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Correlation of Various Shift Factors

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Abstract

The correlation of various shift factors obtained from the flow characteristics are analyzed theoretically and investigated experimentally. The samples used were polymethyl methacrylate resin (to which the method of reduced variables is applicable) and polypropylene resin (to which the method of reduced variables is not applicable). The ratio of the temperature shift factor at constant shear rate to the temperature shift factor at constant shear stress, and the ratio of the pressure shift factor at constant shear rate to the pressure shift factor at constant shear stress, respectively, that is expressed in the form of differential coefficient corresponds to the generalized flow index. These relationships are valid in either case whether the method of reduced variables is applicable or not applicable. Also, these relationships are able to be applied for every kind of fluid.

1. Introduction

The methods of indicating flow characteristics are, for example, for a steady flow a shear stress-shear rate curve, a viscosity-shear rate curve and a viscosity-shear stress curve. These curves can be expressed also by taking respective temperature and hydrostatic pressure as parameters. In the shear stress-shear rate flow curves at constant hydrostatic pressure, taking a temperature as a parameter, the curve at higher temperature is located lower than the curve at lower temperature. It is known that, in the case where influence of hydrostatic pressure is taken into consideration at constant temperature, the curve at higher hydrostatic pressure tends to be located higher than the curve at lower hydrostatic pressure. If such changing states of the flow curves are proved, the flow characteristics in the neighbourhood of experimental value can be estimated by interpolation and extrapolation. Therefore, in die design engineering, it is very important that the flow characteristics is estimated.

It is known that the changing states of the flow curves influenced by the temperature and hydrostatic pressure are expressed conveniently by using a shift factor. For instance, a temperature shift factor can be obtained by measuring the viscosity of a non-Newtonian fluid in the steady state by varying the temperature at constant shear stress or shear rate, respectively. It is known¹⁾ that the values of viscosity are dependent on the measuring conditions. The values of viscosity under the hydrostatic pressure are also dependent on the measuring conditions such as constant shear stress or shear rate. When the data obtained under different measuring conditions are compared with each other, it is desirable to make the correlation of various shift factors clear. Hence, it is useful to obtain the equations for those relations.

In this study respective shift factors at constant shear stress and constant shear rate

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measured at a constant temperature and under constant hydrostatic pressure, are discussed.

2. Relationship between Flow Characteristics and Measuring Condition

In steady flow the viscosity η of non-Newtonian fluid can be thought²⁾ of as a function of the shear stress τ (or the shear rate $\dot{\gamma}$), the temperature T and the hydrostatic pressure P_h . That relation is expressed as follows, in the case where η is function of τ , T and P_h ,

$$\eta = \eta(\tau, T, P_h) \quad (1)$$

Assuming that η to be a function of $\dot{\gamma}$, T and P_h , one obtains,

$$\eta = \eta(\dot{\gamma}, T, P_h) \quad (2)$$

The total differentials of Eqs. (1) and (2) are respectively,

$$d\eta = \left(\frac{\partial \eta}{\partial \tau}\right)_{T, P_h} d\tau + \left(\frac{\partial \eta}{\partial T}\right)_{\tau, P_h} dT + \left(\frac{\partial \eta}{\partial P_h}\right)_{\tau, T} dP_h \quad (3)$$

$$d\eta = \left(\frac{\partial \eta}{\partial \dot{\gamma}}\right)_{T, P_h} d\dot{\gamma} + \left(\frac{\partial \eta}{\partial T}\right)_{\dot{\gamma}, P_h} dT + \left(\frac{\partial \eta}{\partial P_h}\right)_{\dot{\gamma}, T} dP_h \quad (4)$$

where subscript of the parenthesis means a case in which quantity indicated by the subscript is fixed. For a flow under constant hydrostatic pressure and constant the shear stress, from Eqs. (3) and (4),

$$\left(\frac{\partial \eta}{\partial T}\right)_{\tau, P_h} dT = \left(\frac{\partial \eta}{\partial \dot{\gamma}}\right)_{\tau, P_h} d\dot{\gamma} + \left(\frac{\partial \eta}{\partial T}\right)_{\dot{\gamma}, P_h} dT \quad (5)$$

Correlation of η , τ and $\dot{\gamma}$ is expressed by Eq. (6).

$$\eta = \frac{\tau(\dot{\gamma})}{\dot{\gamma}} \quad (6)$$

Differentiating Eq. (6), the following equations are obtained.

$$\frac{\partial \ln \eta}{\partial \ln \dot{\gamma}} = \frac{\partial \ln \tau}{\partial \ln \dot{\gamma}} - 1 \quad (7)$$

$$\frac{\partial \ln \eta}{\partial \ln \tau} = 1 - \frac{\partial \ln \dot{\gamma}}{\partial \ln \tau} \quad (8)$$

Hence, the following relation is obtained from Eqs. (5), (7) and (8).

$$\frac{(\partial \ln \eta / \partial \ln T)_{\dot{\gamma}, P_h}}{(\partial \ln \eta / \partial \ln T)_{\tau, P_h}} = \left(\frac{\partial \ln \tau}{\partial \ln \dot{\gamma}}\right)_{T, P_h} \quad (9)$$

The relation of Eq. (9) is induced also by analyzing the flow under constant shear rate and constant hydrostatic pressure.

For a flow at constant temperature and constant shear stress, from Eqs. (3) and (4),

$$\left(\frac{\partial \eta}{\partial P_h}\right)_{\tau, T} dP_h = \left(\frac{\partial \eta}{\partial \dot{\gamma}}\right)_{\tau, P_h} d\dot{\gamma} + \left(\frac{\partial \eta}{\partial P_h}\right)_{\dot{\gamma}, T} dP_h \quad (10)$$

Eq. (11) is obtained from Eqs. (7), (8) and (10).

$$\frac{(\partial \ln \eta / \partial \ln P_h)_{\dot{\gamma}, T}}{(\partial \ln \eta / \partial \ln P_h)_{\tau, T}} = \left(\frac{\partial \ln \tau}{\partial \ln \dot{\gamma}}\right)_{T, P_h} \quad (11)$$

Eqs. (9) and (11) may be applied for every kind of fluid, for instance, the pseudoplastic

fluid and the dilatant fluid etc.. The right term of Eqs. (9) and (11) that is expressed in the form of differential coefficient agree with the flow index which is obtained from the $\tau-\dot{\gamma}$ flow characteristics. The flow index³⁾ is indicated as follows,

$$n_{\tau\dot{\gamma}} = \frac{\partial \ln \tau}{\partial \ln \dot{\gamma}} \quad (12)$$

where subscript $\tau\dot{\gamma}$ means a value in $\tau-\dot{\gamma}$ co-ordinates.

3. Various Shift Factors

3.1 Temperature shift factor

In the case where the time-temperature superposition principle is applicable, the relationships between temperature shift factor¹⁾ a_T , and the shear stress τ , the shear rate $\dot{\gamma}$, and the viscosity η , is expressed as follows, keeping hydrostatic pressure constant:

$$\tau_T(\dot{\gamma}_T) = \tau_{T_0}(\dot{\gamma}_{T_0}) \quad (13)$$

$$\eta_T(\dot{\gamma}_T) = a_T \eta_{T_0}(\dot{\gamma}_{T_0}) \quad (14)$$

$$\dot{\gamma}_{T_0} = a_T \dot{\gamma}_T \quad (15)$$

where subscript T_0 : a reference temperature, and T : a measuring temperature. It should be noted with Eqs. (13)~(15) that density compensation⁶⁾ in polymer melts is neglected in the case where temperature difference between measuring and reference is not large. The WLF equation^{5)~8)} which expresses a relation between a_T and temperature T is well known for amorphous polymer.

In the case where the so-called method of reduced variables is not applicable, it is useful to obtain a temperature shift factor as a function of τ or $\dot{\gamma}$. In this paper, temperature shift factors in the steady flow are expressed as follows. Temperature shift factor at constant shear stress is,

$$a_{T\tau}(T, \tau) = \left(\frac{\eta}{\eta_0} \right)_{T\tau} \quad (16)$$

$$= \left(\frac{\dot{\gamma}_0}{\dot{\gamma}} \right)_{T\tau} \quad \because \tau_T = \tau_{T_0} \quad (17)$$

Temperature shift factor at constant shear rate is,

$$a_{T\dot{\gamma}}(T, \dot{\gamma}) = \left(\frac{\eta}{\eta_0} \right)_{T\dot{\gamma}} \quad (18)$$

$$= \left(\frac{\tau}{\tau_0} \right)_{T\dot{\gamma}} \quad \because \dot{\gamma}_T = \dot{\gamma}_{T_0} \quad (19)$$

where subscript 0: a value at a reference point. In the same way as in the case where the method of time-temperature reduced variables is applicable, if the measuring temperature T is higher than the reference temperature T_0 , the temperature shift factors $a_{T\dot{\gamma}}$ and $a_{T\tau}$ are smaller than unity. If T is lower than T_0 , $a_{T\dot{\gamma}}$ and $a_{T\tau}$ are larger than unity.

From Eqs. (9), (12) and (16)~(19) one obtains,

$$\left[\frac{(\partial \ln a_{T\dot{\gamma}}) / \{\partial(1/T)\}}{(\partial \ln a_{T\tau}) / \{\partial(1/T)\}} \right]_{P_A} = \left(\frac{\partial \ln a_{T\dot{\gamma}}}{\partial \ln a_{T\tau}} \right)_{P_A} = (n_{\tau\dot{\gamma}})_{T, P_A} \quad (20)$$

The formula of Eq. (20) can be used for the flow characteristics of every kind of fluid. In the case where the method of time-temperature reduced variables is applicable, from the definition of Eqs. (13)~(17), $a_{T\tau}$ is equal to a_T . Hence, substituting $a_{T\tau}=a_T$ into Eq. (20) gives

$$\left(\frac{\partial \ln a_{T\dot{\gamma}}}{\partial \ln a_T} \right)_{P_h} = (n_{T\dot{\gamma}})_{T, P_h} \quad (21)$$

3.2 Pressure shift factor

The method of time-pressure reduced variables is also known as that of time-temperature reduced variables. A few investigations¹⁰⁾ on pressure shift factor for polymer melts have been reported, while many researches^{4), 6), 9)} have been carried out on temperature shift factor. The relationship between the pressure shift factor a_P and τ , $\dot{\gamma}$, η , is expressed as follows, keeping temperature constant:

$$a_P = \left(\frac{\eta}{\eta_o} \right)_{P_h} \quad (22)$$

Pressure shift factor $a_{P\tau}$ at constant shear stress and pressure shift factor $a_{P\dot{\gamma}}$ at constant shear rate are expressed by the following equations, respectively.

$$a_{P\tau}(P_h, \tau) = \left(\frac{\eta}{\eta_o} \right)_{P_h \tau} \quad (23)$$

$$= \left(\frac{\dot{\gamma}_o}{\dot{\gamma}} \right)_{P_h \tau} \quad \because \tau_{P_h} = \tau_{P_h o} \quad (24)$$

$$a_{P\dot{\gamma}}(P_h, \dot{\gamma}) = \left(\frac{\eta}{\eta_o} \right)_{P_h \dot{\gamma}} \quad (25)$$

$$= \left(\frac{\tau}{\tau_o} \right)_{P_h \dot{\gamma}} \quad \because \dot{\gamma}_{P_h} = \dot{\gamma}_{P_h o} \quad (26)$$

In Eqs. (22)~(26), subscript o : a value at a reference point. P_h : a value under a measuring hydrostatic pressure. $P_{h o}$: a value under a reference hydrostatic pressure. The density compensation in the pressure case is neglected also in the same way as in the method of time-temperature reduced variables case. If P_h is higher than $P_{h o}$, the various pressure shift factors are larger than unity. If P_h is lower than $P_{h o}$, those pressure shift factors are smaller than unity.

Eqs. (11), (12) and (23)~(26) one obtains,

$$\left[\frac{(\partial \ln a_{P\dot{\gamma}})/\partial P_h}{(\partial \ln a_{P\tau})/\partial P_h} \right]_T = \left(\frac{\partial \ln a_{P\dot{\gamma}}}{\partial \ln a_{P\tau}} \right)_T = (n_{T\dot{\gamma}})_{T, P_h} \quad (27)$$

Formula of Eq. (27) is able to use in the case as follows, the flow characteristics which the method of time-pressure reduced variables is applicable or not applicable. That is, Eq. (27) can be applied for every kind of fluid. In the case where the reduced variables is applicable, $a_{P\tau}$ becomes equal to a_P .

3.3 Check of validity of $a_{T\dot{\gamma}}-a_{T\tau}-n_{T\dot{\gamma}}$ equation

To check the validity of $a_{T\dot{\gamma}}-a_{T\tau}-n_{T\dot{\gamma}}$ equation which is obtained in the previous section, the following non-Newtonian fluid models^{11)~14)} are used.

$$\tau = \tau_o \left(\frac{a_T a_P \dot{\gamma}}{\dot{\gamma}_o} \right)^{m_{\tau i}(\dot{\gamma}, \dot{\gamma}_o, a_T, a_P)} \quad (28)$$

$$\eta = a_T a_P \eta_o \left(\frac{a_T a_P \dot{\gamma}}{\dot{\gamma}_o} \right)^{m_{\tau i}(\dot{\gamma}, \dot{\gamma}_o, a_T, a_P) - 1} \quad (29)$$

$$= a_T a_P \eta_o \left(\frac{\tau}{\tau_o} \right)^{1 - \{1/m_{\tau i}(\dot{\gamma}, \dot{\gamma}_o, a_T, a_P)\}} \quad (30)$$

$$m_{\tau i}(\dot{\gamma}, \dot{\gamma}_o, a_T, a_P) = \sum_{j=0}^i \left[\frac{(\alpha_{\tau i})_{oj}}{j+1} \sum_{k=0}^j \{ \ln(a_T a_P \dot{\gamma}) \}^{j-k} (\ln \dot{\gamma}_o)^k \right] \quad (31)$$

where α : a constant, subscript $\tau\dot{\gamma}$: a value in τ - $\dot{\gamma}$ flow curve, subscript o : a state under the reference temperature and the reference hydrostatic pressure, and superscript o : standard state.

Eq. (20) is chosen with the object of checking the $a_{T\dot{\gamma}} - a_{T\tau} - n_{\tau\dot{\gamma}}$ relation. In this section, a writing of the subscript P_h is neglected for the purpose of decreasing in complexity in the calculating process. Eq. (32) is obtained from Eq. (20).

$$\frac{\partial \ln a_{T\dot{\gamma}}}{\partial \ln a_{T\tau}} = \frac{(\partial \ln a_{T\dot{\gamma}})/(\partial \ln a_T)}{(\partial \ln a_{T\tau})/(\partial \ln a_T)} \quad (32)$$

Eq. (18) and Eq. (29) under constant hydrostatic pressure P_h give Eq. (33) concerning $a_{T\dot{\gamma}}$.

$$\ln a_{T\dot{\gamma}} = m_{\tau\dot{\gamma}} \left\{ \ln a_T + \ln \left(\frac{\dot{\gamma}}{\dot{\gamma}_o} \right) \right\} + \ln \left(\frac{\eta_o \dot{\gamma}_o}{\eta \dot{\gamma}} \right) \quad (33)$$

Substituting the equation in case of Eq. (31) at $i=1$ into Eq. (33) one obtains,

$$\ln a_{T\dot{\gamma}} = A_2 (\ln a_T)^2 + \left\{ A_1 + A_2 \ln \left(\frac{\dot{\gamma}}{\dot{\gamma}_o} \right) \right\} \ln a_T + \ln \left(\frac{\eta_o}{\eta} \right) + (A_1 - 1) \ln \left(\frac{\dot{\gamma}}{\dot{\gamma}_o} \right) \quad (34)$$

Defining,

$$A_1 \equiv (\alpha_{\tau\dot{\gamma}})_{o0} + A_2 \ln(\dot{\gamma}_o \dot{\gamma}) \quad (35)$$

$$A_2 \equiv \frac{(\alpha_{\tau\dot{\gamma}})_{o1}}{2} \quad (36)$$

Differentiating Eq. (34) at constant shear rate with respect to $\ln a_T$, one obtains,

$$\frac{\partial \ln a_{T\dot{\gamma}}}{\partial \ln a_T} = 2 A_2 \ln a_T + A_1 + A_2 \ln \left(\frac{\dot{\gamma}}{\dot{\gamma}_o} \right) \quad (37)$$

From Eqs. (12), (28) and (31),

$$n_{\tau\dot{\gamma}}(\dot{\gamma}, a_T, a_P) = \sum_{j=0}^i (\alpha_{\tau\dot{\gamma}})_{oj} \{ \ln(a_T a_P \dot{\gamma}) \}^j \quad (38)$$

Eq. (38), at constant hydrostatic pressure and $i=1$, becomes equal to right term of Eq. (37). Therefore,

$$\frac{\partial \ln a_{T\dot{\gamma}}}{\partial \ln a_T} = n_{\tau\dot{\gamma}} \quad (39)$$

From Eq. (16) and Eq. (30) at constant hydrostatic pressure, an equation concerning $a_{T\tau}$ is obtained as follows,

$$m_{\tau\dot{\gamma}} \ln a_{T\tau} = m_{\tau\dot{\gamma}} \left\{ \ln a_T + \ln \left(\frac{\eta_o^\circ \tau}{\eta_o \tau_o^\circ} \right) \right\} - \ln \left(\frac{\tau}{\tau_o^\circ} \right) \quad (40)$$

From Eqs. (6) and (40) and Eq. (31) at $i=1$, one obtains,

$$(B_1 + A_2 \ln a_T - A_2 \ln a_{T\tau}) \ln a_{T\tau} = (B_1 + A_2 \ln a_T - A_2 \ln a_{T\tau}) (\ln a_T + B_2) - B_3 \quad (41)$$

Defining,

$$B_1 \equiv (\alpha_{\tau\dot{\gamma}})_{o0} + A_2 \ln \left(\frac{\dot{\gamma}_o^\circ}{\tau \eta_o} \right) \quad (42)$$

$$B_2 \equiv \ln \left(\frac{\eta_o^\circ}{\eta_o} \right) + B_3 \quad (43)$$

$$B_3 \equiv \ln \left(\frac{\tau}{\tau_o^\circ} \right) \quad (44)$$

Differentiating Eq. (41) at constant shear stress with respect to $\ln a_T$, one obtains,

$$(B_1 + 2A_2 \ln a_T - 2A_2 \ln a_{T\tau}) (\partial \ln a_{T\tau} - \partial \ln a_T) = 0 \quad (45)$$

The following expression is obtained from Eq. (45).

$$\frac{\partial \ln a_{T\tau}}{\partial \ln a_T} = 1 \quad (46)$$

From Eqs. (32), (39) and (46), Eq. (47) is obtained.

$$\frac{\partial \ln a_{T\dot{\gamma}}}{\partial \ln a_{T\tau}} = n_{\tau\dot{\gamma}} \quad (47)$$

Therefore, it is proposed that Eq. (20) is valid.

In the above checking process, the fluid model expressed by Eqs. (28)~(31) was used. Using a fluid model^{(15), (16)} expressed by Eqs. (48)~(50) and checking in the same way in the above, it was verified also that the formula of Eq. (20) was correct, but that verification is ignored here.

$$n_{\tau\dot{\gamma}}(\tau, \dot{\gamma}) = \sum_{j=0}^i (\beta_{\tau\dot{\gamma}})_{oj} (\ln \tau)^j \quad (48)$$

$$\dot{\gamma} = \frac{\dot{\gamma}_o^\circ}{a_T a_P} \left[\frac{(\beta_{\tau\dot{\gamma}})_{o0} + (\beta_{\tau\dot{\gamma}})_{o1} \ln \tau}{(\beta_{\tau\dot{\gamma}})_{o0} + (\beta_{\tau\dot{\gamma}})_{o1} \ln \tau_o^\circ} \right]^{1/(\beta_{\tau\dot{\gamma}})_{o1}} \quad (49)$$

$$\eta = \frac{a_T a_P \eta_o^\circ \tau}{\tau_o^\circ} \left[\frac{(\beta_{\tau\dot{\gamma}})_{o0} + (\beta_{\tau\dot{\gamma}})_{o1} \ln \tau}{(\beta_{\tau\dot{\gamma}})_{o0} + (\beta_{\tau\dot{\gamma}})_{o1} \ln \tau_o^\circ} \right]^{-1/(\beta_{\tau\dot{\gamma}})_{o1}} \quad (50)$$

where β is a constant, Eqs. (49) and (50) are equation at $i=1$.

Eq. (27) is chosen with the object of checking the $a_{P\dot{\gamma}} - a_{P\tau} - n_{\tau\dot{\gamma}}$ relation. Using fluid models and checking the validity of Eq. (27), it was verified also that Eq. (27) was correct. This checking procedure is the same as used in case of the temperature shift factor. Hence, details of checking procedure are ignored.

4. Comparison with Experimental Results

In this section, results of analysis in the previous section are compared with experimental results.

4.1 Comparison with data to which method of time-temperature reduced variables is applicable

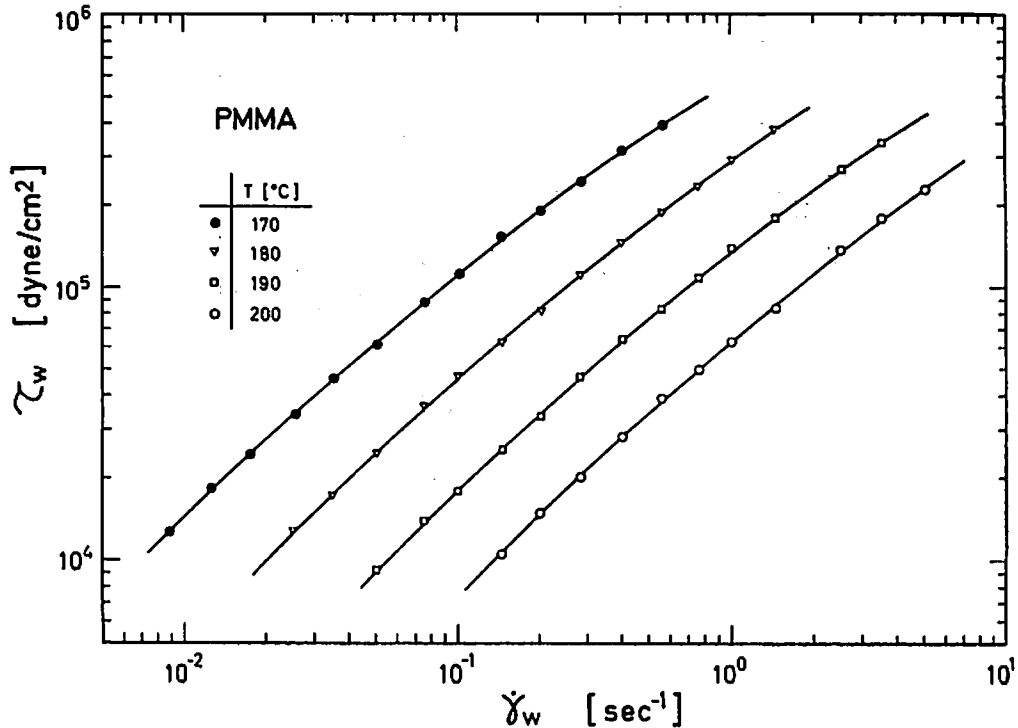


Fig. 1 τ_w - $\dot{\gamma}_w$ flow characteristic curves for PMMA at various temperatures

The samples used in this study were polymethyl methacrylate resin (PMMA, ACRYPET MF of Mitsubishi Rayon). The measurement of flow characteristics was conducted by using the concentric cylindrical rheometer. The τ_w - $\dot{\gamma}$ flow curves under various temperatures and atmospheric pressure are shown in Fig. 1. Subscript w of τ and $\dot{\gamma}$ in the figure indicates at the wall of the measuring system. The temperature shift factor a_T , obtained from the Fig. 1 are plotted in Fig. 2 taking $1/T$ as abscissa. The relationship between a_T and $1/T$ can be approximated by the type of Arrhenius⁹⁾. Hence, the method of time temperature reduced variables can be used for these data.

Results of a_T , $a_{T\dot{\gamma}}$ and $a_{T\tau}$ which are obtained from the τ_w - $\dot{\gamma}_w$ flow characteristics shown in Fig. 1 and Eqs. (13)~(19), where $\dot{\gamma}_{w0}$ (or τ_{w0}) is taken as a parameter, are shown in Fig. 3. In this figure, the reason which $a_{T\tau}$ and a_T can be placed on the same

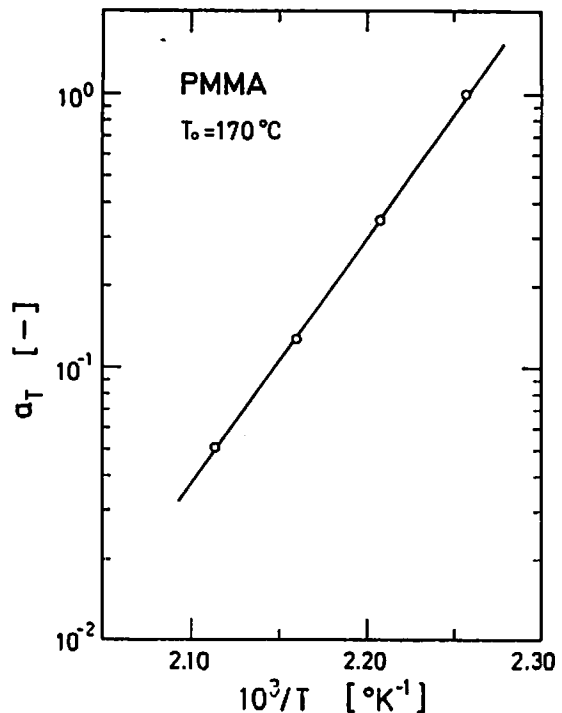


Fig. 2 Variation of a_T with reciprocal of absolute temperature for PMMA

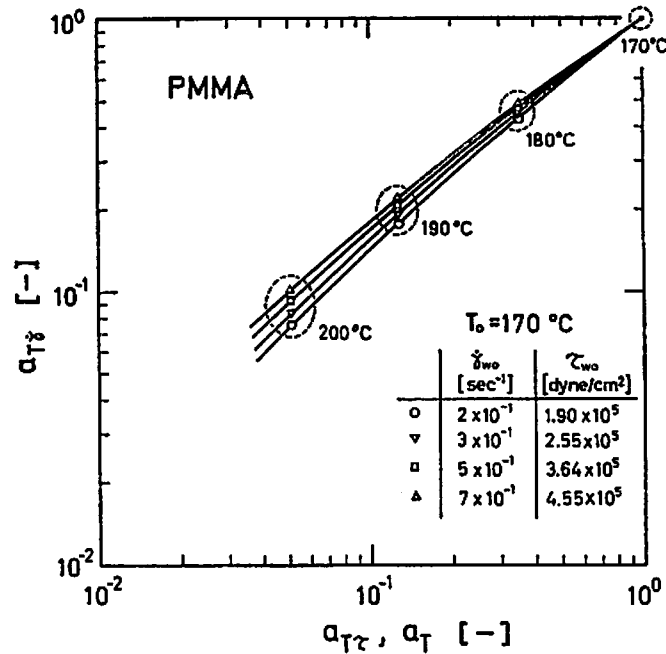


Fig. 3 Relationship $a_{T\gamma}$ relative to $a_{T\tau}$ and a_T for PMMA

abscissa, is that the time-temperature reduced variables method can be used with the data. With the increase in $\dot{\gamma}_{w0}$ (or τ_{w0}), the gradient of $\ln a_{T\gamma} - \ln a_{T\tau}$ shown in Fig. 3 decreases accompanied by the convexity upwardly in its linear relationship. In the figure of $\ln a_{T\gamma} - \ln a_{T\tau}$, points of $a_{T\gamma}$ at the same temperature, stand in a line in the longitudinal direction

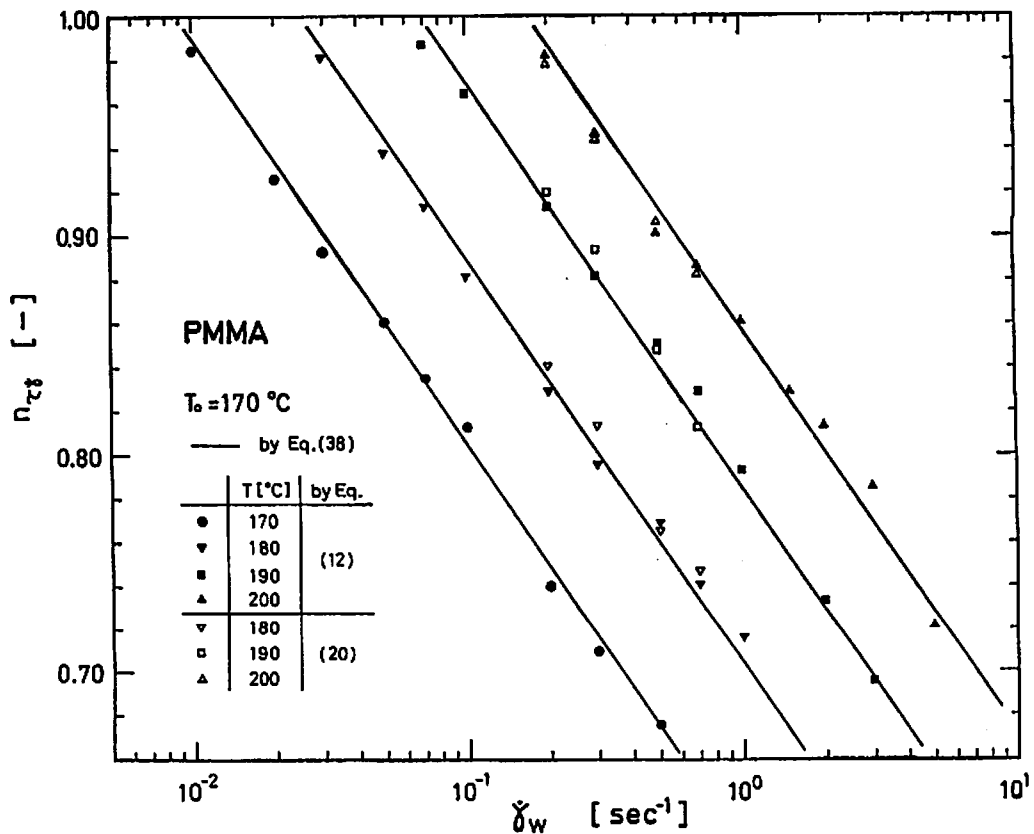


Fig. 4 Relationship between $n_{T\gamma}$ and $\dot{\gamma}_w$ for PMMA at various temperatures

at the same $a_{T\tau}$.

The validity of the theoretical results obtained in the previous section is checked. Eq. (20) is chosen as the object of the check. The values of $(\partial \ln a_{T\dot{\gamma}})/(\partial \ln a_{T\tau})$ obtained by diagrammatical differentiation on $\ln a_{T\dot{\gamma}} - \ln a_{T\tau}$ of Fig. 3, are plotted in Fig. 4 using ∇ , \square and \triangle mark. Fig. 4 includes also the data of flow index $n_{\tau\dot{\gamma}} - \dot{\gamma}_w$ obtained by using the equation on $n_{\tau\dot{\gamma}}$ (Eq. (38)) which is induced from the non-Newtonian fluid model Eqs. (28) ~ (31) and $n_{\tau\dot{\gamma}}$ obtained by diagrammatical differentiation on the $\tau - \dot{\gamma}$ flow curves, using Eq. (12). In Fig. 4 $n_{\tau\dot{\gamma}}$ is a decreasing functional to $\ln \dot{\gamma}_w$. The $n_{\tau\dot{\gamma}} - \ln \dot{\gamma}_w$ curves are shifted to the higher $\dot{\gamma}_w$, with the increase in temperature. The methods of inducing $n_{\tau\dot{\gamma}}$ indicated in Fig. 4 differ from each other. However, it is seen that those values of $n_{\tau\dot{\gamma}}$ agree approximately with one another. Therefore, for the flow characteristics in the case where the method of time-temperature reduced variables is applicable, the relationship among the temperature shift factor $a_{T\dot{\gamma}}$, $a_{T\tau}$ and the flow index $n_{\tau\dot{\gamma}}$ can be expressed by Eq. (20). The relationship among $a_{T\dot{\gamma}}$, $a_{T\tau}$ and $n_{\tau\dot{\gamma}}$ are expressed by Eq. (21).

4.2 Comparison with data to which method of time-temperature reduced variables is not applicable

The theoretical results obtained in previous section 3 and the data to which the method of time-temperature reduced variables is not applicable, are compared in this section. The experimental data are the $\tau_w - \dot{\gamma}_w$ flow curves (indicated by the solid line in Fig. 5) for polypropylene resin (PP) under atmospheric pressure, which were measured by Funatsu¹⁷⁾. Typical results of $n_{\tau\dot{\gamma}}$ which are obtained from the $\tau_w - \dot{\gamma}_w$ flow characteristics shown in Fig. 5 and Eq. (12), are indicated by using the broken line in Fig. 5. If the temperature changes, the $n_{\tau\dot{\gamma}}$ changes with $\dot{\gamma}_w$ and τ_w . This phenomena appears for the flow characteristics in the case where the method of time-temperature reduced variables is not applicable.

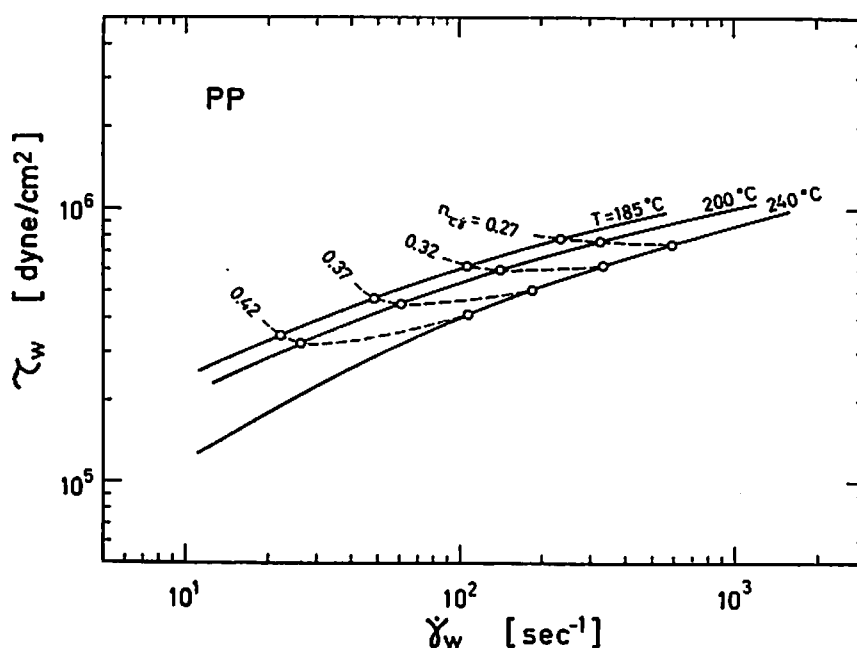


Fig. 5 $\tau_w - \dot{\gamma}_w$ flow characteristic curves for PP at various temperatures

The $a_{T\dot{\gamma}}$ and $a_{T\tau}$ are calculated from the $\tau_w-\dot{\gamma}_w$ flow characteristics shown in Fig. 5 and Eqs. (16)~(19). The relationship between $a_{T\dot{\gamma}}$ and $a_{T\tau}$ where $\dot{\gamma}_{w0}$ (or τ_{w0}) is taken as a parameter is shown in Fig. 6. In the $\ln a_{T\dot{\gamma}}-\ln a_{T\tau}$ curves of Fig. 6, the pattern formed by the group of points at the same temperature, differs remarkably from Fig. 3. That is, the group of points for $a_{T\dot{\gamma}}-a_{T\tau}$ at various temperatures in Fig. 3 is parallel with the $a_{T\dot{\gamma}}$ axis. However, in Fig. 6 this is not so. The pattern which represents the relation between $a_{T\dot{\gamma}}$ and $a_{T\tau}$, becomes such as Fig. 3 in the flow characteristics to which the method of time-temperature reduced variables is applicable, becomes such as Fig. 6 (the group of points for $a_{T\dot{\gamma}}-a_{T\tau}$ at various temperatures is not located parallel with $a_{T\dot{\gamma}}$ axis) in the case where the method of reduced variables is applicable.

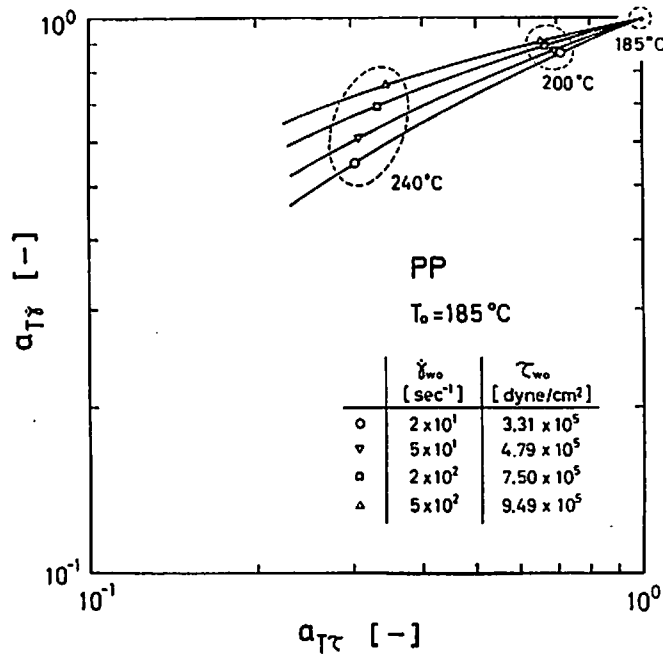


Fig. 6 Relationship between $a_{T\dot{\gamma}}$ and $a_{T\tau}$ for PP

Eq. (20) is applied to the data of Fig. 6. The values of $(\partial \ln a_{T\dot{\gamma}})/(\partial \ln a_{T\tau})$ obtained by diagrammatical differentiation on the curves of Fig. 6, are plotted in Fig. 7 using ∇ and \square mark. Fig. 7 indicates also the data of $n_{T\dot{\gamma}}$ obtained by using the non-Newtonian model and by diagrammatical differentiation on the $\tau-\dot{\gamma}$ curves. The methods of inducing of $n_{T\dot{\gamma}}$ indicated in Fig. 7 is different. However, it is seen that those values of $n_{T\dot{\gamma}}$ agree approximately with each other. Therefore, for the flow characteristics to which the method of time-temperature reduced variables is not applicable, the relationship among the temperature shift factor $a_{T\dot{\gamma}}$, $a_{T\tau}$ and $n_{T\dot{\gamma}}$ can be expressed by Eq. (20).

The validity of Eq. (20) was confirmed by experiment as above. Only the results of the check on the temperature shift factors are described. The results of the check on the pressure shift factors are ignored in this paper.

5. Conclusion

The study on respective shift factors at constant shear stress and constant shear rate

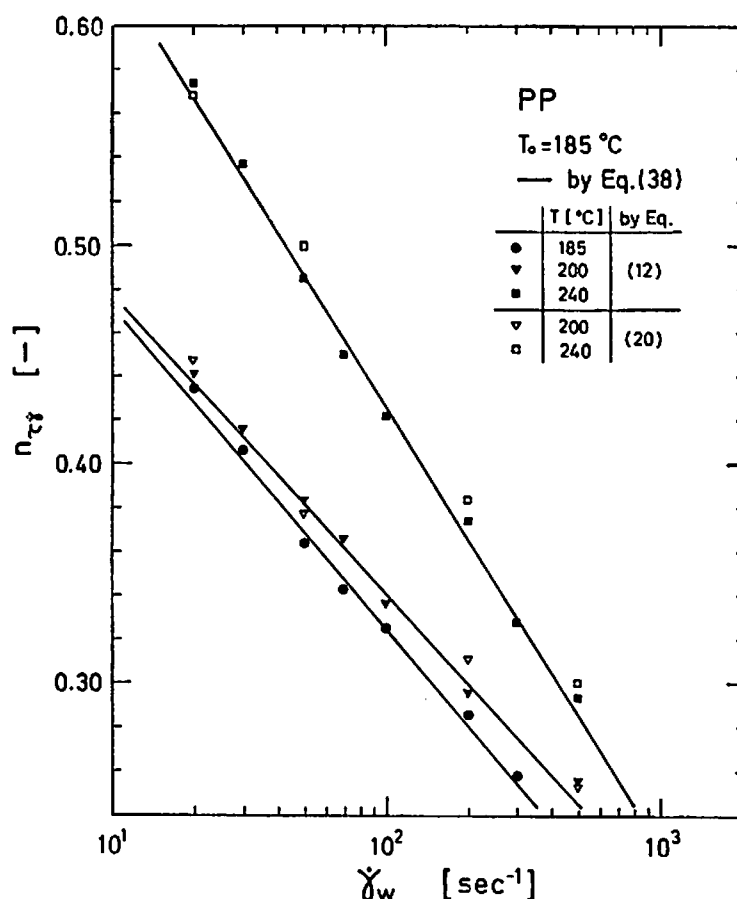


Fig. 7 Relationship between n_{ef} and $\dot{\gamma}_w$ for PP at various temperatures

measured at a constant temperature and under a constant hydrostatic pressure made clear as follows: the ratio of the temperature shift factor at constant shear rate to the temperature shift factor at constant shear stress, and the ratio of the pressure shift factor at constant shear rate to the pressure shift factor at constant shear stress, respectively, that is expressed in the form of differential coefficient corresponds to the generalized flow index. These relationships can be applied to every kind of fluid. And the relationships come into existence whether the method of time-temperature reduced variables or the method of time-pressure reduced variables is applicable or not applicable.

These relationship make a comparative study of the flow characteristics under the different measuring condition easy and also contribute to simplifying the calculation of flow characteristics other than actual values.

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Nomenclature

A_1 = defined in Eq. (35)

A_2 = defined in Eq. (36)
 a_P = pressure shift factor
 $a_{P\dot{\gamma}}$ = pressure shift factor at constant shear rate
 $a_{P\tau}$ = pressure shift factor at constant shear stress
 a_T = temperature shift factor
 $a_{T\dot{\gamma}}$ = temperature shift factor at constant shear rate
 $a_{T\tau}$ = temperature shift factor at constant shear stress
 B_1 = defined in Eq. (42)
 B_2 = defined in Eq. (43)
 B_3 = defined in Eq. (44)
 m = flow index
 n = flow index
 P_h = hydrostatic pressure
 T = temperature
 α = constant
 β = constant
 $\dot{\gamma}$ = shear rate
 η = viscosity
 τ = shear stress
 <Superscript>
 \circ = standard state
 <Subscript>
 \circ = reference point
 P_h = measuring hydrostatic pressure
 $P_{h\circ}$ = reference hydrostatic pressure
 T = measuring temperature
 T_{\circ} = reference temperature
 w = at wall
 $\dot{\gamma}$ = at constant shear rate
 τ = at constant shear stress
 $\tau\dot{\gamma}$ = in flow curve $\tau-\dot{\gamma}$

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