Model Elastic Liquids with Water-Soluble Polymers

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Model liquids with nearly constant viscosity and adjustable elasticity are needed to resolve the role of elasticity in coating and other free-surface flows. Available Boger liquids are not well suited to free-surface flows, because they are solutions in organic solvents and their viscosities exceeding 1 Pa · s fall on the high side. Aqueous liquids are preferred in laboratory studies partly due to environmental hazards. Aqueous polymer solutions with constant shear viscosity and adjustable elasticity were prepared by adding small amounts of a high-molecular-weight polymer to a more concentrated aqueous solution of the same polymer but of a much lower molecular weight. Up to 0.2 wt. % of high-molecular weight poly(ethylene oxide) (PEO, M_w from 400,000 to 4 million g/mol) was added to almost inelastic solutions of low-MW polyethylene glycol (PEG, M_n = 8,000 g/mol). PEG concentrations in these solutions varied between 16.7 and 42.9 wt. %. Shear viscosities of these solutions ranged from about 0.02 to 0.3 Pa · s and were constant up to shear rates of 100 s^{-1}. The stress ratio is one measure of the elasticity of the liquid. Stress ratios up to 0.2 were estimated from small-amplitude oscillatory measurements. Terminal behavior (elastic modulus rising with the square of the frequency) was not observed even at 10^{-2} rad/s. Viscosity and elasticity of the liquids can be manipulated over a wide range by varying the amounts and molecular weights of PEG and PEO within the unentangled and dilute regions of the concentration–molecular weight diagram, respectively. Fits of experimental data to candidate differential and integral constitutive equations are also discussed.

Introduction

Non-Newtonian liquids can possess time-dependent and rate-sensitive viscosity and elasticity, and may also be thixotropic. Effects of these individual properties on coating and other free-surface flows and their instabilities can be studied by experiment only if they are isolated from each other by judicious choice of model liquids. Understanding gained through such experiments can be compared with theoretical predictions. This is ideal. In reality, a complete complement of model liquids does not exist.

Model liquids with nearly constant viscosity and different levels of elasticity are needed to elucidate the role of elasticity in viscous free-surface flows of interest. These liquids should have viscosities between 0.01 and 1 Pa·s, the range typical of coated liquids. Available model liquids (see Table 1), the so-called Boger liquids (Boger, 1977/78; Boger and Nguyen, 1978), are not ideal because of the solvents used, the excessive viscosities, and the temperature sensitivity of their properties (Binnington and Boger, 1986). In the face of environmental regulations, water-based liquids are becoming more relevant. Hence, aqueous polymer solutions are more suitable than solutions in organic solvents as model liquids for coating studies. They are also safe to use and easily disposed.

This study presents a framework for design of aqueous analogs of Boger liquids over a wide range of shear viscosities and elasticity levels. The model liquids consist of poly(ethylene oxide) (PEO) in aqueous solutions of polyethylene glycol (PEG). Their rheological properties are measured and discussed. Aqueous polyacrylamide solutions have been widely used in studies reported in the literature, and even the first

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Table 1. Comparison of Highly Elastic but Nearly Constant Viscosity Liquids Described in the Literature

Work	Viscosity Pa·s	$\tau_{11} - \tau_{22}/\tau_{12}$ at $\dot{\gamma} = 1\ s^{-1}$	Remarks
Boger (1977/78)	22.5	8.5	Water-based. Polyacrylamide in aqueous corn syrup. Temperature sensitive, forms skin on exposure to air.
Boger and Nguyen (1978)	28–72*	~ 2–10*	Polyacrylamide in glucose. Forms skin on exposure to air.
Binnington and Boger (1986)	6–40*	~ 0.28–0.8*	Polyisobutylene in polybutene.
Shaqfeh et al. (1992)	61.4–103.8	0.39–7.79	Low- and high-molecular-weight PS in DOP.
This work	0.02–0.3	Up to 0.2**	Water-based.

*Read from graphs of viscosity and $\tau_{11} - \tau_{22}$ vs. shear rate.
**Estimated from linear viscoelastic data by using $\tau_{11} - \tau_{22}\ (\dot{\gamma}) = 2\ G'(\omega)$.

Boger liquids were prepared by dissolving polyacrylamide in mixtures of corn syrup and water. However, low molecular weight oligomers of polyacrylamide would be needed for comparable model liquids. Because such oligomers are not easily available, PEG/PEO was selected.

Poly(ethylene oxide)

Polymers of ethylene oxide are the most studied among water-soluble polymers. The repeat unit in these polyethers is —CH_2—CH_2—O—. They are available in an enormous range of molecular weights, from a few hundred to a few million g/mol. Those of lowest molecular weights are liquids at room temperature; the rest are solids. Polymers with molecular weight less than about 10,000 g/mol are commonly referred to as polyethylene glycols (PEG), and those above 100,000 g/mol are termed poly(ethylene oxide) or PEO. Several extensive reviews on PEG and PEO exist, for example, by Bailey and Koleske (1976) and Molyneux (1983).

Water solubility

The good solubility of PEG/PEO in water at room temperature is surprising. Bailey and Callard (1959a) compare structurally similar polyethers on the basis of their solubility in water at room temperature. Removing or adding a —CH_2— to the repeat group in PEO, as in poly(methylene oxide) or poly(trimethylene oxide), makes the polymer insoluble in water at room temperature. Further, its isomer polyacetaldehye is also insoluble in water and only low-molecular-weight oligomers of poly(propylene oxide) are water-soluble at room temperature. Also, PEO dissolves in certain chlorinated solvents like chloroform, but not readily in aromatic or aliphatic hydrocarbons at room temperature. This suggests that PEO is readily soluble in polar solvents, and that intermolecular hydrogen bonding between the solvent and polymer molecules is essential to its solubility.

Blandamer et al. (1969) offer the following model. PEO in water has a helical structure with the *gauche* configuration of PEO being most stable (Connor and McLauchlan, 1965). Models indicate that the spacing between ether oxygen atoms of PEO in such a configuration is almost identical to the second neighbor oxygen distance in water at room temperature. Warner (1965) suggests a molecule with such a spacing can be incorporated into water with relatively little distortion of the water structure. This feature may be why PEO is so much soluble in water than other polyethers. It can also account for the observed insensitivity of NMR spectra when PEO is added to water (Blandamer et al., 1969). The second neighbor oxygen distance in water is expected to change with temperature and lessen the solubility of PEO in water as temperature rises. This can explain the lower consolute point in the PEO–water system observed by Bailey and Callard (1959a), and in the PEG–water system by Malcolm and Rowlinson (1957).

Bailey and Callard (1959a, 1959b) measured the precipitation temperature of PEO from water on heating. Their measurements on PEO of 200,000 and 7 million g/mol molecular weight showed only a small difference in precipitation temperature over two decades in concentration, and led them to conclude that the upper temperature limit of solubility is insensitive to molecular weight above a critical value. The temperature they found was 96 ± 3°C, and has since been quoted as the θ-temperature of the PEO–water system.

Hygroscopicity

Many water-soluble polymers are hygroscopic. Hygroscopicity is undesirable in free-surface flow studies, particularly if liquid properties vary strongly with equilibrium water concentration. Polyethylene glycols (PEG) are also hygroscopic, but their hygroscopicity decreases with molecular weight. Little is known about the water take-up by PEG or PEO except from the manufacturers. Union Carbide specifies that PEG-300 (from its Carbowax line of products, and with nominal molecular weight 300 g/mol) shows as much as 45% weight gain in 200 h when exposed to air with 75% relative humidity. Water take-up falls with molecular weight to less than 2% in the case of PEG-8000 (nominal molecular weight 8,000 g/mol) over the same time. Hygroscopicity is reportedly not significant in higher molecular weight PEO.

Degradation

Poly(ethylene oxide) shows limited thermal stability. PEO oxidatively degrades in the presence of oxygen by forming hydroperoxides that decompose into free radicals in the presence of metallic ions. These free radicals in turn cleave other polymer molecules (Bailey and Koleske, 1976). Metallic ions like Fe^{3+} and Cr^{3+} accelerate this process, as does exposure to ultraviolet light. However, the normal rate of degradation at room temperature is slow. Our measurements on aqueous PEO solutions stored away from direct light show that the rate of fall of viscosity and elasticity of aqueous PEO solutions is greater the higher the molecular weight. The viscosity, and elastic modulus, of a 0.5 wt. % aqueous PEO solution of 7 million g/mol molecular weight fell by 5% within 15 days, while that of a 4.1 wt. % solution of 400,000 g/mol fell immeasurably even after 28 days. Allyl, ethyl, and isopropyl alcohol compete for peroxides and free radicals in solution better than PEO and are selectively oxidized, thus stabilizing PEO solutions over longer periods of time (McGary, 1960). Other antioxidants may also be added to delay the onset of degradation.

Like many other polymers, high-molecular-weight PEO ($M_w > 1$ million g/mol approximately) degrades mechanically when subjected to intense deformation for prolonged times. The viscosity of a 0.5 wt. % aqueous PEO solution of 7 million g/mol molecular weight fell by about 10% after shearing for 120 s at 1000 s^{-1} in a Couette fixture. Hence high shear rates should be avoided during solution preparation.

PEO in Aqueous Solutions of Polyethylene Glycol

Low-molecular-weight PEGs are Newtonian liquids. Hence dilute solutions of PEO in PEG were candidates for model liquids. PEGs are hygroscopic, however, and only the lowest molecular-weight PEGs (up to about 500 g/mol) are liquids. Hence these solutions did not meet the requirements of model liquids.

PEO and PEG are both soluble in water, and hence blends of PEO with aqueous solutions of PEG were anticipated to yield the desired highly elastic liquids with nearly constant shear viscosity, and less sensitive to humidity. They were investigated next.

Concentration-molecular weight diagram

Graessley (1980) classified solutions of flexible polymers in thermodynamically good solvents by means of a concentration–molecular weight diagram (Figure 1). Polymer molecules are isolated from each other in the dilute regime. As coils overlap with rising concentration, the solutions become semidilute. The coils shrink with rising concentration in the semidilute regime until they depend only weakly on concentration and approach near-random coil dimensions. This appears to occur anywhere from 5 to 20 wt. % depending on the criterion used, and is taken to be the transition from the semidilute to the concentrated regime. The transition to entangled behavior, that is, where the shear viscosity at vanishingly small rates varies with approximately the fourth power of concentration (Graessley, 1974), is well documented in polymer melts. The same transition can be estimated in the concentrated regime from polymer melt behavior because the polymer coils have near-random coil dimensions. However, it cannot be extended to the semidilute regime. Here, the transition is determined by measuring the shear viscosity of polymer solutions of different concentrations and identifying the critical entanglement concentration. On the other hand, Raspaud et al. (1995) have recently proposed a scaling relationship between viscosity and number of entanglements per molecule to identify the entanglement transition in semidilute solutions.

Water is considered a good solvent for PEO and a similar concentration–molecular weight diagram can be drawn for the PEO–water system from measurements of shear viscosity vs. concentration reported in the literature. Dilute and semidilute regimes can be distinguished by using intrinsic viscosity relationships also reported in the literature (Brandrup and Immergut, 1989). The entanglement molecular weight of PEO is about 4,400 g/mol (Ferry, 1980) and can be used to determine the entanglement transition in the concentrated regime. On this criterion, PEG of 8000 g/mol molecular weight is entangled at concentrations greater than about 50 wt. %, which is well into the concentrated regime.

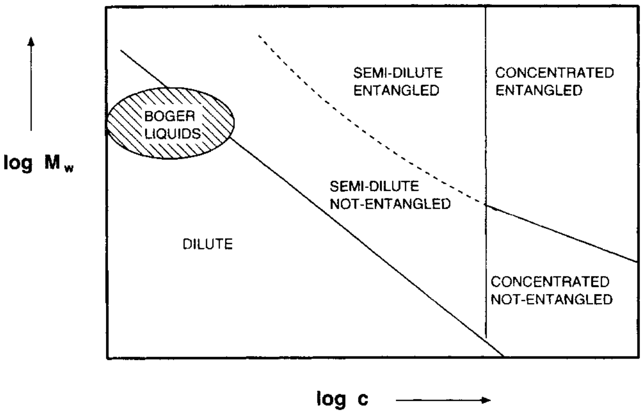

Figure 1. Concentration-molecular-weight diagram of viscoelastic regimes of flexible polymer solutions in "good" solvents (Graessley, 1980) with the range of Boger liquids added.

Different regimes are distinguished by equilibrium molecular conformations.

Recipe

The dependence of viscoelastic properties on concentration and molecular weight (Figure 1) provides a guide to preparing model liquids that are blends of PEO in aqueous PEG solutions. "Solvents" over a wide range of viscosities with little elasticity can be prepared by varying the concentration and molecular weight of PEG in water in the unentangled region. Then adding small quantities of high-molecular-weight PEO yields a dilute solution of PEO in the solvent. The high-molecular-weight polymer coils are isolated from each other, and any increase in elasticity is entirely due to the slower relaxation processes of the large molecules in the viscous solvent (Prilutski et al., 1983).

A subtle point to note is that boundaries in the concentration–molecular-weight diagram shift because the solvent for the high-molecular-weight PEO is no longer water but an aqueous solution of PEG, which is not as good a solvent as water. The dilute regime estimated on the assumption that the solvent is good is always smaller than that estimated by assuming poorer solvents.

Experimental

Aqueous PEG solutions were used as reference solutions. Carbowax PEG-8000 (nominal molecular weight $M_n = 8{,}000$ g/mol) was obtained from Union Carbide (Charleston, SC). Its bulk density was reported to be 1075 kg/m^3. Its polydis-

Table 2. Compositions of Blends of Poly(Ethylene Oxide) (PEO) with Polyethylene Glycol (PEG) in Water Used in this Study.

Liquid	Amount of PEG-8000 wt. %	PEO Additive		Visc.	Elastic Modulus G'** Pa
		Molec. Wt. g/mol	Amount wt. %	10^{-3} Pa·s	
P5	4.8	—	—	2.9	—
P9	9.1	—	—	5.4	—
P17	16.7	—	—	14.4	—
B17.04	16.7	400,000	0.2	20.5	$\sim 10^{-4}$
B17.09	16.7	900,000	0.2	21	$\sim 10^{-4}$
B17.40	16.7	4,000,000	0.1	31	0.002
P33	33.3	—	—	86	$\sim 10^{-4}$
B33.04	33.3	400,000	0.2	106	0.001
B33.40	33.3	4,000,000	0.1	138	0.01
P38	37.5	—	—	134	$\sim 10^{-4}$
B38.04	37.5	400,000	0.2	153	0.001
B38.09	37.5	900,000	0.2	158	0.001
B38.40a	37.5	4,000,000	0.06	151	0.004
B38.40b	37.5	4,000,000	0.08	185	0.01
P43	42.9	—	—	217	$\sim 10^{-4}$
B43.40	42.9	4,000,000	0.05	279	0.002
B43.40r	42.9	4,000,000	0.05	285	0.002

*The nominal molecular weight of PEG is reported as 8000 g/mol; those of PEO (M_w) are listed in the table.

**Measured at $\dot{\gamma} = 1\ s^{-1}$.

persity index (M_w/M_n) was very probably less than 2 (Bailey and Koleske, 1976). Stock solutions containing 4.76, 9.09, 16.67, 33.33, 37.5, and 42.86 wt. % PEG were prepared by adding the oligomer to distilled water (P-series liquids in Table 2). The mixtures were placed in 1-gal bottles on rolls and rotated for at least 24 h at about 18 rpm. The solutions were allowed to stand for another 24 h, after which they were clear, transparent to the eye, and colorless.

Elastic moduli G' of these solutions were first measured in small-amplitude oscillatory ("dynamic") tests. A Rheometrics RFS-II-controlled-strain rheometer (Rheometrics Scientific, Piscataway, NJ) was used, and measurements were made at 20±0.1°C. The rheometer was equipped with a force-rebalance transducer that measures torques between 0.002 g cm (0.196 μNm) and 100 g cm (9,800 μNm) in two ranges to within 1% accuracy. A concentric cylinder geometry with cup diameter 34 mm, bob diameter 32 mm, and bob length 33 mm was used. The fixtures were covered with water-soaked foam-lined covers to avoid any water evaporation from the solutions.

Steady shear viscosities of these solutions were measured vs. shear rate with the strain-controlled rheometer as well as a stress-controlled rheometer (DSR, Rheometrics Scientific, Piscataway, NJ). Finally, temperature sensitivity of the shear viscosity of the solution with the highest PEG concentration (P43) was measured. The temperature was raised from 20°C to 30°C in approximately 2°C increments and then lowered. The fixtures were allowed to equilibrate for 30 min at each temperature before testing began. The cup temperature was measured and controlled; the temperature of the large aluminum bob was not. Each test took about 15 min, and the cup temperature varied at most between ±0.3°C of the set point during this time.

PEO samples of different molecular weights were obtained from Union Carbide. Nominal molecular weights (M_w in this case) reported by the manufacturer were 400,000 g/mol (WSR-1105), 900,000 g/mol (WSR-3333), and 4 million g/mol (WSR-301). Their bulk density was reported to be 1,200 kg/m^3. The polydispersity indices (M_w/M_n) of these samples were very likely to be about four (Bailey and Koleske, 1976). Different amounts of PEO were added to portions of the reference PEG solutions whose shear viscosities were greater than 0.01 Pa·s. These mixtures were stored in 1-gal bottles that were gently rolled for 24 h and allowed to stand for another 24 h. They too were clear, transparent, and colorless to the eye.

Table 2 lists the compositions of the reference solutions and the blends prepared therefrom. Blends B43.40 and B43.40r were independently prepared to test the reproducibility of the solution preparation procedure.

Linear viscoelastic strain limits of these blends were determined with oscillatory tests at fixed frequency (1 rad/s) and rising strain. The linear viscoelastic limit often exceeded 100% strain. Hence strains up to 100% were imposed to produce torques greater than the transducer minimum in dynamic frequency tests. Steady shear viscosities of the blends were measured with the same equipment, fixtures, and conditions as described earlier.

Results and Discussion

Steady shear viscosities of the reference PEG solutions are shown in Figure 2. The filled symbols are data with measured torques below the specified minimum of the transducer, and are less accurate. The shear viscosities denoted by open symbols were all constant and independent of shear rate. This was confirmed by linear regression of measured torque with shear rate. The fits were satisfactory: the coefficient of regression was better than 0.999 in every case. Thus the liquids to be used as solvents for the high-molecular-weight polymeric additives are effectively Newtonian.

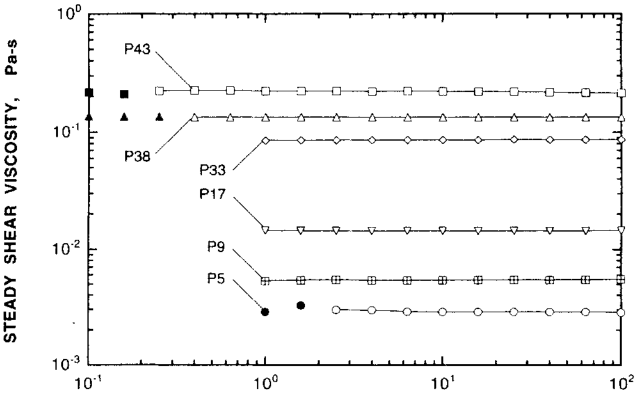

Figure 2. Steady shear viscosities of reference aqueous polyethylene glycol solutions listed in Table 2.

The shear viscosity was measured with concentric cylinders in a Rheometrics RFS-II rheometer. Filled symbols denote measurements at torques less than the specified minimum of the instrument.

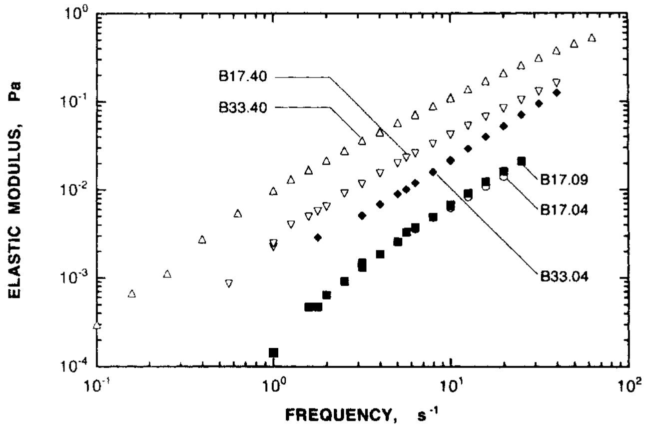

Figure 3. Elastic modulus G' vs. frequency of blends of PEO with P17 and P33.

G' rises markedly with addition of 0.1 wt. % PEO of $M_w = 4$ million g/mol.

Elastic moduli of reference solutions P5, P9, and P17 could not be measured with the RFS-II rheometer. Those of P33, P38, and P43 could be measured accurately only between 1 and 20 s^{-1} because of uncertainties in phase-angle determination at small torques as well as high frequencies, and were about 10^{-4} Pa at a frequency of 1 s^{-1}. Figures 3 and 4 show the elastic moduli of the blends. The elastic moduli of the reference solutions were all less than those of blends B17.04 and B17.09. Adding PEO of 400,000 and 900,000 g/mol molecular weight caused almost identical effects (compare B17.04 with B17.09, and B38.04 with B38.09). One possible reason might be large polydispersity in the samples; another might be the small concentrations of the polymers. On the other hand, shear viscosities of liquids with the 900,000 g/mol additive were always greater than those with the 400,000 g/mol additive (see Figure 5). G' rose markedly with the addition of 0.1 wt. % of the highest molecular weight PEO (M_w = 4 million g/mol). In no case was the terminal slope of 2 achieved at the lowest frequencies tested, which indicates a wide spectrum of relaxation times. The width of the spectrum may be due to polydispersity, or the high frequencies tested. The complex dynamic association between water, PEG, and PEO molecules advanced by Alfrey and Gurnee (1956) may also be rate-dependent and produce a spectrum of relaxation times.

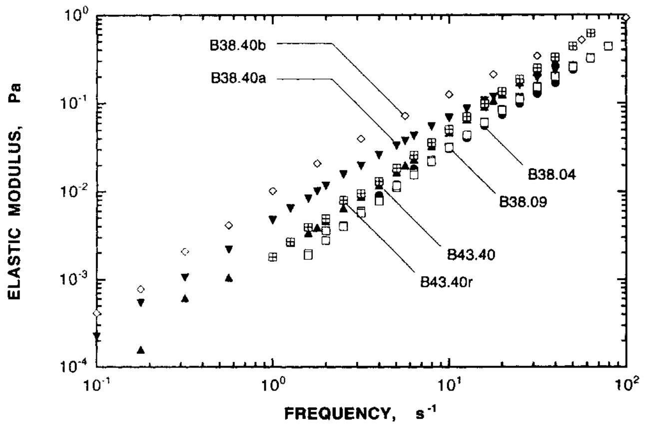

Figure 4. Elastic modulus G' vs. frequency of blends of PEO with P38 and P43.

That blends B43.40 and B43.40r are almost identical in behavior indicates that the solution preparation procedures were reproducible.

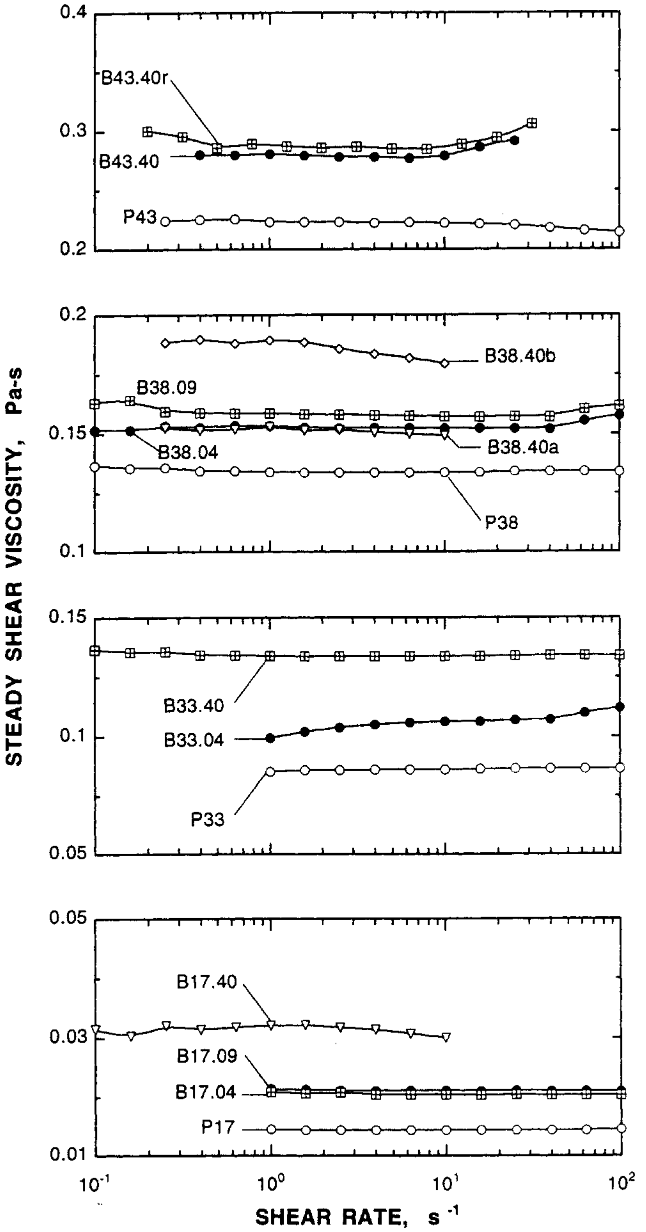

Figure 5. Steady shear viscosities of blends are denoted by open symbols; those of reference solutions are denoted by filled symbols (Table 2).

Rotational flows between concentric cylinders of all blends with PEO of $M_w = 4$ million g/mol became unstable at rates greater than 10 s^{-1}; three are shown in Figure 6. Note linear scale on ordinate.

Figure 5 shows shear viscosities of the blends. Shear viscosities rose with molecular weight and concentration of PEO. Again, the slightest amount of PEO of $M_w = 4$ million g/mol raised the viscosity substantially. Nevertheless, the shear viscosities remained constant in the shear rate range tested. This was confirmed by linear regression of measured torque with shear rate. The fits were again satisfactory: the coefficient of regression was better than 0.99 in each case.

Measured viscosities of blends with PEO of $M_w = 4$ million g/mol abruptly rose at shear rates between 5 and 40 s^{-1} (three are shown in Figure 6). Transient tests revealed that the torque rose beyond about 1 s to a higher value. The torque remained near this value even after 200 s, but oscillated with time with a period of a few seconds. The abrupt rise in measured torque, and consequently in calculated apparent viscosity, is probably due to an elastic instability in the Couette flow between cylinders (Larson et al., 1990; Shaqfeh et al., 1992). Flow visualization with flakes (nominal dimensions 30 $\mu m \times 6\ \mu m \times 0.07\ \mu m$, Kalliroscope Corporation, Groton, MA) in less-controlled experiments with a transparent plexiglass outer cylinder mounted on a Rheometrics DSR rheometer revealed transverse bands, about as thick as the radial clearance between the cylinders, that oscillated in space along the azimuthal direction. Moreover, the free surface was wavy in both space and time when the Couette fixture was half-filled, three-quarters filled, and completely filled with liquid. The shear rate at which the torque rose appeared insensitive to whether the outer or inner cylinder was rotated (RFS-II vs. DSR rheometer). When the cylinders were "flooded," that is, the liquid overflowed from the gap between the cylinders, the torque and hence apparent viscosity rose abruptly at lower shear rates than before.

Normal stresses in steady shearing motions were not measured. Table 1 compares the ratio of the first normal stress difference to the shear stress of various Boger liquids reported in the literature. The stress ratio is one measure of elasticity. The liquids tested here display lower stress ratios. However, the evidence reported here of elastic instabilities in the Couette flow during viscosity measurement indicates that these liquids are elastic enough to use in probing elastic instabilities in prototypical processing flows. Higher elasticity levels can be obtained by using larger amounts of high-molecular-weight PEO.

Fiber spinning and filament stretching best approximate extensional kinematics, but these techniques cannot be used to measure the extensional viscosity of low-viscosity liquids such as those reported here. Opposed-nozzle devices have previously been used to *index* low-viscosity polymer solutions (Hermansky and Roger, 1995; Dontula et al., 1997). A Rheometrics RFX Analyzer with the opposed-nozzle configuration was used to measure the apparent extensional viscosity of the blends. The solution P17 and its blends were not viscous enough, and torques generated with them were smaller than could be reliably measured by this device. On the other hand, the torque measured with blend B43.40 oscillated with time, presumably due to the onset of elastic instabilities elsewhere in the flow cell. Apparent extensional viscosities of other blends could be measured only over a limited range of apparent extension rates. The apparent extensional viscosity of P38 was about 0.5 Pa·s and insensitive to apparent extension rate, whereas that of B38.40b rose with extension rate to about 15 Pa·s at 100 s^{-1} (see Figure 8). This thickening with extension rate is similar to reported measurements on other aqueous PEO solutions (Hudson et al., 1990; Gauri and Koelling, 1997).

The rheological properties of Boger liquids can be rationalized theoretically by considering a liquid comprising dumbbells with Hookean springs dissolved in Newtonian solvents (Prilutski et al., 1983; Mackay and Boger, 1987). The corresponding Oldroyd-B constitutive equation with a single relaxation time representing the high-molecular-weight polymer accounts for the salient behavior. Boger and Mackay (1991) later proposed a two time-constant Oldroyd-B model with a small elasticity attributed to the *solvent* to describe linear viscoelastic behavior at high frequencies. The complex association between polar water, PEG, and PEO molecules in the PEO-PEG-water system may also introduce a spectrum of relaxation times (Alfrey and Gurnee, 1956).

Figure 7 shows the decrease in mean viscosity of solution P43 with temperature. The shear viscosity was measured at shear rates between 1 and 100 s^{-1} at temperatures from 20°C to 30°C. The error bars represent the total variation in viscosity with shear rate during both measurements. Viscosity fell by less than 25% over the 10°C range around room temperature. Its flow-activation energy, $\Delta H/R$, estimated to be 2230

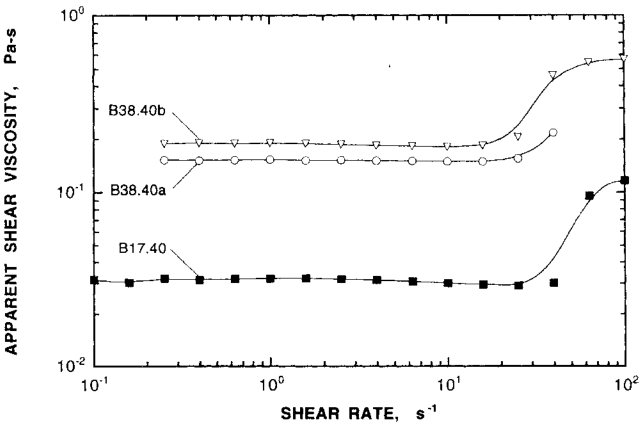

Figure 6. Apparent viscosities of blends B17.40, B38.40, and B38.40b vs. shear rate measured with a concentric-cylinder geometry.

The abrupt rise in measured torque, and consequently in calculated apparent viscosity, is due to an elastic instability in the Couette flow between cylinders (Larson et al., 1990).

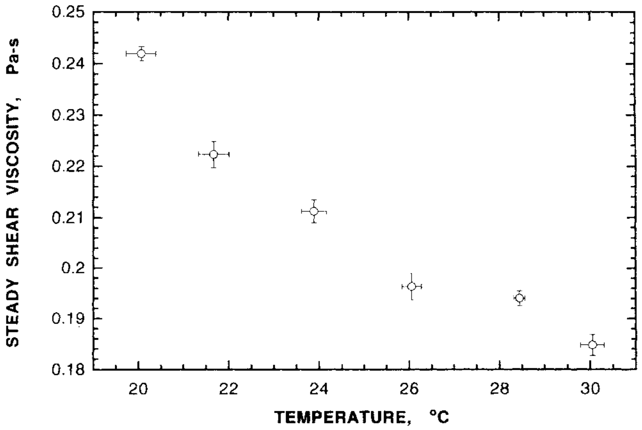

Figure 7. Variation of "mean" steady shear viscosity of reference solution P43 with temperature change.

Shear viscosity reported is the average of two measurements over shear rates of 1-100 s^{-1} at each temperature.

K fell in the middle of the range 1500 to 2800 K reported by Gauri and Koelling (1997) for aqueous PEO solutions. The reference solution P38 behaved similarly.

Shear viscosity of the liquids can be raised by adding more oligomer (PEG) within the unentangled regime of the concentration–molecular-weight diagram. Higher molecular weight PEG can also be used to raise the viscosity of the liquids. However, the transition to entangled polymer behavior, that is, to where the zero-shear viscosity rises with approximately the fourth power of concentration, is at lower concentrations at higher molecular weights. Hence, raising the molecular weight of PEG may make the aqueous PEG solvent elastic without appreciably raising its viscosity, and is not desirable. Salts can also be added to solution. Addition of salts like potassium bromide or magnesium sulfate shrinks the PEO molecules (Bailey and Callard, 1959a), and the dilute limit could be made larger. Their effect on viscosity has not been studied.

Table 3. Relaxation Strengths G_k, Times λ_k, and Other Parameters Estimated from Nonlinear Regression

Liquid	G_k Pa	λ_k s	α (PSM model)	α (Eq. 2)
B33.40	112.575	8.55166×10^{-4}	1.2218×10^{4}	1.2494×10^{4}
	2.18401×10^{-1}	7.96651×10^{-2}		
	2.37257×10^{-2}	7.32302×10^{-1}		
	4.46715×10^{-3}	7.85108		
B38.40a	221.474	5.69356×10^{-4}	4.7084×10^{4}	4.8179×10^{4}
	1.16867×10^{-1}	7.94038×10^{-2}		
	1.6888×10^{-2}	4.55057×10^{-1}		
	9.48407×10^{-4}	4.7901		
B38.40b	265.122	5.0714×10^{-4}	1.5305×10^{4}	1.5484×10^{4}
	2.72585×10^{-1}	7.19447×10^{-2}		
	3.03043×10^{-2}	6.18727×10^{-1}		
	6.63231×10^{-4}	7.83219		
B43.40	397.971	6.23411×10^{-4}	1.9693×10^{5}	1.6452×10^{5}
	7.24527×10^{-1}	8.82649×10^{-2}		
	1.68268×10^{-2}	1.61269		

Fitting constitutive equations to data

Coating and related free-surface flows contain regions of intense mixtures of shear and extension of short duration. Fitting the rheological properties of these liquids to candidate integral and differential constitutive equations makes it possible to estimate shear and extensional viscosities and normal stresses at the large strain rates the liquid experiences in such flows. The elastic and viscous moduli, G' and G'', were simultaneously fitted to a series of Maxwell elements with relaxation times λ_k and relaxation strengths G_k by minimizing the variance measure χ^2 in the average sense of nonlinear regression:

$$\chi^2 = \sum_{k=1}^{np} \left[1 - \frac{G'_{fit}(\omega_i)}{G'(\omega_i)}\right]^2 + \left[1 - \frac{G''_{fit}(\omega_i)}{G''(\omega_i)}\right]^2. \tag{1}$$

Here np is the number of fitted experimental points and N is the number of relaxation times chosen to reduce the residuals to acceptable limits. The resulting system of $2np$ nonlinear algebraic equations was solved by using a modified Levenberg–Marquardt routine (Levenberg, 1944; Marquardt, 1963; IMSL, 1991). The equations are highly nonlinear and can have multiple solutions; the solution found by the iteration routine depends on the domain of convergence the initial estimate falls into (Papanastasiou et al., 1983). Only those liquids whose moduli were measured over two decades of frequency or more were fitted. A fit was considered acceptable if each residual was less than 10^{-2}. Table 3 shows the minimum number of relaxation times and strengths used to fit the linear viscoelastic data from blends B33.40, B38.40a, B38.40b, and B43.40. These values are comparable to those obtained by using the fitting software from Rheometrics Scientific Inc. The shortest relaxation time from these fits is of the order of 10^{-3} s, and cannot be experimentally verified because moduli could not be measured at high frequencies. However, the product of the shortest relaxation time and its relaxation strength, $G_1\lambda_1$, is within 10% of the low-shear rate viscosity of the PEG solutions used as solvents in these blends.

The values of G_k and λ_k were then used to fit the steady shear viscosity to the parameter α in the PSM equation (Papanastasiou et al., 1983), also by using nonlinear regression. The fit was considered acceptable within the range of experimental data if the residuals were less than 10^{-2}. However, the viscosity extrapolated by means of the PSM equation to shear rates above 10,000 s^{-1}, a range commonly encountered in coating processes, falls unacceptably below that of the PEG solution used as solvent, and finally to zero (Figure 8). This behavior stems from the strong damping function in the PSM model (and also in the Wagner model); it can be rectified by adding a Newtonian solvent viscosity contribution to the PSM equation (Kajiwara et al., 1995; but they did not address behavior at high-shear rates):

$$\boldsymbol{\tau}(t) = \eta_s 2\boldsymbol{D} + \boldsymbol{\tau}_p \tag{2a}$$

$$\boldsymbol{\tau}_p = \int_{-\infty}^{t} \left[\sum_{k=2}^{N} \frac{G_k}{\lambda_k} e^{-(t-t')/\lambda_k}\right] \frac{\alpha}{(\alpha-3) + \beta I_{\boldsymbol{B}} + (1-\beta) II_{\boldsymbol{B}}} \times \boldsymbol{B}_t(t')\, dt'. \tag{2b}$$

Here $\boldsymbol{\tau}$ and $2\boldsymbol{D}$ are, respectively, the extra stress tensor and rate of strain tensor, and $I_{\boldsymbol{B}}$ and $II_{\boldsymbol{B}}$ are the first and second invariants of the Finger tensor $\boldsymbol{B}_t(t')$. The parameter β contributes in extensional deformations only. The solvent viscosity η_s was taken to be the product $G_1\lambda_1$ from Table 3, and the summation was then over the remaining relaxation times. The steady shear viscosity data was fitted to this modified PSM equation and values of α are reported in Table 3. Figure 8 compares experimental data on blend B38.40b with the fits of the PSM equation and Eq. 2, and also shows their predictions for the first normal stress difference N_1 and uniaxial extensional viscosity. At low rates, N_1 varies with the square of the shear rate, and should asymptotically approach $2G'$.

Differential constitutive equations are often used to model flows of viscoelastic solutions. The UCM model with Hookean springs predicts a shear-rate-independent viscosity, and an unphysical extensional viscosity because of the infinite extensibility of Hookean springs. The FENE-P differential constitutive equation with a single adjustable nonlinear parameter b (Eq. 13.5-56 in Bird et al., 1987b), the ratio of the maximum stretch to equilibrium length of the springs, was then fitted to the experimental data. The slightly shear-thinning

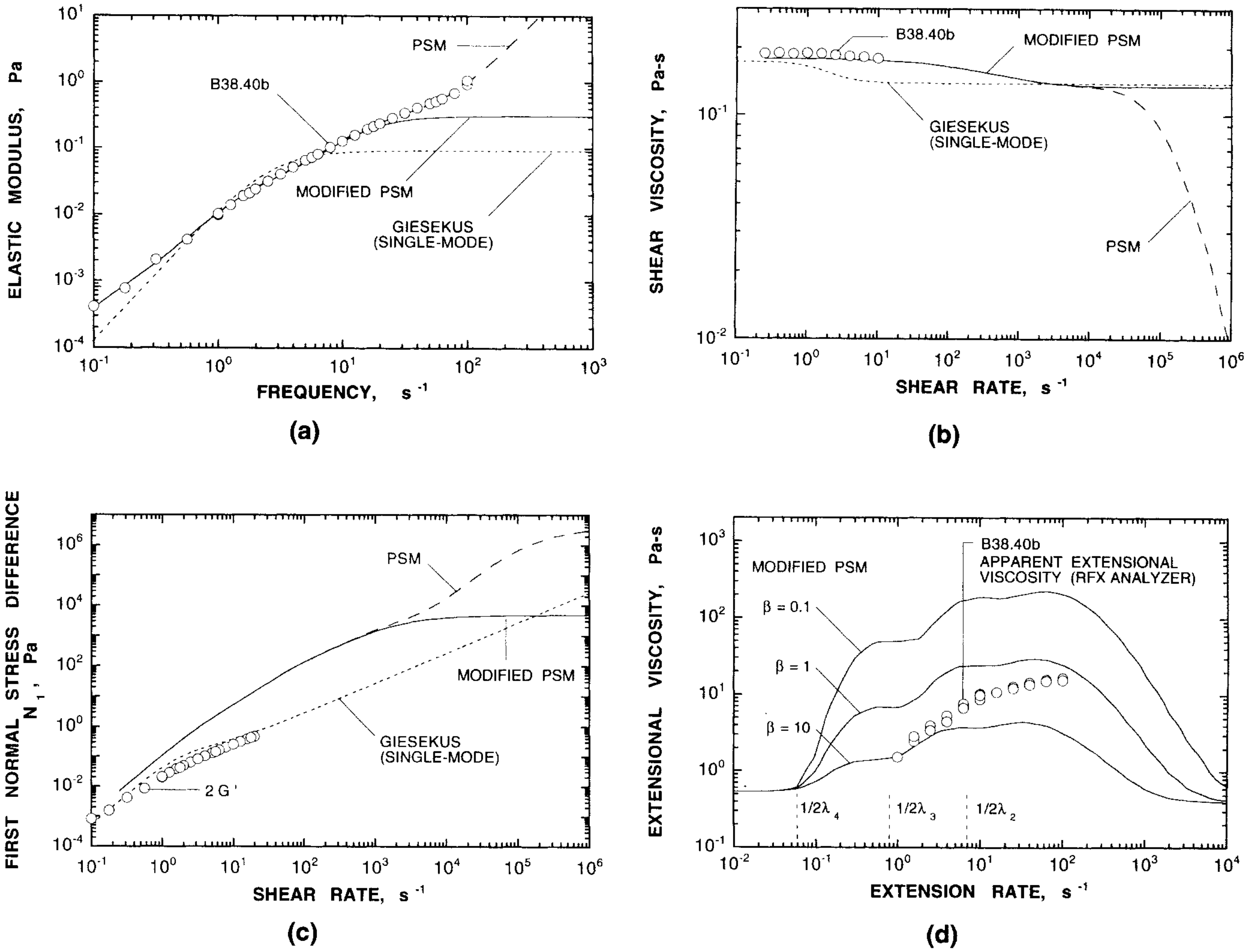

Figure 8. Elastic and viscous moduli, steady shear viscosity, and first normal stress difference for blend B38.40b.

The modified PSM model (Eqs. 2a and 2b) includes a Newtonian solvent viscosity contribution and predicts a more reasonable shear viscosity at high shear rates than the PSM model. The first normal stress difference N_1 should equal $2G'$ at vanishingly low rates and frequencies. The best fit of the Giesekus model with one relaxation time is included for comparison. Also shown is the extensional viscosity *predicted* by the modified PSM model compared with apparent extensional viscosity measured with the RFX indexer.

viscosity in these liquids results in b greater than 10^6 and corresponds to Hookean dumbbell-like behavior. Further, the single Maxwell-like element fails to correlate the experimental measurements of G' and G'', and is not included here. Figure 8 also includes the best fit of the data by the Giesekus model with a single relaxation time (Bird et al., 1987a). This model also does not quantitatively fit the linear viscoelastic and shear viscosity measurements; the agreement between the predicted N_1 and experimental $2G'$ is purely coincidental. The multimode Giesekus model has more than one adjustable nonlinear parameter and can describe the experimental data more accurately. However, more experimental measurements of viscosity, both in shear and extension, and normal stress differences are needed over a wide range of deformation rates to estimate these parameters reliably.

Concluding Remarks

Water-based liquids with adjustable elasticity and nearly constant shear viscosity have been formulated to serve as model liquids in experiments that probe elastic effects in coating and other free-surface flows. Aqueous polymer solutions are convenient to use in laboratory studies, and are now more common in industrial practice.

The solvent, an unentangled solution of low-molecular-weight polyethylene glycol in water, is effectively Newtonian. High-molecular-weight poly(ethylene oxide) (PEO), added in dilute quantities, makes the liquids elastic. Shear viscosities of the liquids range from about 0.02 to 0.3 Pa·s and are constant up to shear rates of 100 s^{-1}. Small-amplitude oscillatory tests indicate stress ratios up to 0.2. Shear viscosity and elasticity can be adjusted by varying the concentration and molecular weight of the oligomer and polymer within the unentangled regions of the concentration–molecular-weight diagram (Graessley, 1980).

Differential constitutive equations with a single relaxation time, like the FENE-P or Giesekus model, do not accurately describe the salient rheological properties of these liquids. The multimode Giesekus model can be used, but to fit all of the parameters involved requires measurements of viscosity and normal stress differences over a wider range of shear rates than was accessible in this study. The PSM integral constitutive equation modified by addition of a solvent contribution to viscosity, fits both the data and the expected high-shear-rate asymptote of viscosity.

Flow-induced degradation of these liquids has not been studied. High-molecular-weight polymers are more susceptible to degradation than lower molecular weight ones, more so in extension than in shear. However, in current slot coating studies with these liquids, a progressive cavity pump has been found to degrade them much less than a gear pump used previously in the pumping system.

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