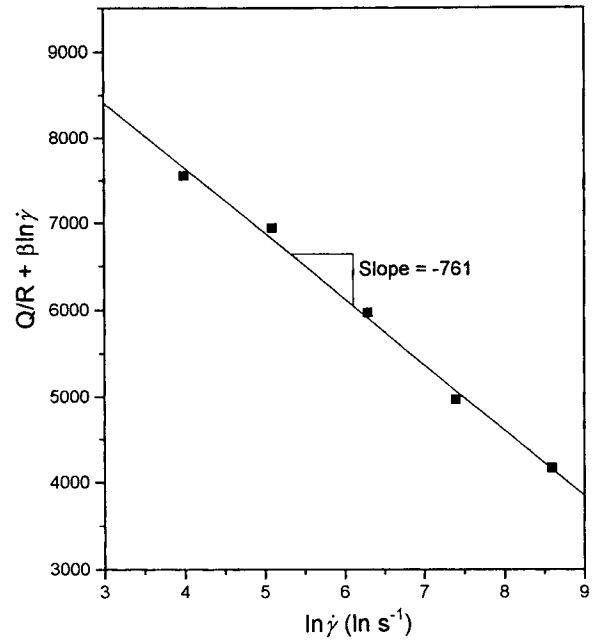


Figure 2 $Q/R + \beta \ln \dot{\gamma}$ vs. $\ln \dot{\gamma}$.

various temperatures. Result shows that the steady-state shear viscosities were linearly dependent on the shear rate in log scale at a fixed temperature. Again, the values of $\alpha + \beta/T$ (or $n - 1$) can be determined from the slopes of the plot in Figure 3 (the value of the slope in Fig. 3 being equal to $\alpha + \beta/T$). The values of $n - 1$ at various temperatures

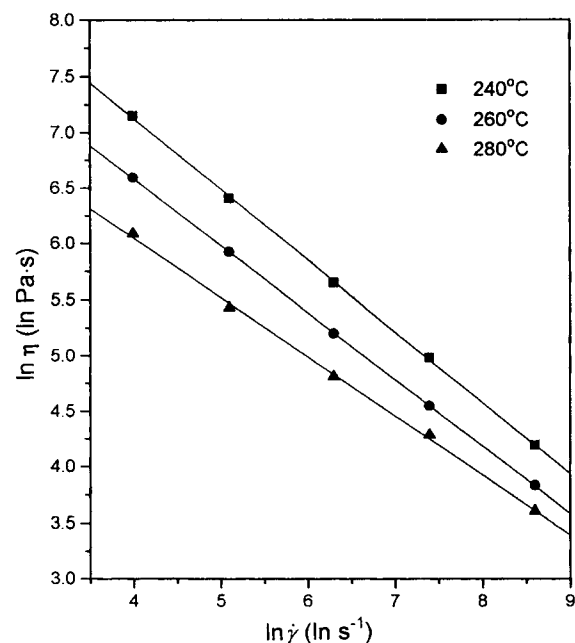


Figure 3 Variation of melt viscosity with shear rate: (■) 240°C ; (●) 260°C ; (▲) 280°C .

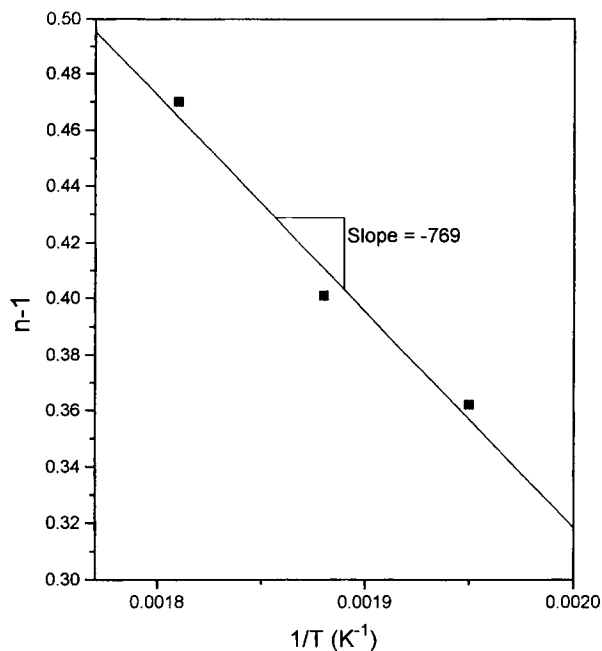


Figure 4 $n - 1$ vs. $1/T$.

were determined and plotted against $1/T$ in Figure 4. From eq. (8), D can be determined from the slope of the plot in Figure 4 and the value of D is -769 .

The difference between J and D negligible ($<1\%$), so that eq. (3) satisfies the thermodynamic criterion. It shows that the rheological equation of state [eq. (3)] is a state function and that the steady-state shear viscosity of toughened PMMA can be described by the rheological equation of state expressed in eq. (3).

When β is chosen by the mean value ($=-765$) of J and D , the values of Q/R and α can be calculated from eqs. (4) and (5), respectively. Based on results shown in Figures 2 and 4, the values of Q/R and α were determined and summarized in Tables II and III.

Because the values of Q/R and material constant α are $10719K$ and 0.85 , respectively, the value of \bar{K} can be calculated from eq. (3) and summarized as

Table II Values of Q/R

$\ln \dot{\gamma}$	$Q/R - 765 \ln \dot{\gamma}$	Q/R
3.99	7555	10,608
5.09	6943	10,839
6.29	5968	10,782
7.40	4964	10,622
8.60	4166	10,742
Average \pm SD		10,719 \pm 101

Table III Values of α

$1/T$	$\alpha - 765/T$	α
0.00195	-0.64	0.85
0.00188	-0.60	0.84
0.00181	-0.53	0.86
Average \pm SD		0.85 \pm 0.01

shown in Table IV. From the results shown in Table IV, the value of \bar{K} is 1.37×10^{-5} .

From the previous results, eq. (3) can be rewritten as

$$\ln \eta = -11.2 + \left(0.85 - \frac{765K}{T}\right) \ln \dot{\gamma} + \frac{10719K}{T} \quad (9)$$

To compare measured viscosities with calculated viscosities from eq. (9), measured and calculated viscosities were plotted as functions of temperature and shear rate in Figure 5. As shown in Figure 5, steady-state shear viscosities calculated from the proposed rheological equation of state in this study agree very well with measured viscosities. Thus, we can use the proposed rheological equation of state in this study to predict and describe steady-state shear viscosities of our polymer system.

CONCLUSION

A useful laboratory method for determining the steady-state shear viscosity of toughened PMMA

Table IV Values of $\ln \bar{K}$

$\ln \eta$	$\ln \dot{\gamma}$	$1/T$	$\ln \bar{K}$
6.09	3.99	0.00195	-11.17
5.43	5.09	0.00195	-11.24
4.81	6.29	0.00195	-11.22
4.28	7.40	0.00195	-11.15
3.61	8.60	0.00195	-11.19
6.59	3.99	0.00188	-11.18
5.92	5.09	0.00188	-11.21
5.20	6.29	0.00188	-11.23
4.55	7.40	0.00188	-11.24
3.83	8.60	0.00188	-11.25
7.15	3.99	0.00181	-11.18
6.41	5.09	0.00181	-11.22
5.65	6.29	0.00181	-11.21
4.98	7.40	0.00181	-11.17
4.19	8.60	0.00181	-11.19
Average \pm SD			-11.20 \pm 0.03

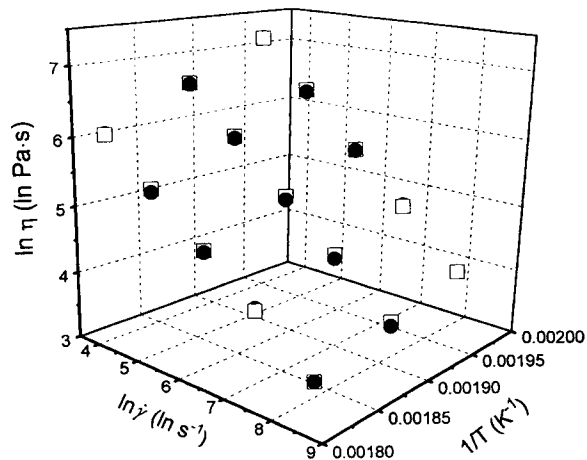


Figure 5 Melt viscosity as functions of temperature and shear rate: (●) measured; (□) calculated using eq. (9).

has been developed. This constitutive rheological equation also successfully describes and predicts the effects of temperature and shear rate on the steady-state shear viscosity of thermoplastic polymer melts.

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