

Ch 15

Rheology of emulsions and immiscible blends

Steady shear viscosity, normal stresses

Dilute suspension of Newtonian drops or bubbles in a Newtonian medium

$$\eta_r \equiv \frac{\eta}{\eta_s} = 1 + \frac{1 + \frac{5}{2}M}{1 + M} \phi$$

For higher concentration

$$(\eta_{r,0})^{1/K_1} = \exp\left(\frac{2.5\phi}{1 - \phi/\phi_m}\right)$$

$$K_1 \equiv \left(\frac{0.4 + M}{1 + M}\right)$$

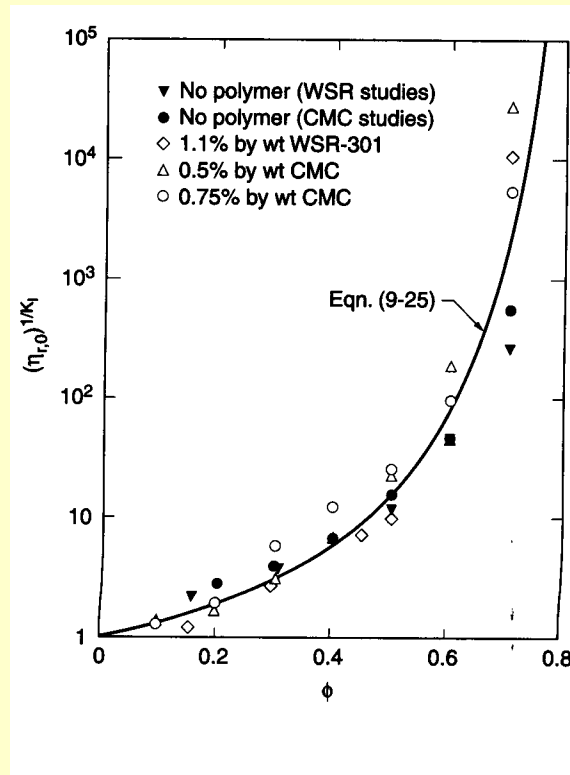


Figure 9.15 Zero-shear relative viscosity $\eta_{r,0}$ to the power $1/K_1$ versus droplet concentration ϕ for emulsions of petroleum oil in aqueous solutions of Triton X-100 surfactant and 1.1% polyethylene oxide (Polyox WSR), or sodium carboxymethyl cellulose (CMC). K_1 is given by Eq. (9-26), and the line is the fit using Eq. (9-25) with $\phi_m = 0.91$. (From Pal 1992, with permission from the Journal of Rheology.)

Steady shear viscosity, normal stresses

At high shear rate, $(\eta_{r,0})^{1/K_1} = \exp\left(\frac{2.5\phi}{1 - \phi/\phi_m}\right)$

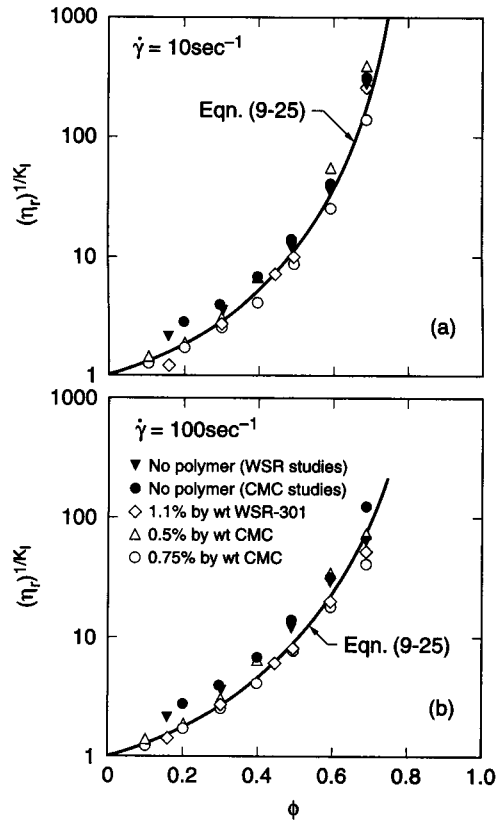


Figure 9.16 Relative viscosity to the power $1/K_1$ versus droplet concentration ϕ at shear rates of 10 sec^{-1} and 100 sec^{-1} , for emulsions described in the caption to Fig. 9-15. K_1 is given by Eq. (9-26), and the lines are the fits using Eq. (9-25) with $\phi_m = 1.05$ for $\dot{\gamma} = 10 \text{ sec}^{-1}$ and $\phi_m = 1.18$ for $\dot{\gamma} = 100 \text{ sec}^{-1}$. (From Pal 1992, with permission from the Journal of Rheology.)

The volume fraction at maximum packing was used as a fitting parameter for the best fit

Linear viscoelasticity

Oldroyd theory; LVE of suspensions of one Newtonian fluid in another

$$G^* = i\omega\eta_s \left(\frac{1 + \frac{3}{2}\phi \frac{E}{D}}{1 - \phi \frac{E}{D}} \right) \quad \begin{aligned} E &\equiv 2i\omega(\eta_d - \eta_s)(19\eta_d + 16\eta_s) + \frac{8\Gamma}{a}(5\eta_d + 2\eta_s) \\ D &\equiv i\omega(2\eta_d + 3\eta_s)(19\eta_d + 16\eta_s) + \frac{40\Gamma}{a}(\eta_d + \eta_s) \end{aligned}$$

Can be rewritten in the following form;

$$\begin{aligned} G' &= G'_{bulk} + G'_{interface} & G'_{bulk} &= 0, & G''_{bulk} &= \omega\mu \frac{\tau_2}{\tau_1} & G'_{interface} &= \frac{\mu}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1}\right) \frac{\omega^2 \tau_1^2}{1 + \omega^2 \tau_1^2} \\ G'' &= G''_{bulk} + G''_{interface} & & & & & G''_{interface} &= \frac{\mu}{\tau_1} \left(1 - \frac{\tau_2}{\tau_1}\right) \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \end{aligned}$$

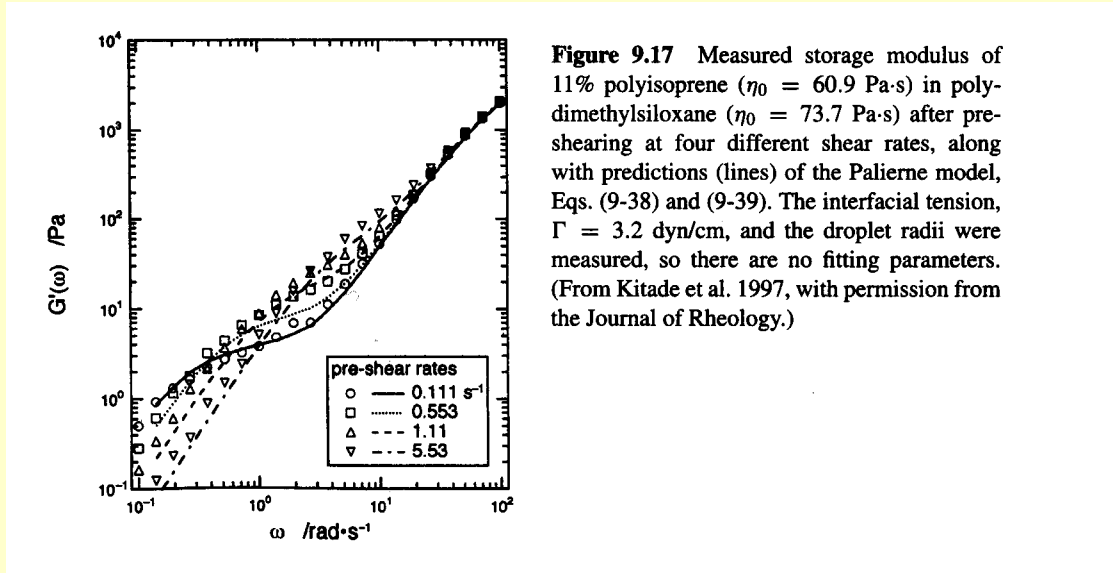
Palierne model when both phases are viscoelastic;

in the limit of a constant interfacial tension and no interfacial viscosity

$$G^* = G_s^* \left(\frac{1 + \frac{3}{2}\phi \frac{E}{D}}{1 - \phi \frac{E}{D}} \right) \quad \begin{aligned} E &\equiv 2(G_d^* - G_s^*)(19G_d^* + 16G_s^*) + \frac{8\Gamma}{a}(5G_d^* + 2G_s^*) \\ D &\equiv (2G_d^* + 3G_s^*)(19G_d^* + 16G_s^*) + \frac{40\Gamma}{a}(G_d^* + G_s^*) \end{aligned}$$

Linear viscoelasticity

Predictions of Palierne model



Nonlinear viscoelasticity; The Doi-Otta theory

If flow is continuous, or strains are large;

Doi-Otta developed a theory for blends of two immiscible Newtonian fluids of equal viscosity and roughly equal density (to avoid settling)

Valid at $0.1 < M < 4$

Q ; area of interface per unit volume; increases in response to an increase in shear rate

Shearing not only increases the surface area of interface, but also orients the interface, so it becomes more nearly parallel to the shearing surfaces

\mathbf{q} ; interface tensor $\mathbf{q} \equiv \frac{1}{V} \int_A dA (\mathbf{nn} - \delta)$

$$\frac{\partial}{\partial t} \mathbf{q} = -\mathbf{q} \cdot \nabla \mathbf{v}^T - \nabla \mathbf{v} \cdot \mathbf{q} + \frac{2}{3} \delta \nabla \mathbf{v} : \mathbf{q} - \frac{Q}{3} (\nabla \mathbf{v} + \nabla \mathbf{v}^T) + \frac{1}{Q} \mathbf{q} : \nabla \mathbf{v} \mathbf{q}$$

$$\frac{\partial}{\partial t} Q = -\nabla \mathbf{v} : \mathbf{q}$$

$$\boldsymbol{\sigma} = 2\eta_0 \mathbf{D} - \Gamma \mathbf{q}$$

Nonlinear viscoelasticity; The Doi-Otta theory

Additional terms to account for coarsening must be added to the right sides

$$\left(\frac{\partial}{\partial t} \mathbf{q}\right)_{relax} = -\Lambda Q \mathbf{q} \quad \left(\frac{\partial}{\partial t} Q\right)_{relax} = -\Lambda \mu Q^2$$

Scaling law can be derived; which implies that all components of the stress tensor are linear in the shear rate

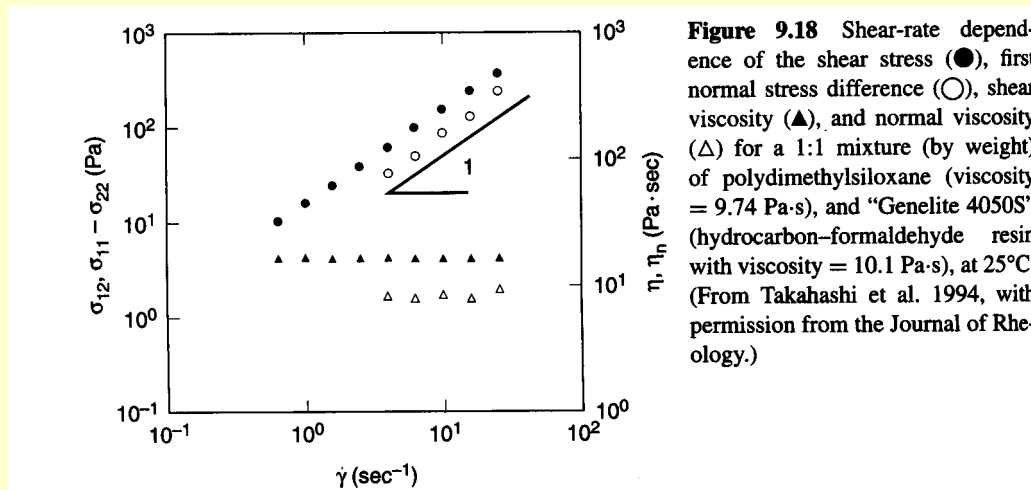


Figure 9.18 Shear-rate dependence of the shear stress (●), first normal stress difference (○), shear viscosity (▲), and normal viscosity (△) for a 1:1 mixture (by weight) of polydimethylsiloxane (viscosity = 9.74 Pa·s), and “Genelite 4050S” (hydrocarbon–formaldehyde resin with viscosity = 10.1 Pa·s), at 25°C. (From Takahashi et al. 1994, with permission from the Journal of Rheology.)

Individual components do not have normal stresses -> the normal stress difference must be attributed entirely to the presence of interfaces

Nonlinear viscoelasticity; The Doi-Otta theory

Scaling onto a single curve due to the lack of an intrinsic relaxation time

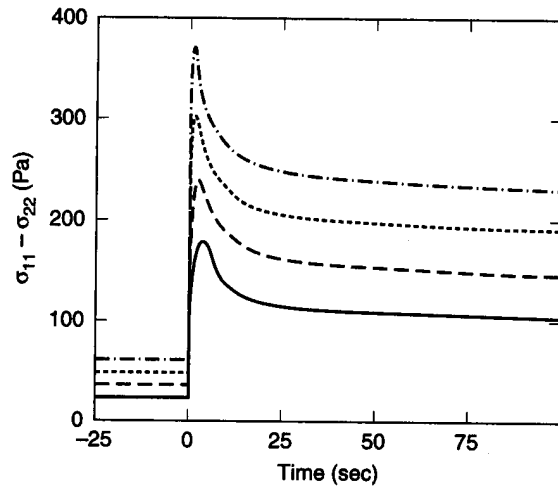


Figure 9.20 First normal stress difference versus time after step increases in shear rate. The shear rates before the step increase, $\dot{\gamma}_i$, and after it, $\dot{\gamma}_f$, are given by $(\dot{\gamma}_i, \dot{\gamma}_f) = (3,12), (4,16), (5,20),$ and $(6,24)$, from the bottom curve to the top one. (From Takahashi et al. 1994, with permission from the Journal of Rheology.)

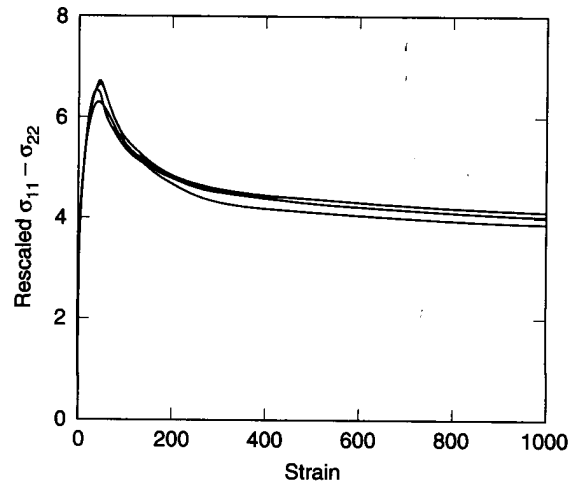
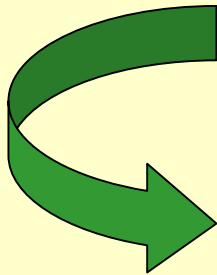


Figure 9.21 The data of Fig. 9-20 re-plotted as normalized stress $N_1/N_1^{ss}(\dot{\gamma}_i)$ versus strain $\dot{\gamma}_f t$. (From Takahashi et al. 1994, with permission from the Journal of Rheology.)