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## **Capillary Rheometry**

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Rheometers are instruments for measuring rheological properties of liquids and (soft) solids. Typical rheological properties are viscosity, modulus, compliance, yield stress, and relaxation times. These properties depend on the microstructure of the material and, hence, depend on stress or strain-induced structural changes, and on time (aging or ripening of structure). For rheometry, a test sample gets mounted into the rheometer and subjected to well-defined stress or strain. In strain-controlled experiments, the strain or strain rate is prescribed and the stress response gets recorded. Stress-controlled instruments prescribe the stress and record the strain. Typically, rheometers are designed for one or the other mode of operation.

This chapter deals with the capillary rheometer, which is one of the oldest rheometer types. Hagen and Poiseuille already found that the pressure drop,  $\Delta p$ , for flow in a capillary (radius  $R$ , length  $L$ ) at a volume flow rate,  $Q$ , depends on the shear viscosity

$$\eta = \frac{\Delta p}{L} \frac{\pi R^4}{8Q} \quad (1),$$

provided that the flow is laminar and the fluid is *Newtonian*. The following will describe capillary rheometry that also applies to *non-Newtonian* fluids.

Capillary rheometers are designed for characterizing polymer melts at high shear rates, typically from 10 to 10,000s<sup>-1</sup>. Such shear rates can be reached easily in capillary flow and also in polymer processing (extrusion, injection molding). Excessive heat generation due to viscous dissipation (Winter, 1977), flow instabilities (Ramamurthy, 1986), or wall slip (Mooney, 1931) determine the upper limit of such high shear rate experiments with capillary rheometers and require special attention.

The measurement principle is simple. A pump (extruder, gear pump, ram) pushes test fluid through a capillary of constant cross section (circular or slit cross section). The volume flow rate,  $Q$ , and the pressure gradient,  $p'$ , in the region of fully developed flow are measured for determining the shear viscosity.

A typical capillary rheometer is shown in figure 1. Some capillary rheometers use a single pressure transducer at the die inlet and recover the pressure gradient through repeat measurements as described further below. The volume flow rate is determined from the measured piston speed,  $v_p$ , and the piston cross sectional area,  $A_p$ .

$$Q = A_p v_p \quad (1).$$

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Figure 1: Capillary rheometer which consists of a feed system (1), a connector channel (2), a temperature controlled housing (3) which contains the sample reservoir (4) and is wrapped by heaters (5), a measurement die (6) with an insulated head (7), pressure sensors (8), temperature sensor (9), piston (10) to push the sample through the die, and mechanical drive system (11 - 13). The feed system (1) is convenient for extensive sample testing but requires larger samples. Mounted on the capillary (6) are pressure transducers for a direct measurement of the pressure gradient in the fully developed flow region.

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Figure 2: Slit capillary with pressure transducers (Eswaran et al., 1963; Robens and Winter, 1975).

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## Data Treatment

The overall purpose of the capillary flow experiment is the measurement of the steady shear viscosity

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (3),$$

of non-Newtonian fluids such as polymer melts and solutions. While the experiment itself is straight forward, the data analysis is unduly involved. Difficulties arise from the fact that neither the shear stress,  $\tau$ , nor the shear rate,  $\dot{\gamma}$ , are measured directly. Their value has to be extracted from the pressure readings and the measured volume flow rate,  $Q$ . This is the topic of most of the remaining chapter.

The data analysis depends on the geometry of the capillary. Here we consider capillaries with circular cross section (radius  $R$ ; area  $\pi R^2$  for) and slit cross section (height  $H$ ; width  $W$ ; area  $HW$ ). Equations need to be derived for the shear stress and the shear rate which take into account that neither one is constant throughout the capillary cross section.

*a) Shear Stress* The shear stress in fully developed capillary flow grows linearly with the distance from the center of the capillary ( $r=0$  or  $y=0$ ) to its maximum value, the wall shear stress  $\tau_w$ :

$$\text{circular geometry} \quad \tau(r) = \tau_w r / R \quad \text{with} \quad \tau_w = -\frac{R}{2} p' \quad (4),$$

$$\text{slit geometry} \quad \tau(y) = \tau_w 2y / H \quad \text{with} \quad \tau_w = -\frac{H}{2} p' \quad (5).$$

This shows that we need to measure the pressure gradient,  $p'$ , in the capillary before we can determine the shear stress distribution. The pressure gradient can be approximated by the measured pressure drop  $\Delta p$  over the entire capillary

$$p' = -\frac{\Delta p}{L} \quad (6).$$

However, this approximate value overestimates the real  $p'$  value since it includes pressure losses at the inlet and the outlet of the capillary. These so-called ‘end effects’ can be subtracted out by repeating the measurements (same volume flow rate  $Q$  again and again) with capillaries of different length (Bagley, 1960). The pressure gradient is then determined as (when using two capillaries, for instance)

$$p' = -\frac{\Delta p_1 - \Delta p_2}{L_1 - L_2} \quad (7).$$

This is the preferred method of determining  $p'$ .

b) *Shear Rate* The shear rate in fully developed capillary flow grows sharply with increasing distance from the center of the capillary. The shear rate distribution is a characteristic property of the test sample and can not be predicted beforehand. There is, however, a possibility of determining the share rate at the wall by combining data from measurements at different volume flow rates  $Q_1, Q_2, Q_3$ , etc. and determining the slope of the curve  $Q(p')$  for each of the flow rate values. With this information, the shear rate at the capillary wall can be calculated as

circular geometry  $\dot{\gamma}_w = -\frac{Q}{\pi R^3} \left( 3 + \frac{p'}{Q} \frac{\partial Q}{\partial p'} \right)$  (8),

slit geometry  $\dot{\gamma}_w = -\frac{2Q}{WH^2} \left( 2 + \frac{p'}{Q} \frac{\partial Q}{\partial p'} \right)$  (9).

These equations were first proposed by Rabinowich (1929). Determining the gradient ( $\partial Q/\partial p'$ ) for these formulas is somewhat tedious and often marred with error. An alternative approach will be explained in section (c) below.

Capillary flow experiments together with the above analysis (using equations 4, 7, 8, or equations 5, 7, and 9, respectively) lead to the final result, the shear rate dependent viscosity. In all cases, the viscosity value belongs to the shear rate at the wall

$$\eta(\dot{\gamma}_w) = \frac{\tau_w}{\dot{\gamma}_w} \quad (10).$$

A typical data set is shown in **Table 1** together with the data from the analysis.

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Table 1: Evaluation of capillary flow experiments at a range of shear rates.

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c) *Approximate Determination of Shear Rate Values* Much complication can be avoided with the help of an approximate method that was proposed by Schümmer (1969) and Giesekus et al. (1977). They realized that shear thinning fluids, such as polymer melts, adopt a shear rate of

$$\text{circular geometry} \quad \dot{\gamma}_\kappa \approx -\kappa \frac{4Q}{\pi R^3} \quad \text{at } r = \kappa R \quad (11),$$

$$\text{slit geometry} \quad \dot{\gamma}_\kappa \approx -\kappa \frac{6Q}{WH^2} \quad \text{at } y = \kappa H/2 \quad (12),$$

with  $\kappa = 0.75$  (about). This is called the “representative shear rate” and belongs to some intermediate position  $r$  or  $y$  as defined in eqs. 11 and 12. The shear stress at these positions is known from the pressure gradient measurements

$$\text{circular geometry} \quad \tau_\kappa = \frac{\kappa R}{2} p' \quad (13),$$

$$\text{slit geometry} \quad \tau_\kappa = \frac{\kappa H}{2} p' \quad (14).$$

The corresponding viscosity belongs to this new shear rate value at  $\kappa R$  or  $\kappa H/2$

$$\eta(\dot{\gamma}_\kappa) = \frac{\tau_\kappa}{\dot{\gamma}_\kappa} = \frac{\pi R^4}{8Q} p' \quad \left( \text{or } \frac{WH^3}{12Q} p' \text{ for slit} \right) \quad (15).$$

The new viscosity values are shown in **table 2**.

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Table 2: Evaluation of capillary viscosity data according to Schümmmer.

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Figure 3: Comparison of viscosity values (left) and flow curves (right) from gradient evaluation procedure (Rabinowich) and representative shear rate procedure (Schümmmer-Giesekus). The Rabinowitsch methods delivers data that reach to higher shear rates. This is recognizable in the figures.

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## Temperature Effects

The viscosity is preferably measured under isothermal conditions. The temperature is uniform throughout the sample and experiments are repeated at temperatures  $T_1, T_2, T_3$ , etc. However, isothermal experiments are not possible at high shear rates where flow energy is converted into large amounts of internal energy of the sample. This effect is called viscous dissipation (Winter, 1977). Dissipation effects are minimized in capillary rheometry by using very thin capillaries (Robens and Winter,

Many materials follow the so-called time-temperature superposition principle (Williams et al., 1955; Ferry, 1980). For these, the temperature dependent viscosity

$$\eta(\dot{\gamma}, \tau) = \eta(\dot{\gamma}, T_o) \frac{a_T(T; T_o)}{b_T(T; T_o)} \quad (16)$$

can be expressed with a reference viscosity at  $T_o$  that gets shifted to the new temperature  $T$  by applying both, the horizontal shift factor  $a_T(T; T_o)$  and the vertical shift factor  $b_T(T; T_o)$ .

Temperature shift factors are defined as

$$\alpha_T(T;T_o) = \exp\left\{\frac{E}{R}\left(\frac{1}{T-T_v} - \frac{1}{T_o-T_v}\right)\right\} \quad (17),$$

$$b_T(T;T_o) = \frac{T_o \rho(T_o)}{T \rho(T)} \quad (\text{for polymers}) \quad (18),$$

with parameters  $E/R$ ,  $T_v$ ,  $\rho(T)$ ,  $\rho(T_o)$  and a reference temperature,  $T_o$ . The vertical shift factor has values close unity for many polymer melts (an is often falsely omitted from the data analysis), but can adopt very small or very large values for other materials. Here we have to emphasize that by far not all materials obey the time-temperature superposition principle (Colby, 1989); it needs to be confirmed for each class of materials.

### Approximation of Viscosity Curves for Shear Thinning Liquids

Many formulas have been suggested for approximating the shear thinning behavior of polymer melts. Very convenient for modeling calculations is the powerlaw relation

$$\eta(\dot{\gamma}, T) = \frac{m[T_o]}{b(T;T_o)} (\dot{\gamma} a_T(T;T_o))^{n-1} \quad (19).$$

More realistic is the Carreau Yasuda formula (Yasuda, 1981)

$$\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{(1 + (\lambda \dot{\gamma})^\alpha)^{\frac{1-n}{\alpha}}} \quad (20),$$

which can be reformulated as

$$\eta(\dot{\gamma}, T) = \frac{a_T(T;T_o)}{b_T(T;T_o)} \left\{ \eta_\infty(T_o) + \frac{\eta_0(T_o) - \eta_\infty(T_o)}{(1 + [\dot{\gamma} \lambda(T_o) a_T(T;T_o)]^\alpha)^{\frac{1-n}{\alpha}}} \right\} \quad (21)$$

to also include *non-isothermal* flows. Parameters are the zero shear viscosity  $\eta_0$ , the high shear rate viscosity  $\eta_\infty$ , the characteristic relaxation time  $\lambda$ , the powerlaw exponent  $n$ , and the broadening exponent  $\alpha$ . Temperature shift factors account for the temperature dependence.

A *shear thickening* viscosity, as found with concentrated suspensions (Egres and Wagner, 2005), cannot be described by such approximation. It is difficult to express such shear-induced viscosity upturn (called “jamming”) in a simple approximation formula.

### Additional Uses of Capillary Rheometers

a) *Mini Extruder* The capillary rheometer often serves as mini extruder when it is combined with a stretching unit for the extrudate. Wagner (2001) shows typical data of this type and proposes a powerful analysis of this experiment.

b) *Extensional Rheometer* (Cogswell method) Cogswell (1972) noticed that extensional material properties dominate the converging flow from the wide reservoir (position 4 in Fig. 1) into the narrow capillary. He separated the entrance pressure drop (from the Bagley correction, see above) into shear and extension dominated components.

The extensional component was then rearranged into an empirical expression for the steady *extensional* viscosity. Binding (1988) proposed an alternative empirical relation that also may be used. The Cogswell-Binding methods are very attractive since it is still impossible to reach very large strains and deformation rates with the existing extensional rheometers (Morrison 2001)

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Table 1

Q	p'	Q	p'	gradient	shear stress	shear rate	viscosity
cm <sup>3</sup> /s	bar/cm	[m <sup>3</sup> /s]	[Pa/m]	term [-]	[Pa]	[1/s]	[Pa s]
0.0011	1.1	3.66667E-10	11000000	1.01	2860	3.3	859
0.0018	1.7	6E-10	17000000	1.02	4420	5.5	809
0.0024	2.3	8E-10	23000000	1.05	5980	7.3	815
0.0037	3.4	1.23333E-09	34000000	1.12	8840	11.5	768
0.0054	4.9	1.8E-09	49000000	1.2	12740	17.1	744
0.0073	6.3	2.43333E-09	63000000	1.26	16380	23.5	698
0.0111	8.8	3.7E-09	88000000	1.3	22880	36.0	635
0.0182	12.2	6.06667E-09	1.22E+08	1.56	31720	62.6	506
0.0255	14.8	8.5E-09	1.48E+08	1.73	38480	91.0	423
0.0365	18	1.21667E-08	1.8E+08	1.88	46800	134.4	348
0.0548	21.5	1.82667E-08	2.15E+08	2.31	55900	219.6	255
0.0729	24.3	2.43E-08	2.43E+08	2.83	63180	320.7	197
0.1096	28	3.65333E-08	2.8E+08	3.09	72800	503.7	145
0.1425	30.3	4.75E-08	3.03E+08	3.4	78780	688.2	114
0.1827	32.6	6.09E-08	3.26E+08	3.7	84760	923.7	92
0.2137	34.1	7.12333E-08	3.41E+08	3.8	88660	1096.6	81
0.2549	35.8	8.49667E-08	3.58E+08	4.12	93080	1369.6	68
0.3614	39	1.20467E-07	3.9E+08	4.31	101400	1993.6	51

Table 2

Q	p'	shear stress	shear rate	viscosity
[m <sup>3</sup> /s]	[Pa/m]	[Pa]	[1/s]	[Pa s]
3.66667E-10	11000000	2145	2.5	861
6E-10	17000000	3315	4.1	814
8E-10	23000000	4485	5.4	825
1.23333E-09	34000000	6630	8.4	792
1.8E-09	49000000	9555	12.2	782
2.43333E-09	63000000	12285	16.5	743
3.7E-09	88000000	17160	25.1	683
6.06667E-09	1.22E+08	23790	41.2	577
8.5E-09	1.48E+08	28860	57.7	500
1.21667E-08	1.8E+08	35100	82.6	425
1.82667E-08	2.15E+08	41925	124.1	338
2.43E-08	2.43E+08	47385	165.0	287
3.65333E-08	2.8E+08	54600	248.1	220
4.75E-08	3.03E+08	59085	322.6	183
6.09E-08	3.26E+08	63570	413.6	154
7.12333E-08	3.41E+08	66495	483.8	137
8.49667E-08	3.58E+08	69810	577.1	121
1.20467E-07	3.9E+08	76050	818.2	93



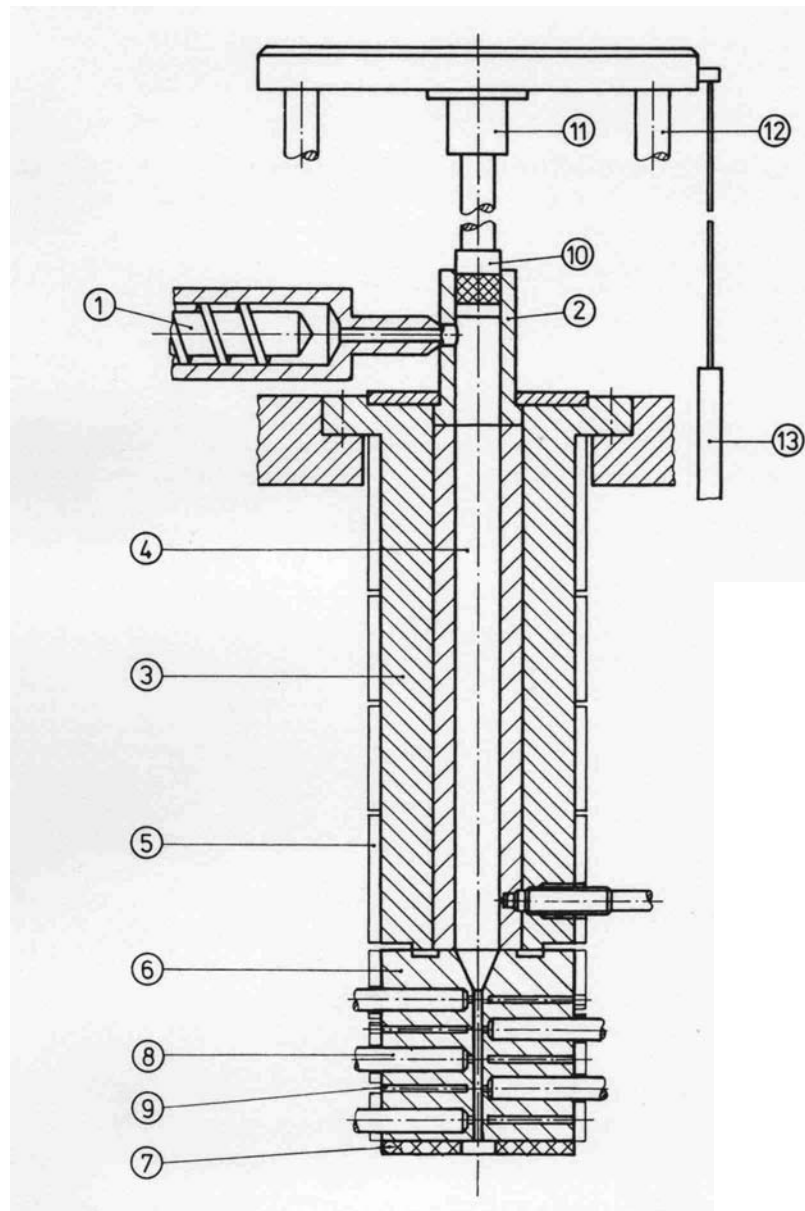


Figure 1

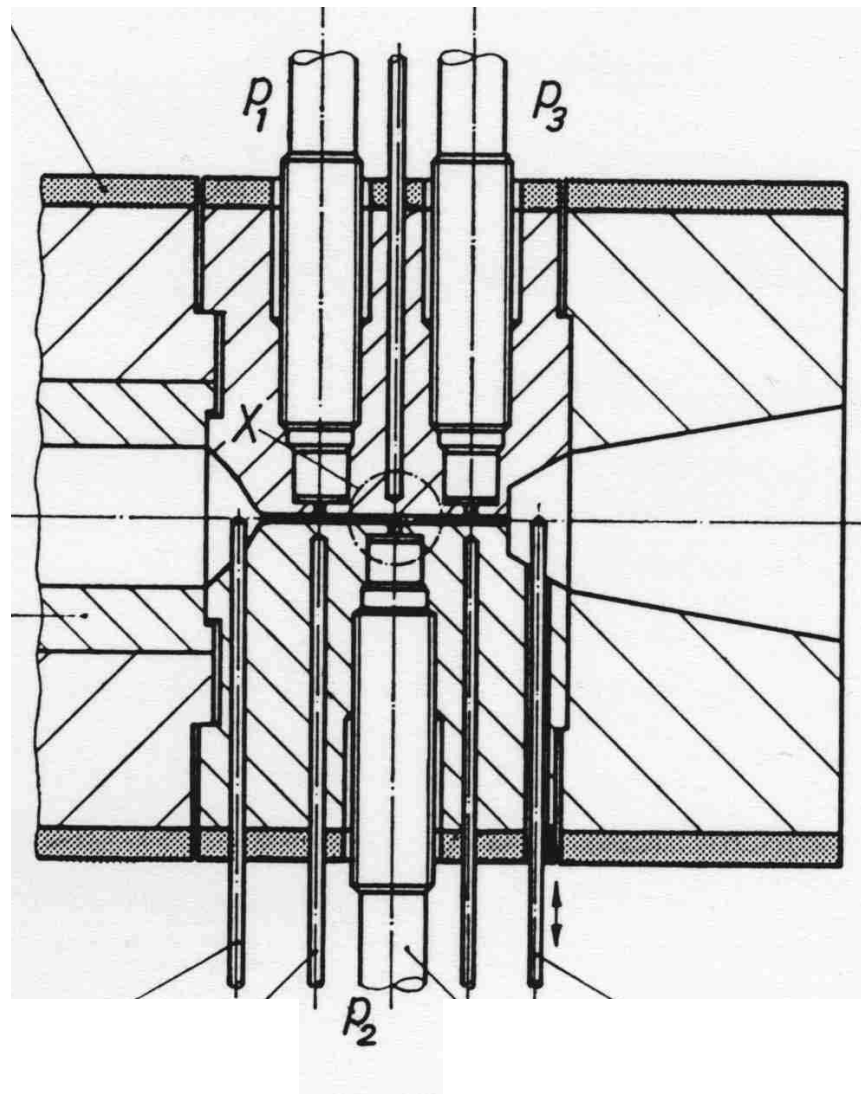


Figure 2

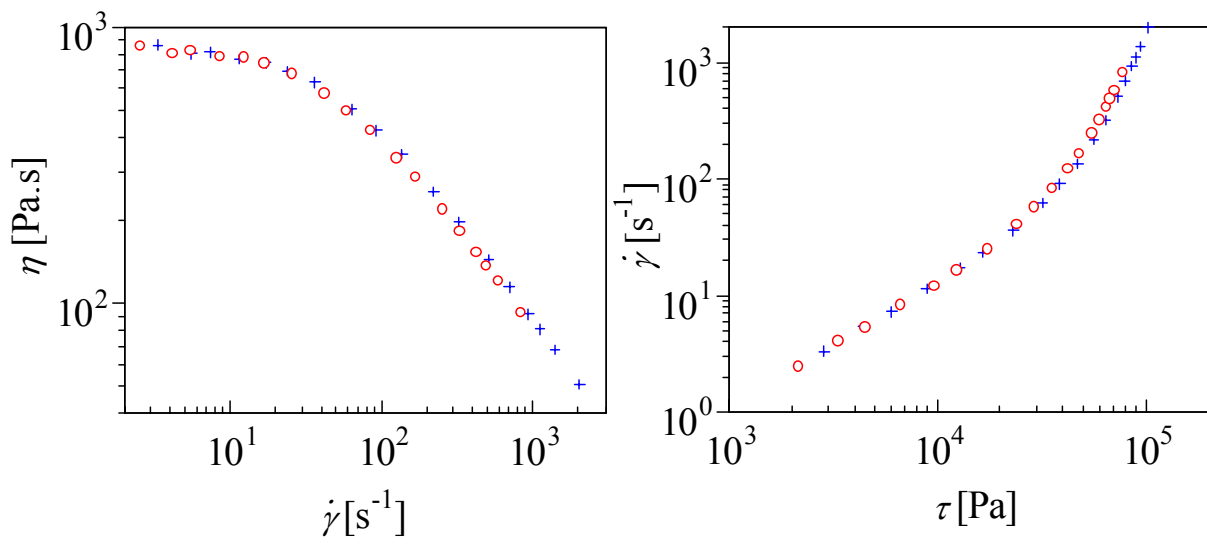


Figure 3