

Melt Viscosities of Molten Poly(ethylene Terephthalate) Calculated from Modified Bueche-Harding Equation

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Synopsis

The semiempirical Bueche-Harding equation was successfully modified to allow the calculation of experimentally verified melt viscosities of molten poly(ethylene terephthalate) (PET) for shear stresses $>9.65 \times 10^6$ dynes/cm² by accounting for the definite Newtonian region in the flow behavior of PET for shear stresses $\leq 9.65 \times 10^6$ dynes/cm². Melt viscosity values calculated from the modified Bueche-Harding equation agreed within $\pm 12\%$ of the values calculated from the equations based on experimental data.

INTRODUCTION

Bueche and Harding proposed a universal master curve for the viscous behavior of concentrated polymer solutions¹:

$$\frac{\eta_0}{\eta} = 1 + 0.6 (\dot{\gamma} D)^{0.75} \quad (1)$$

where η_0/η is the ratio of the zero shear viscosity to the viscosity at some shear rate, $\dot{\gamma}$; D is the parameter (relaxation time) defined as

$$D = \frac{12\eta_0 M}{\pi^2 \rho R T} \quad (2)$$

where M is the molecular weight, ρ is the density (for melts) or concentration (for solutions), R is the universal gas constant, and T is the absolute temperature. From the master curve it is possible to determine the melt viscosity-shear rate flow curve of many linear polymers at any temperature, if the zero shear viscosity, the molecular weight, and the density (or concentration) of the polymer are known. The work of Bueche and Harding has been extended with varying degrees of success to a number of molten polymer systems.²⁻⁸

Van der Vegt⁶ found that an expression similar to that of Bueche and Harding was satisfactory for polypropylene melts. Kraus and Gruver⁴ showed that for polymers of similar molecular weight distribution and minimum branching, all viscometric data could be reduced to a single curve by a reduced variable technique. The general rheological behavior for poly-

(dimethylsiloxanes) over a wide range of variables was obtained by Collins² through extension of the Bueche and Harding standard curve.

Sabia³ and Brodnyan et al.⁵ found Bueche's standard curve to be unsatisfactory for describing the non-Newtonian flow of several polymer melts including polyethylene³ and poly(methyl methacrylate).⁵ Porter et al.⁷ showed that variations in molecular weight distributions cause marked deviations from general reduced variable curves for non-Newtonian flow. Middleman⁸ modified Bueche's theory to account for the effect of polydispersity on the viscosity of polymeric fluids.

The steady-state flow properties of molten poly(ethylene terephthalate) (PET) were recently reported in graphic form by Gregory and Watson.⁹ A single, complete master flow curve was constructed in that work; the curve interrelates shear stress, shear rate, temperature, and molecular weight. Gregory, in more recent work,¹⁰ derived generalized rheological equations from the master curve. The objective of this current paper is to compare the results of the earlier work¹⁰ with results calculated from the Bueche-Harding equation applied to molten PET.

RESULTS AND DISCUSSION

Rheological equations for molten PET which were developed by Gregory¹⁰ and were based on the earlier experimental work of Gregory and Watson⁹ are

$$\eta_0 = 1.13 \times 10^{-13} \left[\left[\exp \left(-11.9755 + \frac{6802.1}{T} \right) \right] (\bar{M}_w)^{3.5} \right] \quad (3)$$

where η_0 = zero shear viscosity, poises; T = absolute temp., °K; \bar{M}_w = weight-average molecular weight; and

$$\eta = 4.89 \times 10^{-8} \left[\left[\exp \left(-11.9755 + \frac{6802.1}{T} \right) \right] (\bar{M}_w)^{3.5} \right]^{0.707} (\dot{\gamma}_w)^{-0.293} \quad (4)$$

where $\dot{\gamma}_w$ = shear rate at wall, sec⁻¹. Equation (3) is valid for $0 < \tau_w \leq 9.65 \times 10^5$ dynes/cm², and eq. (4) is valid for $9.65 \times 10^5 < \tau_w \leq 4.14 \times 10^6$ dynes/cm² (τ_w is the shear stress at the wall, dynes/cm²).

Melt viscosities of PET calculated using the Bueche-Harding equation, eq. (1), are compared in Table I with melt viscosities calculated from eqs. (3) and (4). Agreement is reasonable at high shear rates when an \bar{M}_w/\bar{M}_n ratio of 3.5 (ratio based on ebulliometry)¹¹ is used, but agreement is poor (even at high shear rates) when an \bar{M}_w/\bar{M}_n ratio of 2 (determined by osmometry)¹¹ is used. Large systematic differences exist, however, between values of melt viscosity calculated using eq. (1) and those based on experimental work and calculated from eqs. (3) and (4) at low shear rates approaching the shear rate of departure from Newtonian behavior.

TABLE I
Melt Viscosities of PET Calculated Using the Bueche-Harding Equation

I. V.	\bar{M}_w	\bar{M}_n	$\bar{M}_n(2.0)^d$	$\bar{M}_n(3.5)^b$	T, °C	η_0 , poise	ρ , g/cc	$\dot{\gamma}$, sec ⁻¹	$\eta[\bar{M}_n(2)]^c$	$\eta[\bar{M}_n(3.5)]^d$	η (this work) ^e	Difference for $\eta[\bar{M}_n(2)]$, % ^f	Difference for $\eta[\bar{M}_n(3.5)]$, % ^g
	37,200	18,600	10,630	→	295	1122	1.155	500	934	991	1121	-16.7	-11.6
	→	→	→	→	→	→	→	1000	838	918	1038	-19.3	-11.6
	→	→	→	→	→	→	→	2000	715	817	847	-15.6	-3.5
	→	→	→	→	290	1248	1.157	500	1024	1091	1246	-17.8	-0.6
	→	→	→	→	→	→	→	1000	912	1005	1119	-18.5	-10.2
	→	→	→	→	→	→	→	2000	771	887	913	-15.6	-2.8
	→	→	→	→	280	1560	1.162	500	1237	1331	1551	-20.2	-14.2
	→	→	→	→	→	→	→	1000	1083	1210	1306	-17.1	-7.4
	→	→	→	→	→	→	→	2000	897	1050	1066	-15.9	-1.5
	→	→	→	→	→	→	→	5000	631	793	815	-22.6	-2.7
	→	→	→	→	270	1948	1.166	500	1484	1616	1878	-21.0	-14.0
	→	→	→	→	→	→	→	1000	1277	1448	1532	-16.6	-5.5
	→	→	→	→	→	→	→	2000	1034	1232	1251	-17.3	-1.5
	→	→	→	→	→	→	→	5000	707	904	956	-26.0	-5.4

^a Number-average molecular weight from osmometry¹¹; $\bar{M}_w/\bar{M}_n = 2$.

^b Number-average molecular weight from ebulliometry¹¹; $\bar{M}_w/\bar{M}_n = 3.5$.

^c Melt viscosity calculated using number-average molecular weight of footnote (a).

^d Melt viscosity calculated using number-average molecular weight of footnote (b).

^e Values calculated from eqs. (3) and (4) derived from experimental data.^{9,10}

^f Comparison of melt viscosity from experimental data^{9,10} with melt viscosity of footnote (c).

^g Comparison of melt viscosity from experimental data^{9,10} with melt viscosity of footnote (d).

TABLE II
Melt Viscosities of PET of 0.40-0.95 I.V. Calculated Using Modified Bueche-Harding Equation

I. V.	\bar{M}_w	$\bar{M}_n(3.5)^a$	T, °C	η_0 , poise	ρ , g/cc	$\dot{\gamma}$, sec ⁻¹	$\dot{\gamma} - \dot{\gamma}_{depart}$	$\eta[\bar{M}_n(3.5)]^b$	η (this work) ^c	Difference for $\eta[\bar{M}_n(3.5)]$, %
0.40	20,500	5,857	295	139.4	1.155	10,000	3100	130.3	116.6	+11.7
	→	→	280	193.7	1.162	10,000	5000	171.5	160.9	+ 6.6
	→	→	270	271.8	1.166	10,000	6000	227.8	227.3	+ 0.2
0.50	28,460	8,130	295	438.6	1.155	3,000	800	407.6	373.6	+ 9.1
	→	→	280	610.6	1.162	3,000	1450	528.8	519.3	+ 1.8
	→	→	270	856.6	1.166	5,000	3750	607.1	627.2	- 3.2
0.60	37,200	10,630	295	1122	1.155	1,000	140	1068	1038	+ 2.9
	→	→	280	1560	1.162	5,000	4390	831	815	+ 2.0
	→	→	270	1948	1.166	5,000	4500	942	956	- 1.5
0.70	46,660	13,330	295	2478	1.155	2,000	1610	1473	1484	- 0.7
	→	→	280	3430	1.162	1,000	720	2312	2288	+ 1.0
	→	→	270	4302	1.166	1,000	775	2668	2686	- 0.7
0.95	73,100	20,900	305	9702	1.152	200	100	7314	7649	- 4.4
	→	→	295	11,930	1.155	200	120	8272	8856	- 6.6
	→	→	280	16,510	1.162	200	142	10,000	11,140	-10.2

^a Number-average molecular weight from ebulliometry¹¹; $\bar{M}_w/\bar{M}_n = 3.5$.

^b Melt viscosity calculated using number-average molecular weight of footnote (a).

^c Values calculated from eq. (4) derived from experimental data.^{9,10}

The Bueche-Harding equation is intended for use in the non-Newtonian region only. It predicts that η will equal η_0 only when $\dot{\gamma} = 0$ or when $D = 0$. A definite Newtonian region for molten PET has been shown to exist at shear rates well above zero.⁹ The shear rate for departure from Newtonian behavior for PET as a function of temperature and molecular weight has recently been determined.¹² It is not surprising then that the Bueche-Harding equation fails to predict accurate viscosities at shear rates near the departure values. The Bueche-Harding equation was modified for PET (and for any other polymeric system with a distinguishable Newtonian region) to account for the shear rate of departure from Newtonian behavior as shown in eq. (5):

$$\frac{\eta_0}{\eta} = 1 + 0.6 [D(\dot{\gamma} - \dot{\gamma}_{\text{depart}})]^{0.75} \quad (5)$$

where $\dot{\gamma}_{\text{depart}}$ = shear rate for departure from Newtonian behavior,¹² sec⁻¹.
For PET,¹²

$$\dot{\gamma}_{\text{depart}} = \frac{62.1}{\left[\exp \left(-11.9755 + \frac{6802.1}{T} \right) \right] (I.V.)^{5.145}} \quad (6)$$

where *I.V.* is the inherent viscosity determined from the solution viscometry of 0.25 g polyester in 100 ml of a 60/40 mixture of phenol/tetrachloroethane.

Melt viscosities were calculated using eq. (6) for PET of inherent viscosities ranging from 0.40 to 0.95 and are included in Table II. Good agreement between these calculated values and those calculated from eq. (4) (derived from experimental data) resulted at all *I.V.* and temperature levels when an \bar{M}_w/\bar{M}_n ratio of 3.5 (from ebulliometry) was used.

CONCLUSIONS

Large systematic differences existed between values of melt viscosity calculated from the Bueche-Harding equation and those calculated from equations derived from experimental data for molten PET. The Bueche-Harding equation was successfully modified, however, to allow calculation of reasonable melt viscosity data for shear stresses $>9.65 \times 10^6$ dynes/cm² by accounting for the definite Newtonian region in the flow behavior of PET at shear stresses $\leq 9.65 \times 10^6$ dynes/cm².

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