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Limitation of Stress-Optical Rule for Polymeric Liquids

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The stress-optical rule states that the deviatoric components of the refractive index tensor, $\Delta\mathbf{n}$, and those of the stress tensor, $\boldsymbol{\sigma}$, are proportional to each other in flowing liquids.[1,2] The rule is believed to be valid for polymeric liquids in the steady shear flow and slowly varying shear flows. In this note, we deduce from existing experimental data for real polymers that the rule is valid only approximately and may not be valid even approximately for polymers with low stress-optical coefficients.

The correspondence between the stress and the birefringence was verified first in steady shear flow. In the steady shear flow with the rate of shear $\dot{\gamma}$, the deviatoric components of stress can be represented by the shear stress, σ_{12}, the first normal stress difference, $\sigma_{11} - \sigma_{22}$, and the second normal stress difference, $\sigma_{22} - \sigma_{33}$. The deviatoric components of the refractive index tensor can be represented by three quantities, n_{12}, $n_{11} - n_{22}$, and $n_{22} - n_{33}$, corresponding to the stress components, respectively. Extensive studies[1,2] following pioneering works[3,4] have revealed the following relations:

$$n_{12} = C_F\sigma_{12} \tag{1a}$$

$$n_{11} - n_{22} = C_F(\sigma_{11} - \sigma_{22}) \tag{1b}$$

where C_F, the stress-optical coefficient, is independent of the rate of shear. These relations imply that the angle between a principal axis of stress and the flow direction, χ_s, is equal to that of the refractive index, χ_0, called the extinction angle. The relation is often written as

$$2\cot(2\chi_0) = (\sigma_{11} - \sigma_{22})/\sigma_{12} \tag{2}$$

Afterward the relations (1) and (2) were exhibited to be good for time-dependent flows related to the steady shear flow such as the transient states at the start up and on the cessation of steady shear flow.[2,5,6] These observations are consistent with the modern theory of polymer dynamics based on flexible polymer models.[7] The relation between $n_{22} - n_{33}$ and $\sigma_{22} - \sigma_{33}$ has not been examined so much.[1,2]

It has been known that the simple proportionality does not hold valid for rapidly varying flows like oscillatory shear of high frequency.[8] It was revealed that the birefringence, n_{12}, corresponding to the stress, σ_{12}, in linear viscoelasticity measurements over wide frequency or time ranges can be described well by a modified stress-optical rule for many polymers.[9] In the regime of linear viscoelasticity,[10] the shear stress can be derived from the relaxation modulus, $G(t)$

$$\sigma_{12}(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t')\,\mathrm{d}t' \tag{3}$$

Likewise the corresponding component of the refractive index can be derived from a function $M(t)$, representing the refractive index corresponding to a unit step strain

$$n_{12}(t) = \int_{-\infty}^{t} M(t - t')\dot{\gamma}(t')\,\mathrm{d}t' \tag{4}$$

The modified stress-optical rule, a modification of the stress-optical rule to include the deviation at short times, is written as[9]

$$G(t) = G_R(t) + G_G(t) \tag{5a}$$

$$M(t) = C_RG_R(t) + C_GG_G(t) \tag{5b}$$

Here the function $G_R(t)$ dominates the flow behavior of the polymeric liquids and agrees with $G(t)$ in the terminal flow zone and the rubbery plateau zone; the function $G_G(t)$ is associated with only short relaxation times corresponding to the glass-to-rubber transition zone and the glassy zone. C_R and C_G are material constants.

One may be tempted to assume that the stress and the refractive index at long times or in slowly varying flows like steady shear are determined by the quantities with the subscript R and so the stress-optical rule is valid. We show below that this is not the case.

In order to avoid lengthy equations, we employ a simple model in which the functions $G_R(t)$ and $G_G(t)$ include only one relaxation time, respectively.

$$G_R(t) = G_R{}^0\exp(-t/\tau_R), \qquad G_G(t) = G_G{}^0\exp(-t/\tau_G) \tag{6}$$

Here τ_R and τ_G ($<\tau_R$) are relaxation times and $G_R{}^0$ and $G_G{}^0$ are constants. Extension to more general cases is trivial.

For the stress relaxation after an instantaneous deformation, γ, one obtains

$$n_{12} = \gamma[C_RG_R(t) + C_GG_G(t)] \tag{7a}$$

$$\sigma_{12} = \gamma[G_R(t) + G_G(t)] \tag{7b}$$

In the ratio of n_{12} to σ_{12} the G component becomes negligible at long times. Thus the stress-optical ratio at the limit of long times in stress relaxation process is

$$C^r = C_R \qquad (t \gg \tau_G) \tag{8}$$

It is easily shown that eq 8 applies to any stress relaxation at a fixed shape of the material following an arbitrary flow history.

For the steady shear flow, or at the long time limit of creep measurement, one obtains from eqs 3 and 4

$$n_{12} = \dot{\gamma}[C_RG_R{}^0\tau_R + C_GG_G{}^0\tau_G] \tag{9a}$$

$$\sigma_{12} = \dot{\gamma}[G_R{}^0\tau_R + G_G{}^0\tau_G] \tag{9b}$$

and so the stress-optical ratio for the shear stress in steady shear is

$$C^s = (C_RG_R{}^0\tau_R + C_GG_G{}^0\tau_G)/(G_R{}^0\tau_R + G_G{}^0\tau_G) \tag{10}$$

Evidently C^s is not equal to C^r.

It is well established that the first normal stress difference in steady shear can be evaluated from $G(t)$ with the following relation in the second-order approximation, *i.e.*, up to the second power of the rate of shear.[11]

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$$\sigma_{11} - \sigma_{22} = 2\dot{\gamma}^2 \int_0^\infty G(t)t \, \mathrm{d}t \tag{11a}$$

In the same way, one obtains

$$n_{11} - n_{22} = 2\dot{\gamma}^2 \int_0^\infty M(t)t \, \mathrm{d}t \tag{11b}$$

The stress-optical ratio for the first normal stress difference in steady shear is

$$C^{\mathrm{N}} = \frac{n_{11} - n_{22}}{\sigma_{11} - \sigma_{22}} = \frac{C_{\mathrm{R}} G_{\mathrm{R}} {\tau_{\mathrm{R}}}^2 + C_{\mathrm{G}} G_{\mathrm{G}} {\tau_{\mathrm{G}}}^2}{G_{\mathrm{R}} {\tau_{\mathrm{R}}}^2 + G_{\mathrm{G}} {\tau_{\mathrm{G}}}^2} \tag{12}$$

This value is not equal to either C^{r} or C^{s}.

From these observations, one may conclude that the deviatoric components of the refractive index tensor are not proportional to those of the stress tensor in steady shear flow. Since C^{N} is not equal to C^{s}, the correspondence of the stress and the birefringence is steady shear flow is not as simple as in eq 1. The extinction angle does not coincide with the direction of the principal axis of the stress; eq 2 does not hold valid.

Direct observations for polymeric liquids in the flow zone have not detected the proposed discrepancies.[1,2] For most of the polymers investigated so far, the coefficient C_{R} is at least an order of magnitude larger than C_{G}.[9] In addition, the quantity $G_{\mathrm{R}}{}^0\tau_{\mathrm{R}}$ is usually much larger than $G_{\mathrm{G}}{}^0\tau_{\mathrm{G}}$. Thus the discrepancy from the stress-optical rule is too small to detect with the present technique. On the other hand, the coefficient C_{R} can be small for some polymers: *e.g.*, C_{R} changes sign at a certain temperature for poly(methyl methacrylate).[12] A test of the validity of the rule may be possible for this polymer provided that the temperature is precisely controlled to the point where $C_{\mathrm{R}} = 0$. The difference between $G_{\mathrm{R}}{}^0\tau_{\mathrm{R}}$ and $G_{\mathrm{G}}{}^0\tau_{\mathrm{G}}$ may not be extremely large for polymeric systems that do not exhibit the rubbery plateau zone due to chain entanglement. Thus the discrepancy may be detected for low molecular weight polymers even if the C_{R} is not precisely equal to zero.

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