The Rheology and Spin Coating of Polyimide Solutions

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The rheological properties of five types of concentrated polyamic acid and polyimide solutions are characterized by non-Newtonian shear viscosity $\eta(\dot{\gamma})$ and primary normal stress coefficient $\Psi_1(\dot{\gamma})$ measurements over a wide range of shear rates. Onset of non-Newtonian flow of the polyamic acid solutions was observed in the shear rate range 30 to $400s^{-1}$ and of the fully imidized polyimide solution at below $3 \times 10^{-2}s^{-1}$. Significant viscoelastic properties exemplified by normal stresses were observed in all the solutions. The solution rheology results are discussed in the context of spin coating for the deposition of thin films. The relative magnitude of effects of non-Newtonian flow on the dynamics of spin coating is assessed with a Deborah number characteristic of the flow.

INTRODUCTION

Polyimide coatings are currently of considerable interest for application in various microelectronic devices (1-3). This interest stems from the excellent thermal stability, dielectric properties, chemical resistance, and mechanical properties of the fully imidized solid polyimide films and the ease of processing the polymeric liquid precursors by spin coating to obtain films with relatively planar surfaces. Nearly all recent and current work on polyimides have been devoted to the properties of their thin solid films (1-4). By contrast very little has been done on the solution properties (5-6) and the relation of solution properties to the spin-coating process for forming their films. Most polyimide coatings are commercially supplied as concentrated polyamic acid (PAA) solutions in organic solvents, usually with 14 to 40 percent solids. Other polyimide coatings are concentrated solutions of the fully imidized polyimide (PI) resin.

In early theoretical analysis of the hydrodynamics of the spin-coating process for the deposition of thin films, Emslie, *et al.* (7), showed that, for Newtonian fluids, uniform fluid distribution (planar surfaces) resulted from any initial fluid-surface contour. However, subsequent theoretical analysis of the case of non-Newtonian liquids by Acrivos, *et al.* (8), predicted *nonuniform coatings*. In a recent extensive experimental study of the final film thickness and film uniformity of spin-coated polyimides and photoresists, Givens and Daughton (9) have shown the strong dependence on fluid viscosity, spin speed, and spinning time. This is to be expected and, indeed, in accord with the theoretical analyses previously mentioned. Thus the fundamental rheological properties of polymeric liquids are important for understanding and controlling the process of spin coating for forming

their films. No such data are available for polyimide coatings.

In this paper, results of an investigation of the rheology of five types of polyimide coatings by non-Newtonian shear viscosity $\eta(\dot{\gamma})$ measurements are presented. The implication of the rheology of polyimide coatings for the spin-coating technique for forming their films on wafers is discussed. The relative magnitude of non-Newtonian effects on the dynamics of spin coating is analyzed using a Deborah number characteristic of the flow.

EXPERIMENTAL

Materials

The polyimide coatings, PI2555 and PI2566, hereafter referred to as (I) and (II) respectively, were obtained from DuPont Co. as polyamic acid (PAA) solutions in N-methyl-2-pyrrolidone (NMP)/aromatic hydrocarbon (AH) mixed solvent system. Others, PIQ-13 (III) and PIX-3400 (IV) were obtained from Hitachi Chemical Co., as PAA solutions in NMP. The polyimide solution 2080-D (V) was obtained from UpJohn Co. as a fully imidized resin soluble in N, N-dimethylformamide (DMF). All materials were used as supplied. *Table 1* summarizes the concentrations and properties of the solutions.

Table 1. Concentration and Density of Polyamic Acid and Polyimide Solutions.

Polyimide Solution	Resin Type	Solvent	Concentration (%wt)	Density (Kg/m³) (25°C)
I	PAA	NMP/AH	19	1.06 × 10³
II	PAA	NMP	18	1.055 × 10³
III	PAA	NMP	14.5	1.05 × 10³
IV	PAA	NMP	18.5	1.05 × 10³
V	PI	DMF	22	1.02 × 10³

Rheological Measurements

Measurements of the steady-state shear stress $\sigma_{12}(\dot{\gamma})$ and primary normal stress difference $N_1(\dot{\gamma})$ were made on a fully automated Rheometrics System Four (Rheometrics, Inc., Springfield, N.J.) using the cone and plate geometry. The relevant viscometric equations at steady shear flow are:

$$\dot{\gamma} = \frac{\omega}{\theta} \tag{1}$$

$$\sigma_{12} = \frac{3M}{2\pi R^3} \tag{2}$$

$$N_1 = \sigma_{11} - \sigma_{22} = \frac{2F_z}{\pi R^2} \tag{3}$$

$$\eta = \frac{\sigma_{12}}{\dot{\gamma}} \tag{4}$$

$$\Psi_1 = \frac{N_1}{\dot{\gamma}^2} \tag{5}$$

where $\dot{\gamma}$ is shear rate (s^{-1}), ω is rotational speed (rad/s), θ is cone angle (rad), M is torque, R is radius of cone and plate, F_z is thrust, Ψ_1 is primary normal stress coefficient, and η is shear viscosity. The cone and plate radius was 2.5 cm and θ was 0.04 rad. All measurements reported here were at room temperature.

RESULTS

Non-Newtonian Viscosity

In *Figs.* 1-3 are shown logarithmic plots of the non-Newtonian viscosity as a function of shear rate for five polyimide solutions (I-V) at room temperature. All the PAA solutions exhibited a prominent constant viscosity region at low shear rates followed by shear thinning at high shear rates. The fully imidized polyimide solution (V) showed no zero-shear viscosity limit at down to $3.0 \times 10^{-2} s^{-1}$.

The zero-shear viscosity, η_o, and shear rate at onset of non-Newtonian flow, $\dot{\gamma}_o$, are collected together in *Table 2*. It is seen that η_o has values in the range 1.4 to 15.0 Pa.s at room temperature. The viscosity of a polymer solution is generally determined by the concentration, polymer molecular properties such as structure, molecular weight, and molecular-weight distribution, and solvent. The solvent of the PAA solutions investi-
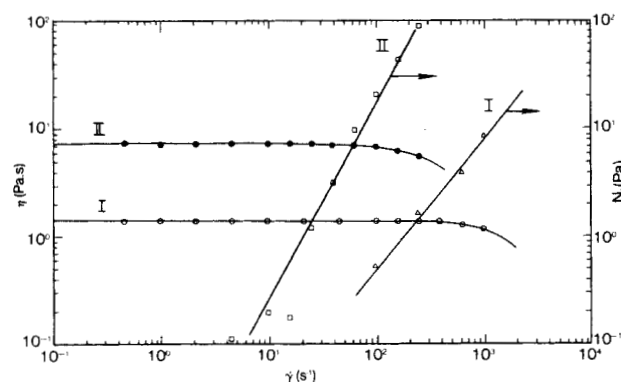

Fig. 1. Non-Newtonian viscosity $\eta(\dot{\gamma})$ and primary normal stress difference $N_1(\dot{\gamma})$ of PAA solutions I and II at 25°C and 22°C respectively.
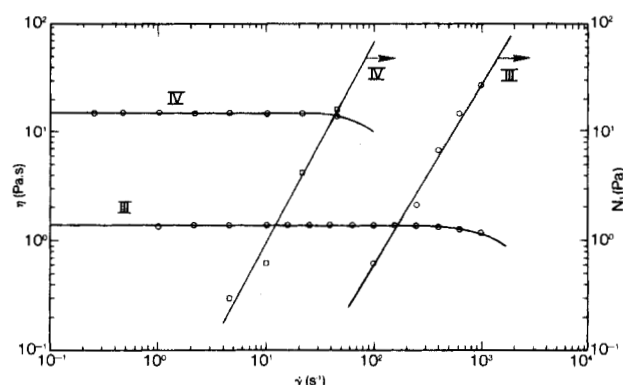

Fig. 2. Non-Newtonian viscosity $\eta(\dot{\gamma})$ and primary normal stress difference $N_1(\dot{\gamma})$ of PAA solutions III and IV at 23°C.
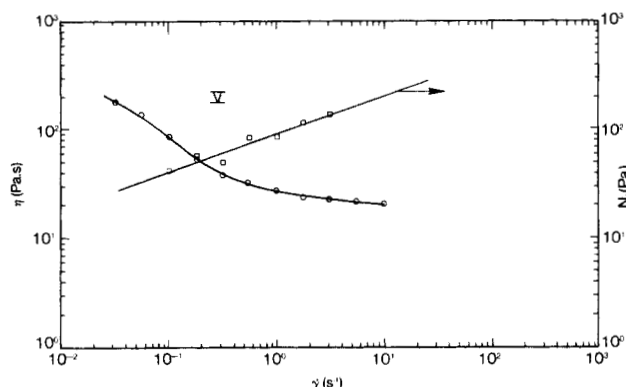

Fig. 3. Non-Newtonian viscosity $\eta(\dot{\gamma})$ and primary normal stress difference $N_1(\dot{\gamma})$ of PI solution V at 23°C.

gated here is essentially the same, NMP which appears to be a good solvent. The polymer concentration is 14.5 to 19 percent in the four PAA solutions. At this high concentration, the solutions can be considered to be in the network regime where the density of chain entanglement is expected to be very high, minimizing the difference in viscosity due to concentration difference. Indeed solutions I and III which have 19 percent and 14.5 percent polymer in solution have identical zero shear viscosity. Thus the observed difference in zero shear viscosity of PAA solutions is attributable to the considerable difference in molecular structure, molecular weight, and molecular-weight distribution of the polymers (1,5-6).

Also shown in *Table 2* is the reduced solution viscosity η_r, defined as the ratio of the zero-shear viscosity to the solvent viscosity η_s. The solution viscosity exceeds

Table 2. Zero-shear-rate viscosity (η_0) and shear rate at onset of non-Newtonian behavior ($\dot{\gamma}_0$) for 5 polyimide solutions at room temperature.

Polyimide Solution	Temperature (°C)	η_0 (Pa.s)	$\dot{\gamma}_0$ (s⁻¹)	$\eta_r = \dfrac{\eta_0{}^*}{\eta_s}$
I	25	1.4	440	840
II	22	7.4	60	4,400
III	23	1.4	300	840
IV	23	15.0	30	9,000
V	23	≥183.3	<3×10^{-2}	≥228,500

*Newtonian solvent viscosity and density at 25°C:
NMP: $\eta_s = 1.666 \times 10^{-3}$ Pa.s, $\rho = 1.0279$ g/cm³; DMF: $\eta_s = 8.02 \times 10^{-4}$ Pa.s, $\rho = 0.9445$ g/cm³. (Ref. 10)

that of the Newtonian solvent by 840 to 9000 in the low shear limit. Note that $\eta_o - \eta_s \simeq \eta_o$. The explanation for the difference in the reduced viscosity among the PAA solution is as given for η_o.

The shear rate at the onset of non-Newtonian flow $\dot{\gamma}_o$ has values in the range 30 to 400 s^{-1} as shown in *Table 2*. At shear rates higher than $\dot{\gamma}_o$ the solutions become shear thinning, with the viscosity decreasing relative to η_o as is common in polymer solutions and melts (11). It is to be noted that the onset of non-Newtonian flow is a strong function of the zero-shear viscosity, $\dot{\gamma}_o$ decreasing with increasing η_o.

A rheological model which appears to best describe the observed non-Newtonian viscosity of PAA solutions is a three-parameter equation of the form:

$$\frac{\eta}{\eta_o} = [1 + (\lambda\dot{\gamma})^2]^{\frac{n-1}{2}} \tag{6}$$

where λ is a characteristic time constant, and n is a dimensionless power law index. This is the so-called Carreau model (11); it exhibits shear thinning at high shear rates and constant viscosity at low shear rates. The power law index n could not be determined for the PAA solutions because of experimental limitation of the cone and plate geometry at high shear rates. The sample between the cone and plate begins to squeeze out at the high rates. The observed values of n for most polymer solutions and melts fall in the range 0.15 to 0.60 (11).

Primary Normal Stress Difference

In *Figs. 1-3* are shown logarithmic plots of the primary normal stress difference $N_1(\dot{\gamma})$ as a function of shear rate for both PAA and PI solutions at room temperature. It is to be noted that N_1 achieves significant magnitudes at higher shear rates the lower the zero-shear viscosity. Thus, for instance, at $100s^{-1}$ the value of N_1 is 5 and 200 Pa for solutions with zero-shear viscosity of 1.4 Pa.s and 7.4 Pa.s, respectively. It must be mentioned that for Newtonian fluids in steady shear flow normal stresses are zero and hence both the primary and secondary normal stress coefficients should be zero. The non-zero values of N_1 for the PAA and PI solutions suggest that they are viscoelastic fluids.

Figure 4 shows primary normal stress coefficient data for PAA solutions at room temperature. Note that in over 5 decades of shear rate $(10^{-2} - 10^3 \, s^{-1})$ the primary normal stress coefficient changes by 6 to 8 orders of magnitude. The shear thinning in Ψ_1 is considerably more pronounced than that observed in non-Newtonian viscosity. All the data of PAA solutions exhibited a prominent power law region. The anticipated low shear limit of Ψ_1 analogous to the zero-shear viscosity was not reached. In solutions I, II, and IV, some leveling off in Ψ_1 was observed at the high shear rates. These normal stress results are similar to those commonly observed in polymer solutions (11-12).

DISCUSSION

The spin-coating process for the deposition of thin polyimide films has also been widely used in other areas including photoresists (9,13,14) and electron re-
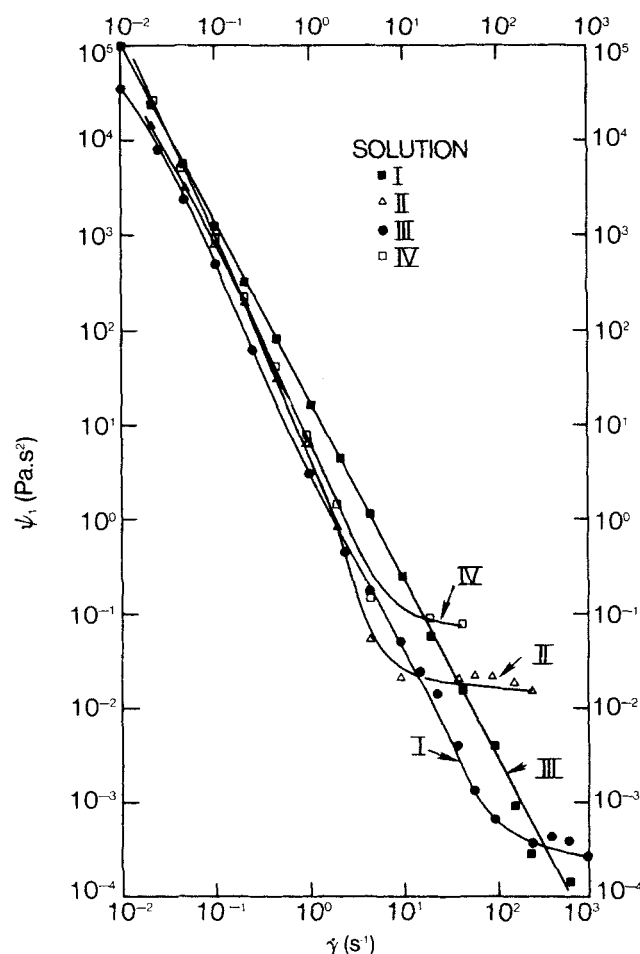

Fig. 4. The primary normal stress coefficient Ψ_1 $(\dot{\gamma})$ of PAA solutions at room temperature.

sists (15). The major concern with this technique is the ability to deposit films with desirable characteristics, especially film thickness uniformity. Several experimental studies investigating this problem have been reported (9,13-15). These studies have generally tried to correlate the *final film thickness* with such parameters as spinning speed, polymer concentration in solution, solvent evaporation rate, fluid viscosity, spinning time, volume of fluid dispensed, and acceleration of spinning disk. All the experimental facts seem to point to one aspect or another of the effect of fluid rheological properties on the hydrodynamics of spin coating. For instance, even if significant evaporation of solvent occurs during spin coating, the effects show by way of changing rheological properties.

The flow of liquids on rotating flat disks for forming their thin films has been modeled with simplifying assumptions as to the nature of their rheological properties (7,8,14,16). Newtonian and power law flows have been analyzed with different conclusions regarding film thickness and film-thickness uniformity (7,8). A detailed analysis of the flow of polymeric liquids, considered as non-Newtonian and viscoelastic fluids, on the spinning disk is being made to be presented elsewhere (17). Here effects of fluid rheological properties on the dynamics of spin coating are discussed qualitatively in the light of polyimide solution rheology data.

The basic equation of motion, with appropriate assumptions of steady radial flow, cylindrical symmetry about the axis of rotation, isothermal flow, etc., (7,8,17) is given by

$$\frac{\partial \sigma_{rz}}{\partial z} = \rho \omega^2 r \qquad (7)$$

where ω is the angular speed of the disk, ρ is density of fluid, and (r,θ,z) is the cylindrical polar coordinate. The constitutive equation is given by

$$\sigma_{rz} = \eta(\dot\gamma) \frac{\partial V_r}{\partial z} \qquad (8)$$

where $\eta(\dot\gamma)$ is as in *Eq. 6* and $\dot\gamma = \partial Vr/\partial z$. The boundary conditions $V_r = 0$ at $z = 0$ (no slip at the surface of the disk) and $\partial V_r/\partial z = 0$ at $z = h$ (zero shear at the free liquid surface), where h is the thickness of the liquid film, combined with *Eqs. 7 and 8* yield the velocity profile for a power-law fluid (Carreau model at high shear rates)

$$V_r(z) = \left(\frac{n}{n+1}\right)\left(\frac{\rho\omega^2 r}{K}\right)^{1/n}\left[h^{(n+1)/n} - (h-z)^{(n+1)/n} \right] \qquad (9)$$

where K is the ratio of η_0 to $(\lambda)^{1-n}$. In order to estimate the relative importance of effects of non-Newtonian flow and viscoelastic behavior, a dimensionless Deborah number (De) characterizing the radial flow of polymeric liquids on a flat spinning disk may be defined as the ratio of a characteristic time of the fluid λ to a characteristic time scale of flow T(11,17-19):

$$De = \frac{\lambda}{T} \qquad (10)$$

The parameter λ for the Carreau model is taken to be $1/\dot\gamma_0$ where $\dot\gamma_0$ is the shear rate at onset of non-Newtonian flow. The parameter T is taken to be $1/\dot\gamma_{max}$ where $\dot\gamma_{max}$ is the maximum shear rate of the flow calculated as,

$$\dot\gamma_{max} = \left(\frac{\partial V_r}{\partial z}\right)_{z=0} = \left(\frac{\rho\omega^2 rh}{K}\right)^{1/n} \qquad (11)$$

Thus we obtain,

$$De = \left(\frac{\omega^2 rh}{\nu_0 \dot\gamma_0}\right)^{1/n} \qquad (12)$$

where $\nu_0 = \eta_0/\rho$. The Deborah number defined in *Eq. 12* provides a measure of the relative magnitude of non-Newtonian flow and associated phenomena on a spinning disk in terms of the pertinent fluid rheological properties and parameters of the flow. For a Newtonian fluid, the power law index is 1, $\dot\gamma_0 \rightarrow \infty$ and hence De = 0, indicative of a purely viscous flow (18,19). In this case thin uniform films are always obtained by spin coating (7,17). In polymeric liquids which are usually non-Newtonian, $\dot\gamma_0$ is finite, $0 < n < 1$, and consequently De is non-zero and its magnitude is determined by non-Newtonian effects. The consequence of non-Newtonian flow or elastic effects on spin coating would include significant changes of the velocity field from the Newtonian and hence

changes in the film-thickness uniformity (17). Also, normal stresses would tend to increase forces lifting the fluid from the surface of the spinning disk. In general, as defined in *Eq. 12*, non-Newtonian effects become significant at De of order unity. However, such a Deborah number does not include elastic effects. In order to include effects of elasticity of flow on the spinning disk a time constant $\lambda = \Psi_1/2\eta_0$ may be combined with *Eqs. 10* and *11* to give

$$De^* = \left[\frac{\rho\omega^2 rh \Psi_1}{2\eta_0^2}\right]^{1/n} \qquad (13)$$

The Deborah number (De*) defined in *Eq. 13* measures the relative magnitude of viscous and elastic-effects. Elasticity of flow becomes comparable to viscous effects whenever De* is of order unity.

It is instructive to consider the specific case of polyimide coatings in microelectronic processing where h is typically of the order 1 to $100\mu m$, r can be taken as the radius of the wafer being coated (and in the calculations let $r = 3.81$ cm), and angular speed ω is typically in the range 100 to 1500 rad/s. *Figure 5* shows the logarithmic plot of De (ω) for the polyimide solutions I, IV, and V, assuming $n = 1$. Other cases of n can be considered, but the analysis and conclusions are similar to the case $n = 1$; the sensitivity of De to n is obvious from *Eq. 12*. The slope of the parallel lines is 2, as is obvious from *Eq. 12*. The factor $\nu_0\dot\gamma_0$ is 0.528 and 0.429 m^2/s^2, respectively, for solutions I and IV and about 5.4×10^{-3} for solution V. Thus, at the same film thickness, e.g. $100\mu m$, higher De values are obtained at all angular speeds the lower the factor $\nu_0\dot\gamma_0$. A similar statement obtains for fixed $\nu_0\dot\gamma_0$ and variable h or variable r. At the range of angular speeds considered, De is in the range 0.10 to 20.0 for 1 to $100\mu m$ films for solutions I, II, III, and IV. De approaches 10^2 to 10^3 at angular speeds of about $10^3\ s^{-1}$ for 10 to $100\mu m$ thicknesses for solution V. It will be virtually impossible to obtain uniform films at values of De much higher than 1, such as for solution V at speeds as low as 100 rad/s.

These estimates of departure from Newtonian flow are qualitatively in accord with experimental observation on film deposition by spin coating; the larger the radius of disk and film thickness and the higher the
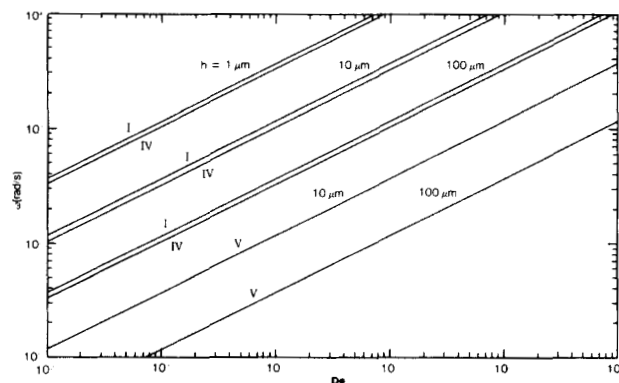

Fig. 5. The Deborah number (De) as a function of angular speed ω for the flow of PAA and PI solutions on a rotating flat disk of radius 3.81 cm. De dependence on film thickness and rheological properties is also shown.

spinning speed, the poorer the quality (thickness and morphology) of films. Though the question as to what De does the film thickness non-uniformity become significant in spin coating polymeric fluids has not been precisely answered, the order of magnitude analysis shows the influence of rheological properties on the dynamics of spin coating. Furthermore, the Deborah number seems to be an ideal group of parameters for correlating studies of film thickness and film thickness uniformity of spin coated polymer films.

CONCLUSION

New data on the rheological properties of polyamic acid and fully imidized polyimide solutions are reported. Onset of non-Newtonian flow of the PAA solutions was observed in the shear rate range 30 to $400s^{-1}$ and of the fully imidized PI solution at below 3×10^{-2} s^{-1}. The Carreau model, which exhibits constant viscosity at low shear rates and shear thinning at high shear rates, appears to best describe the non-Newtonian shear viscosity $\eta(\dot{\gamma})$ of PAA solutions. A Deborah number characteristic of the flow on a spinning disk is used to estimate the relative magnitude of non-Newtonian flow effects. At the highest angular speeds ($\sim 10^3$ rad/s) typically employed in polyimide coating for thin film (1 to $100\mu m$) deposition, De is of the order 10^{-1} to 2×10^1 for PAA solutions and much higher for PI solution. The Deborah number could also be a useful group of parameters for correlating experimental spin coating data.

ACKNOWLEDGEMENT

NOMENCLATURE

h	= film thickness (m)
n	= power law index
r	= radius of spinning disk (m)
V_r	= radial velocity component, $V_r(z)$
D_e	= Deborah number, non-Newtonian effects, eqn. (12)
D_e^*	= Deborah number, elastic effects, eqn. (13)
F_z	= Normal Force
K	= power law parameter ($= \eta_0 \lambda^{n-1}$)
M	= torque
N_1	= primary normal stress difference
R	= cone and plate radius (m)
T	= time scale of flow (s)

Greek Letters

ω	= angular speed (rad/s)
η	= non-Newtonian shear viscosity (Pa.s)
η_0	= zero-shear viscosity
η_s	= solvent viscosity
η_r	= reduced viscosity ($= \eta_0/\eta_s$)
$\dot{\gamma}$	= shear rate (s^{-1})
$\dot{\gamma}_0$	= onset of non-Newtonian flow
$\dot{\gamma}_{max}$	= maximum shear rate of fluid on spinning disk
ν_0	= kinematic viscosity (m^2/s) ($= \eta_0/\rho$)
ρ	= density (kg/m^3)
λ	= characteristic time of fluid (s)
θ	= cone angle (rad)
σ_{ij}	= shear stresses ($i, j = 1, 2,$ or r, z)
σ_{jj}	= normal stresses ($j = 1, 2$ or r, z)
Ψ_1	= primary normal stress coefficient (Pa.s^2)

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