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(出版者 / Publisher)
法政大学工学部
(雑誌名 / Journal or Publication Title)
Bulletin of the Technical College of Hosei University / 法政大学工学部研究集報
(巻 / Volume)
16
(開始ページ / Start Page)
85
(終了ページ / End Page)
96
(発行年 / Year)
1980-03
(URL)
https://doi.org/10.15002/00004137

Flow Behaviors of Molten Polymers

Masayuki KASAJIMA* and Katsuhiko ITO*

Abstract

Flow characteristics of poly(methyle methacrylate) polymer melts were measured. The temperature shift factor at constant shear rate $a_{T\dot{\gamma}}$ is larger than the temperature shift factor a_T and the temperature shift factor at constant shear stress $a_{T\tau}$. Inclinations of the $a_{T\dot{\gamma}}$-temperature T lines are less than inclinations of the a_T, $a_{T\tau}-T$ lines. The various flow indices ($n_{\tau\dot{\gamma}}, n_{\eta\dot{\gamma}}, n_{\eta\tau}, m_{\tau\dot{\gamma}}, m_{\eta\dot{\gamma}}, m_{\eta\tau}$: wherein subscripts indicate the flow characteristics) show a great dependency on the shear rate $\dot{\gamma}_w$ or the shear stress τ_w. The indices decrease with increasing $\dot{\gamma}_w$ or τ_w. $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\ln\dot{\gamma}_w$ and $n_{\eta\dot{\gamma}}$, $m_{\eta\dot{\gamma}}-\ln\dot{\gamma}_w$ relations can be represented by straight lines, respectively. $n_{\eta\tau}$, $m_{\eta\tau}-\ln\dot{\gamma}_w$ and $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\ln\tau_w$ relations are curvilineal, respectively. Inclinations of $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\ln\dot{\gamma}_w$ lines agree with inclinations of $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\ln a_T$ lines.

1. Introdution

Flow characteristics of polymers are influenced not only by factors based on their molecular structure[1~6] but also by such factors as temperature, shear rate and shear stress which are external operating conditions in the polymer processing. Polymer processing is usually done with the polymer in a melting state as the result of heating. In such state the flow depends[7~12] strongly on the temperature, and also is non-Newtonian generally. Under isothermal and simple shear for non-Newtonian fluid various empirical and theoretical formulae[9,13,14], which are used to represent relationships among the shear stress, viscosity and the shear rate, have been presented. The power law epuation, which is one of the constitutive equations for the flow, is very useful because the equation can be treated easily and used practically. Flow index, represented by an exponent of the power law equation, is a value[15] to indicate degree of fluidity and can be used conveniently to grasp the deformating property of the fluid. In the studies[16~22] the rlationships between the flow index and the polymer processing have been investigated. Such relationships include: the relationship between the uniformity[16,18] of T-die extrusions and the flow index, the relationship between average fluidity[19], used in the case where the flow in the mold is investigated, and the flow index, the relationship which is a factor of compressibility[20,21] of polymer melts, conditions of polymer pocessing and the flow index, for thermoplastic resins relationship between the temperature and the flow index. However, in all these case the fiow index is a constant. That is, the flow index is not a function of the shear rate or the shear stress. By other studies[12,23,24], it has been made known that the flow index depends on the shear rate. For the polymer melts many date of the flow index as a function of the shear rate or the shear stess have not been measured. These have been only a few investigations of various flow indices. Hence

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it is useful from the engineering viewpoint to get informations on the flow index.

In this study the flow characteristics of the thermoplastic resin were measured for various temperature. Various temperature shift factors and various flow indices are discussed in terms of polymer processing.

2. Flow Indices and Temperature Shift Factors

In cases where the flow index is not constant and is a function of the shear rate $\dot{\gamma}$ or the shear stress τ, various shift factors[24)~27)] obtained from various flow characteristics under steady flow are expressed by Eqs. (1)~(3).

$$n_{\tau\dot{\gamma}}=\frac{\partial \ln \tau}{\partial \ln \dot{\gamma}} \tag{1}$$

$$n_{\eta\dot{\gamma}}=\frac{\partial \ln \eta}{\partial \ln \dot{\gamma}} \tag{2}$$

$$n_{\eta\tau}=\frac{\partial \ln \eta}{\partial \ln \tau} \tag{3}$$

wherein subscripts $\tau\dot{\gamma}$, $\eta\dot{\gamma}$ and $\eta\tau$ mean value obtained respectively from the characteristics such as the $\tau-\dot{\gamma}$, viscosity $\eta-\dot{\gamma}$ and $\eta-\tau$. Relationships among $n_{\tau\dot{\gamma}}$, $n_{\eta\dot{\gamma}}$ and $n_{\eta\tau}$ are expressed by the following equations.

$$n_{\eta\dot{\gamma}}=n_{\tau\dot{\gamma}}-1 \tag{4}$$

$$n_{\eta\tau}=1-\frac{1}{n_{\tau\dot{\gamma}}} \tag{5}$$

$$=\frac{n_{\eta\dot{\gamma}}}{n_{\eta\dot{\gamma}}+1} \tag{6}$$

Eqs. (4)~(6) may be applied to every kind of fluid, for instance, the pseudoplastic fluid and the dilatant fluid etc.. Models[12),24)~26)] of $n_{\tau\dot{\gamma}}$ as a function of $\dot{\gamma}$ or τ are expressed by Eqs. (7) and (8). Where a_T

$$n_{\tau\dot{\gamma}}(\dot{\gamma},\ a_T,\ a_P)=\sum_{j=0}^{i}(\alpha_{\tau\dot{\gamma}})_{oj}\{\ln(a_Ta_P\dot{\gamma})\}^j \tag{7}$$

$$n_{\tau\dot{\gamma}}(\tau,)=\sum_{j=0}^{i}(\beta_{\tau\dot{\gamma}})_{oj}(\ln\tau)^j \tag{8}$$

means the temperature shift factor, a_P means the pressure shift factor, α and β mean constant, subscript $\tau\dot{\gamma}$ means a value in the $\tau-\dot{\gamma}$ flow curve, and subscript $\circ$ means a value under the reference temperature and hydrostatic pressure. When $n_{\tau\dot{\gamma}}$ is indicated by Eq. (7), the flow characteristics for non-Newtonian fluid models[12),24)~26)] can be expressed by Eqs. (9)~(12). Where superscript $\circ$ means a value under the standard state. In such formulae as

$$\tau=\tau_o^\circ\left(\frac{a_Ta_P\dot{\gamma}}{\dot{\gamma}_o^\circ}\right)^{m_{\tau\dot{\gamma}}(\dot{\gamma},\dot{\gamma}_o^\circ,a_T,a_P)} \tag{9}$$

$$\eta=a_Ta_P\eta_o^\circ\left(\frac{a_Ta_P\dot{\gamma}}{\dot{\gamma}_o^\circ}\right)^{m_{\eta\dot{\gamma}}(\dot{\gamma},\dot{\gamma}_o^\circ,a_T,a_P)} \tag{10}$$

$$\eta=a_Ta_P\eta_o^\circ\left(\frac{\tau}{\tau_o^\circ}\right)^{m_{\eta\tau}(\tau,\tau_o^\circ)} \tag{11}$$

$$m_{\tau\dot{\gamma}}(\dot{\gamma},\ \dot{\gamma}^{\circ}_{o},\ a_T,\ a_P)=\sum_{j=0}^{i}\left[\frac{(\alpha_{\tau\dot{\gamma}})_{oj}}{j+1}\sum_{k=0}^{i}\{\ln(a_Ta_P\dot{\gamma})\}^{j-k}(\ln\dot{\gamma}^{\circ}_{o})^{k}\right] \tag{12}$$

type of power law, flow index $m_{\tau\dot{\gamma}}$ has relations to $m_{\eta\dot{\gamma}}$ and $m_{\eta\tau}$ such as follows.

$$m_{\eta\dot{\gamma}}=m_{\tau\dot{\gamma}}-1 \tag{13}$$

$$m_{\eta\tau}=1-\frac{1}{m_{\tau\dot{\gamma}}} \tag{14}$$

$$=\frac{m_{\eta\dot{\gamma}}}{m_{\eta\dot{\gamma}}+1} \tag{15}$$

When $n_{\tau\dot{\gamma}}$ is indicated by Eq. (8), non-Newtonian fluid at $i=1$ is expressed as follows.

$$\dot{\gamma}=\frac{\dot{\gamma}^{\circ}_{o}}{a_Ta_P}\left[\frac{(\beta_{\tau\dot{\gamma}})_{00}+(\beta_{\tau\dot{\gamma}})_{01}\ln\tau}{(\beta_{\tau\dot{\gamma}})_{00}+(\beta_{\tau\dot{\gamma}})_{01}\ln\tau^{\circ}_{o}}\right]^{1/(\beta_{\tau\dot{\gamma}})_{01}} \tag{16}$$

$$\eta=\frac{a_Ta_P\eta^{\circ}_{o}\tau}{\tau^{\circ}_{o}}\left[\frac{(\beta_{\tau\dot{\gamma}})_{00}+(\beta_{\tau\dot{\gamma}})_{01}\ln\tau}{(\beta_{\tau\dot{\gamma}})_{00}+(\beta_{\tau\dot{\gamma}})_{01}\ln\tau^{\circ}_{o}}\right]^{-1/(\beta_{\tau\dot{\gamma}})_{01}} \tag{17}$$

In the case where the method of time-temperature reduced variables is applicable, it is known[28),29)] that density compensation in polymer melts is neglected in the case where temperature difference between measuring and reference is not large. Therefore, relationships among the temperature shift factor[30)] a_T, τ, $\dot{\gamma}$ and η are expressed as follows[28),31)], keeping hydrostatic pressure constant:

$$\tau_T(\dot{\gamma}_{T},)=\tau_{T_o}(\dot{\gamma}_{T_o},) \tag{18}$$

$$\eta_T(\dot{\gamma}_{T},)=a_T\eta_{T_o}(\dot{\gamma}_{T_o},) \tag{19}$$

$$\dot{\gamma}_{T_o}=a_{T_o}=a_T\dot{\gamma}_T \tag{20}$$

In the case where the so-called method of time-temperature reduced variables is not applicable, it is convenient to use a temperature shift factor as a function of τ or $\dot{\gamma}$. Various temperature shift factors in the steady flow are expressed as follows[12),26)]. Temperature shift factor at constant shear stress $a_{T\tau}$ is,

$$a_{T\tau}(T,\ \tau)=\left(\frac{\eta}{\eta_o}\right)_{T\tau} \tag{21}$$

$$=\left(\frac{\dot{\gamma}_o}{\dot{\gamma}}\right)_{T\tau}\quad \because\quad \tau_T=\tau_{T_o} \tag{22}$$

Temperature shift factor at constant shear rate $a_{T\dot{\gamma}}$ is,

$$a_{T\dot{\gamma}}(T,\ \dot{\gamma})=\left(\frac{\eta}{\eta_o}\right)_{T\dot{\gamma}} \tag{23}$$

$$=\left(\frac{\tau}{\tau_o}\right)_{T\dot{\gamma}}\quad \because\quad \dot{\gamma}_T=\dot{\gamma}_{T_o} \tag{24}$$

In the same way in the case of a_T, if T is higher than T_o, $a_{T\tau}$ and $a_{T\dot{\gamma}}$ are larger than 1.

3. Experimental

The samples used in this study were poly(methyle methacrylate) resin (PMMA, ACRYPET MF of Mitsubishi Rayon Co., Ltd.). The measurement of flow characteristics was conducted by using the concentric cylindrical rheometer. The temperature was measured at temperature intervals of 10°C over the range of from 170°C to 200°C. In this study $\eta-\dot{\gamma}$ and $\eta-\tau$ flow characteristics were measured, because it is known[32)] that the viscosity in flow state is different at condition of $\dot{\gamma}$ constant or τ constant.

The flow index can be obtained by diagrammatical differentiation on the flow characteristic curve, for instance, $\ln\tau$ (or $\ln\eta$)$-\ln\dot{\gamma}$ curve. By the naked eye the diagrammatical differentiation can not be seen easily and a satisfactory result can not be obtained, because the flow characteristic curve of the polymer melts generally has a small curvature. The authors used[24] a transparent glass bar as the object of the diagrammatical differentiation. We put such bar on the flow characteristic curve. The bar presents as if there is a curve having large curvature. Thereby the diagrammatical differentiation can be done easily. And the value of n may be obtained accurately.

4. Results and Discussion

Viscosity η_w-shear rate $\dot{\gamma}_w$ flow characteristic curves are shown in **Fig. 1**, taking temperature T as a parameter. Subscript w indicates a value at the wall of the measuring system. η_w decreases with increasing $\dot{\gamma}_w$. That is, such η_w has a structural viscosity[33]. The $\eta_w-\dot{\gamma}_w$ curves at low temperature are higher above than the curve at high temperature. η_w dependence of $\dot{\gamma}_w$ in the small $\dot{\gamma}_w$ region is larger than in its at large $\dot{\gamma}_w$. Such behavior occurs remarkably at high temperature. At small $\dot{\gamma}_w$ region the $\ln\eta_w-\ln\dot{\gamma}_w$ curves are located approximately parallel to the $\ln\dot{\gamma}_w$ axis.

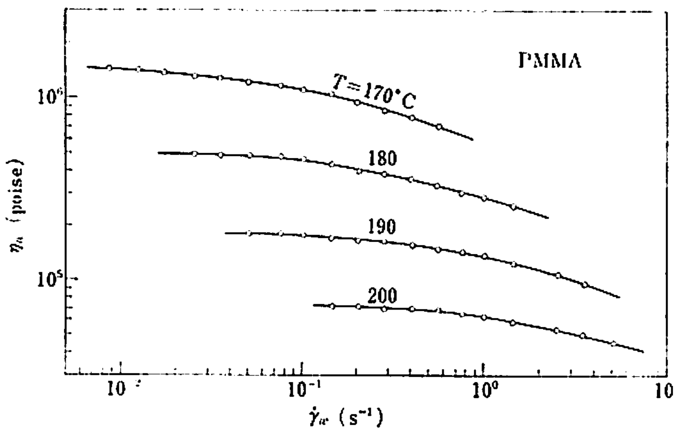

Fig. 1 $\eta_w-\dot{\gamma}_w$ flow characteristic curves for PMMA at various temperatures.

η_w-shear stress τ_w flow characteristic curves, having a parameter T, are shown in **Fig. 2.** The η_w decreases with increasing τ_w. The η_w has a large dependency on τ_w. The same as in the case of the $\ln\eta_w-\ln\dot{\gamma}_w$ flow characteristic curves, the $\ln\eta_w-\ln\tau_w$ curves at high temperature are located at the top of Fig. 2. The tendency of η_w to change to τ_w is larger at region of τ_w than at region of small τ_w. The shapes of $\ln\eta_w-\ln\tau_w$ curves at various temperature are similar. Therefore, if such curves are moved in parallel along the η_w axis, respective $\ln\eta_w-\ln\tau_w$ curves can be superimposed. By comparing Figs. 1 and 2, it is seen that the η_w dependence of $\dot{\gamma}_w$ differs from the η_w dependence of τ_w.

Various temperature shift factors obtained from data of Figs. 1 and 2 are shown in **Fig. 3.** The reference temperature T_o is 170°C. The value of a_T, $a_{T\tau}$ and $a_{T\dot{\gamma}}$ decrease

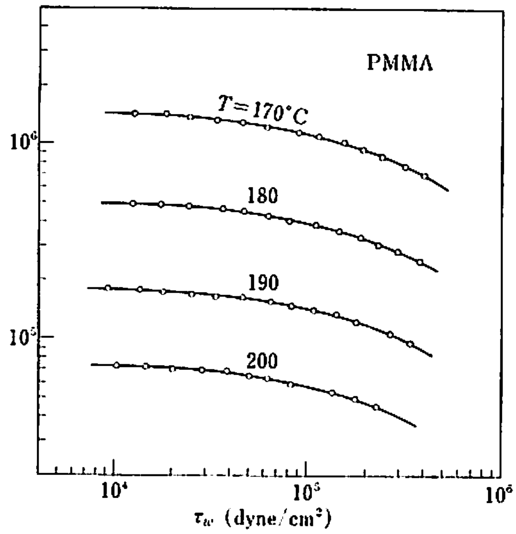

Fig. 2　$\eta_w - \tau_w$ flow characteristic curves for PMMA at various temperatures.

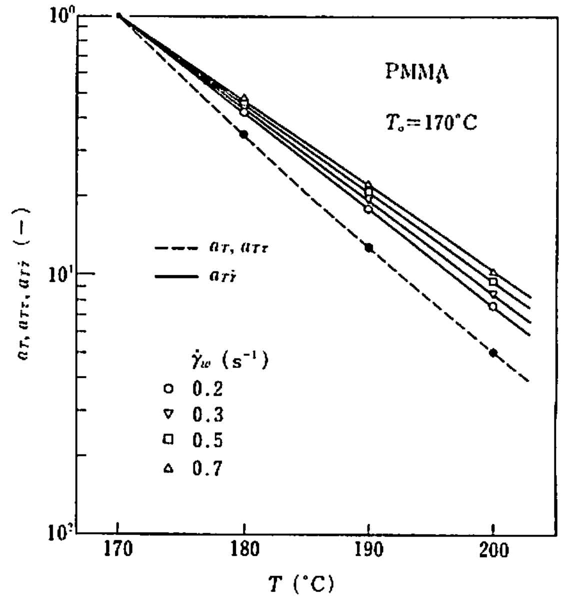

Fig. 3　Relationships among various temperature shift factors for PMMA.

with the increase in temperature. Because the method of time-temperature reduced variables to the data shown in Figs. 1 and 2 can be applied, the $a_{T\tau}$ agrees with the a_T. The relationship between T and $\ln a_T$ or $\ln a_{T\tau}$ is slightly curvilinear having small curvature. The relationship between $\ln a_T$ and $1/T$ can be approximated (Figure is neglected) by the type of Arrhenius[34]. The $\ln a_T - T$ lines are located radially with center at $T=$ 170°C. Changing tendency of the $\ln a_T - T$ lines to $\dot{\gamma}_w$ decreases with increasing $\dot{\gamma}_w$. Inclinations of the $\ln a_T$, $\ln a_{T\tau} - T$ lines are larger than inclinations of the $\ln a_{T\dot{\gamma}} - T$ lines. The is, the a_T, $a_{T\tau}$ dependence of T is larger than of the $a_{T\dot{\gamma}}$. From Fig. 3 difference the η_w dependence of $\dot{\gamma}_w$ and η_w dependence of τ_w may be known quantitatively.

Flow index $n_{\tau\dot{\gamma}}$ obtained by the diagrammatical differentiation (using Eq. (11)) on the $\ln \tau_w - \ln \dot{\gamma}_w$ flow characteristic curves of the previous paper[26], are plotted in **Fig. 4** using ● mark. The $n_{\tau\dot{\gamma}}$ decreases with increasing $\dot{\gamma}_w$. When the value of $\dot{\gamma}_w$ differs one figure, the value of $n_{\tau\dot{\gamma}}$ differs about 0.2. Hence, the $n_{\tau\dot{\gamma}}$ dependence of $\dot{\gamma}_w$ is considerably large. In the region of small $\dot{\gamma}_w$ the $n_{\tau\dot{\gamma}}$ has a value of near 1. This means that the flow behavior is similar to Newtonian flow behavior. The relationship between $n_{\tau\dot{\gamma}}$ and $\ln \dot{\gamma}_w$ can be approximated by the straight line. Broken lines in shown Fig. 4 indicate the $n_{\tau\dot{\gamma}} - \ln \dot{\gamma}_w$ relation expressed by Eq. (7) at $i=1$ and $T_0=170$°C. The $n_{\tau\dot{\gamma}} - \ln \dot{\gamma}_w$ lines at $T=180\sim200$°C, induced by the $n_{\tau\dot{\gamma}} - \ln \dot{\gamma}_w$ line at $T_0=170$°C and the a_T, agree substantially with the $n_{\tau\dot{\gamma}}$ obtained by the diagrammatical differentiation. Therefore, if the method of time-temperature reduced variables is applicable, the value of τ_w does not change, and also the value of $n_{\tau\dot{\gamma}}$ does not change. However, comparing values of $n_{\tau\dot{\gamma}}$ in various temperatures at a certain $\dot{\gamma}_w$, it is seen that the $n_{\tau\dot{\gamma}}$ at high temperature has large value. Flow index $m_{\tau\dot{\gamma}}$ obtained from the data of $\ln \tau_w - \ln \dot{\gamma}_w$, Eqs. (9) and (12) are shown by the solid lines in Fig. 4. Inclination of the $m_{\tau\dot{\gamma}} - \ln \dot{\gamma}_w$ line is equal to half inclination of the $n_{\tau\dot{\gamma}} - \ln \dot{\gamma}_w$. Such result agrees with Eq. (25) induced from

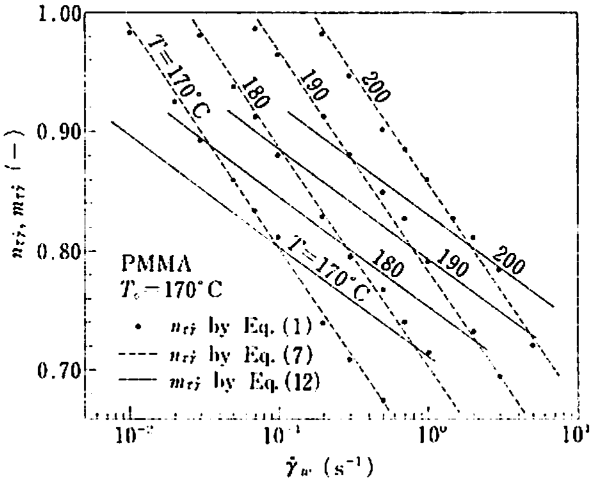

Fig. 4 Relationships $n_{\tau\dot{\gamma}}$ and $m_{\tau\dot{\gamma}}$ relative to $\dot{\gamma}_w$ for PMMA at various temperatures.

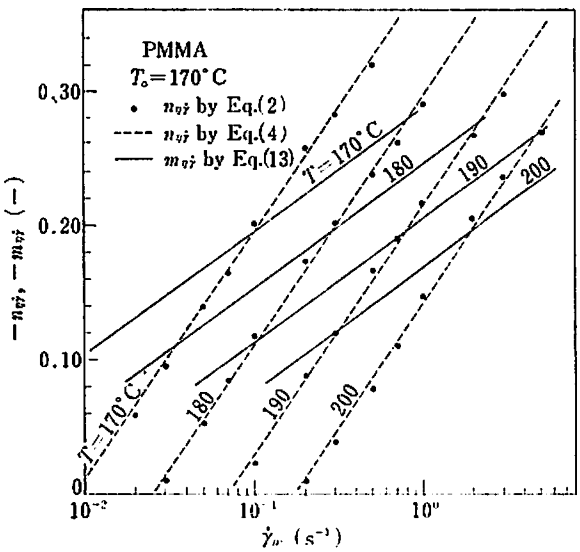

Fig. 5 Relationships $n_{\eta\dot{\gamma}}$ and $m_{\eta\dot{\gamma}}$ relative to $\dot{\gamma}_w$ for PMMA at various temperatures.

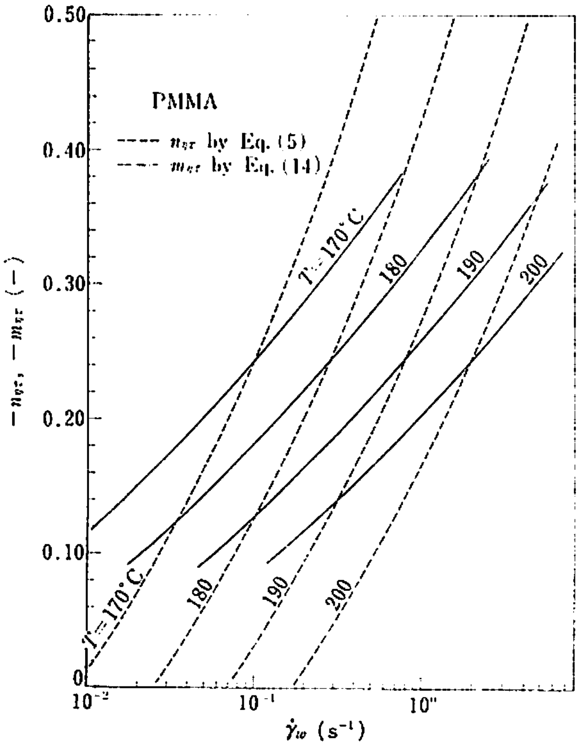

Fig. 6 Relationships $n_{\eta\tau}$ and $m_{\eta\tau}$ relative to $\dot{\gamma}_w$ for PMMA at various temperatures.

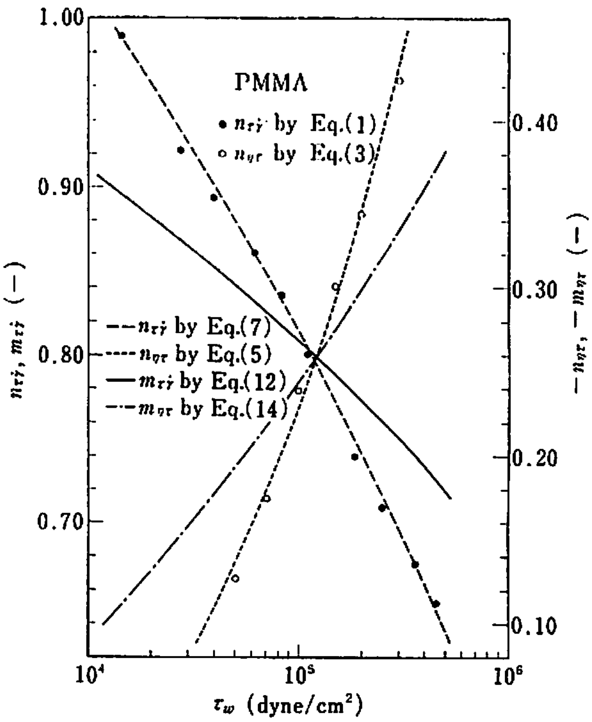

Fig. 7 $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\tau_w$ and $n_{\eta\tau}$, $m_{\eta\tau}-\tau_w$ relationships for PMMA.

Eqs. (7) and (12). With increasing T, the $m_{\tau\dot{\gamma}}-\ln\dot{\gamma}_w$ lines are shifted along the $\ln\dot{\gamma}_w$ axis

$$\frac{\partial n_{\tau\dot{\gamma}}}{\partial \ln\dot{\gamma}}=2\frac{\partial m_{\tau\dot{\gamma}}}{\partial \ln\dot{\gamma}} \tag{25}$$

in the direction of increasing $\dot{\gamma}_w$.

$n_{\eta\dot{\gamma}}$ obtained by the diagrammatical differentiation (using Eq. (2)) on the flow characteristic curves shown in Fig. 1, are plotted in **Fig. 5** using ● mark. It should be noted that the $n_{\eta\dot{\gamma}}$ axis has a minus value. The value of $n_{\eta\dot{\gamma}}$ changes largely with the $\dot{\gamma}_w$. The $n_{\eta\dot{\gamma}}$ dependence on $\dot{\gamma}_w$ is large. Comparing values of $n_{\eta\dot{\gamma}}$ at a certain $\dot{\gamma}_w$, it is seen that the $n_{\eta\dot{\gamma}}$ at low temperature has a small value. The data shown in Fig. 5 can be approximated by the straight line. The $n_{\eta\dot{\gamma}}-\ln\dot{\gamma}_w$ (indicated by the broken lines) in Fig. 5 are obtained from the $n_{\tau\dot{\gamma}}-\ln\dot{\gamma}_w$ lines (indicated by the broken lines) shown in Fig. 4 and Eq. (4). Hence, $n_{\eta\dot{\gamma}}$ indicated by ● mark and the broken lines which are obtained by the methods of different inducement, agree substantially with each other. The solid lines shown in Fig. 5 indicate the $m_{\eta\dot{\gamma}}-\ln\dot{\gamma}_w$ relation obtained from the $m_{\tau\dot{\gamma}}-\ln\dot{\gamma}_w$ lines and Eq. (13). The ratio between inclinations of the $n_{\eta\dot{\gamma}}$ and $m_{\eta\dot{\gamma}}$ lines is 1:2. With increasing T, the $n_{\eta\dot{\gamma}}-\ln\dot{\gamma}_w$ and the $m_{\eta\dot{\gamma}}-\ln\dot{\gamma}_w$ lines are shifted along the $\ln\dot{\gamma}_w$ axis in the direction of increasing $\dot{\gamma}_w$. From the characteristics to which the method of time-temperature reduced variables is applicable, inclinations of the $n_{\eta\dot{\gamma}}(m_{\eta\dot{\gamma}})-\ln\dot{\gamma}_w$ lines at various temperatures are the same, so the lines at different temperatures can be superimposed by being shifted along the $\ln\dot{\gamma}_w$ axis.

The relationship between $n_{\eta\tau}$ and $\dot{\gamma}_w$, and the relationship between $m_{\eta\tau}$ and $\dot{\gamma}_w$ are shown in **Fig. 6** using the broken lines and the solid lines, respectively. Such $n_{\eta\tau}$ are obtained by the $n_{\tau\dot{\gamma}}-\ln\dot{\gamma}_w$ lines shown in Fig. 4 and Eq. (5). The $m_{\eta\tau}$ are obtained by the $m_{\tau\dot{\gamma}}-\ln\dot{\gamma}_w$ lines shown in Fig. 4 and Eq. (14). From Fig. 6 it is seen that, the $n_{\eta\tau}$ and the $m_{\eta\tau}$ decrease with increasing $\dot{\gamma}_w$, $n_{\eta\tau}$ and $m_{\eta\tau}$ have large dependency on $\dot{\gamma}_w$. The $n_{\eta\tau}$, $m_{\eta\tau}-\ln\dot{\gamma}_w$ relations shown in Fig. 6, being different from Figs. 4 and 5, are curvilinear. The $n_{\eta\tau}$, $m_{\eta\tau}-\ln\dot{\gamma}_w$ curves having T as a parameter can be superimposed by

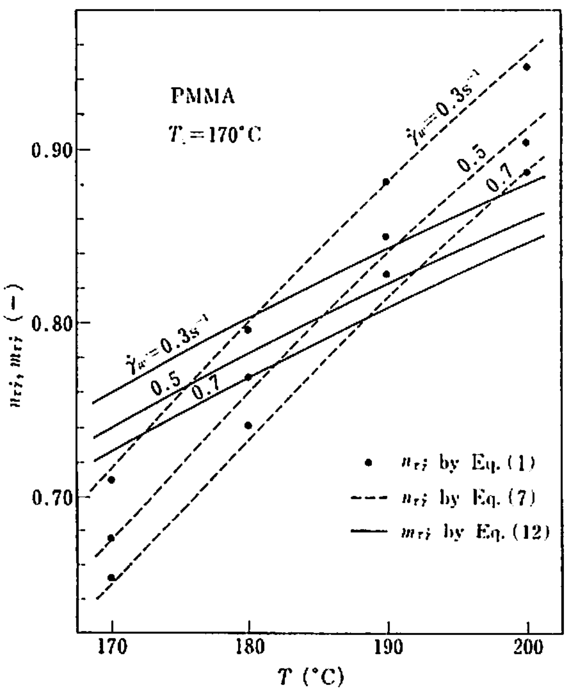

Fig. 8　Relationships $n_{\tau\dot{\gamma}}$ and $m_{\tau\dot{\gamma}}$ relative to T for PMMA.

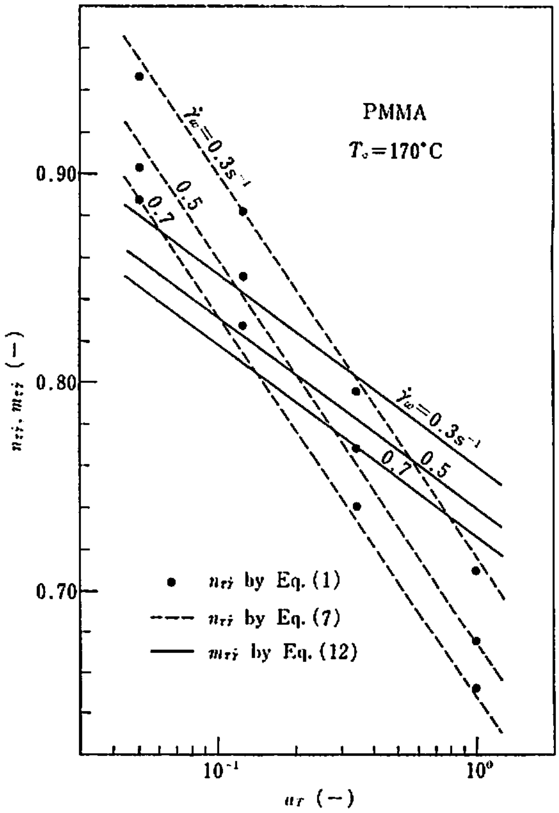

Fig. 9　Relationships $n_{\tau\dot{\gamma}}$ and $m_{\tau\dot{\gamma}}$ relative to a_T for PMMA.

being shifted along the $\dot{\gamma}_w$ axis.

The relationship between $n_{\tau\dot{\gamma}}$ and τ_w, obtained by the $\ln\tau_w - \ln\dot{\gamma}_w$ flow characteristic curves and Eq. (1), is shown in **Fig. 7** using ● mark. The $n_{\tau\dot{\gamma}}$ decreases with increasing τ_w. The relationship between $n_{\eta\tau}$ and $\ln\tau_w$ (the value of τ_w can be obtained by the value of $\dot{\gamma}_w$ and the $\ln\tau_w - \ln\dot{\gamma}_w$ flow characteristics), obtained by the $n_{\tau\dot{\gamma}} - \ln\dot{\gamma}_w$ lines (indicated by the broken lines) shown in Fig. 4, the temperature shift factor in Fig. 3 and Eq. (7), are shown in Fig. 7 using --- mark. Such --- line agrees substantially with ● mark. The line of --- mark is an upward convexity. It is possible that the $n_{\tau\dot{\gamma}} - \ln\tau_w$ relation indicated by ● mark can be approximated by the straight line expressed by Eq. (8) at $i=1$. However, if the $n_{\tau\dot{\gamma}} - \ln\dot{\gamma}_w$ relation is expressed by the straight line, the $n_{\tau\dot{\gamma}} - \ln\tau_w$ relation become exactly curvilinear such as the long broken line shown in Fig. 7. Conversely, if the $n_{\tau\dot{\gamma}} - \ln\tau_w$ relation is approximated by the straight line, the $n_{\tau\dot{\gamma}} - \ln\dot{\gamma}_w$ relation become curvilinear. The relationship between $n_{\eta\tau}$ and τ_w, obtained by the $\ln\eta_w - \ln\tau_w$ flow characteristic curves and Eq. (3), is shown in Fig. 7 using ○ mark. The $n_{\eta\tau}$ has large dependency on τ_w. The value of $n_{\eta\tau}$ decreases with increasing τ_w. The $n_{\eta\tau}$ obtained by Eq. (5) and the $n_{\tau\dot{\gamma}} - \ln\tau_w$ curves, shown in Fig. 7 using the long broken line, are shown using ...... mark. The $n_{\eta\tau} - \ln\tau_w$ cuves indicated by ...... mark agrees substantially with ○ mark. The $n_{\eta\tau}$ has large dependency on τ_w. The relationship between $m_{\tau\dot{\gamma}}$ and $\ln\tau_w$, obtained by the $m_{\tau\dot{\gamma}} - \ln\dot{\gamma}_w$ lines (indicated by the solid lines) shown in Fig. 4, the temperature shift factor in Fig. 3 and Eq. (12), are shown in Fig. 7 using the solid line. The $m_{\tau\dot{\gamma}} - \ln\tau_w$ relation is an upward convexity. The $m_{\tau\dot{\gamma}}$ dependence of τ_w is smaller than the $n_{\tau\dot{\gamma}}$ dependence of τ_w. The $m_{\eta\tau}$ indicated by the —·— mark is obtained by Eq. (14) and the $m_{\tau\dot{\gamma}} - \ln\tau_w$ indicated in Fig. 7 using the solid line. Comparing the $n_{\eta\tau} - \ln\tau_w$ curve and $m_{\eta\tau} - \ln\tau_w$ curve, it is seen that the $m_{\eta\tau}$ dependence on τ_w is less than of $n_{\tau\dot{\gamma}}$.

The relationship between $n_{\tau\dot{\gamma}}$ and T as a parameter $\dot{\gamma}_w$ are shown in **Fig. 8.** ● mark indicate the $n_{\tau\dot{\gamma}}$ obtained by Eq. (1) and the $\ln\tau_w - \ln\dot{\gamma}_w$ flow characteristic curves. The $n_{\tau\dot{\gamma}} - T$ curves indicated by the broken line are obtained from the $n_{\tau\dot{\gamma}} - \ln\dot{\gamma}_w$ lines shown in Fig. 4 using the broken line. The $n_{\tau\dot{\gamma}} - T$ curve is an upward convexity. Shapes of the $n_{\tau\dot{\gamma}} - T$ curves at various $\dot{\gamma}_w$ are nearly similar. With increasing $\dot{\gamma}_w$, the $n_{\tau\dot{\gamma}} - T$ curve is shifted along the $\dot{\gamma}_w$ axis in the direction of increasing T. Comparing the $n_{\tau\dot{\gamma}}$ at various $\dot{\gamma}_w$ and constant temperature, it is seen that the $n_{\tau\dot{\gamma}}$ decreases with increasing $\dot{\gamma}_w$. $m_{\tau\dot{\gamma}} - T$ relation is shown in Fig. 8 using the solid line. Such $m_{\tau\dot{\gamma}} - T$ curves are obtained from the $m_{\tau\dot{\gamma}} - \ln\dot{\gamma}_w$ lines shown in Fig. 4 using the solid line. The $m_{\tau\dot{\gamma}} - T$ curves are upward convexity. The $m_{\tau\dot{\gamma}}$ increases with increasing T. With decreasing $\dot{\gamma}_w$, the $m_{\tau\dot{\gamma}} - T$ curves are moved along the $m_{\tau\dot{\gamma}}$ axis in the direction of increasing $m_{\tau\dot{\gamma}}$.

The relationship between $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}$ and a_T is shown in **Fig. 9**, taking $\dot{\gamma}_w$ as a parameter. ● mark indicate the $n_{\tau\dot{\gamma}}$ obtained by Eq. (1), the $\ln\tau_w - \ln\dot{\gamma}_w$ flow characteristic curves and the $a_T - T$ relation (Fig. 3). The $n_{\tau\dot{\gamma}}$ dependence of a_T is very large. And the $n_{\tau\dot{\gamma}}$ decrease with increasing a_T. The relationship between the $n_{\tau\dot{\gamma}}$ and $\ln a_T$, obtained by the temperature shift factor shown in Fig. 3, the $n_{\tau\dot{\gamma}} - \ln\dot{\gamma}_w$ lines (broken line) indic-

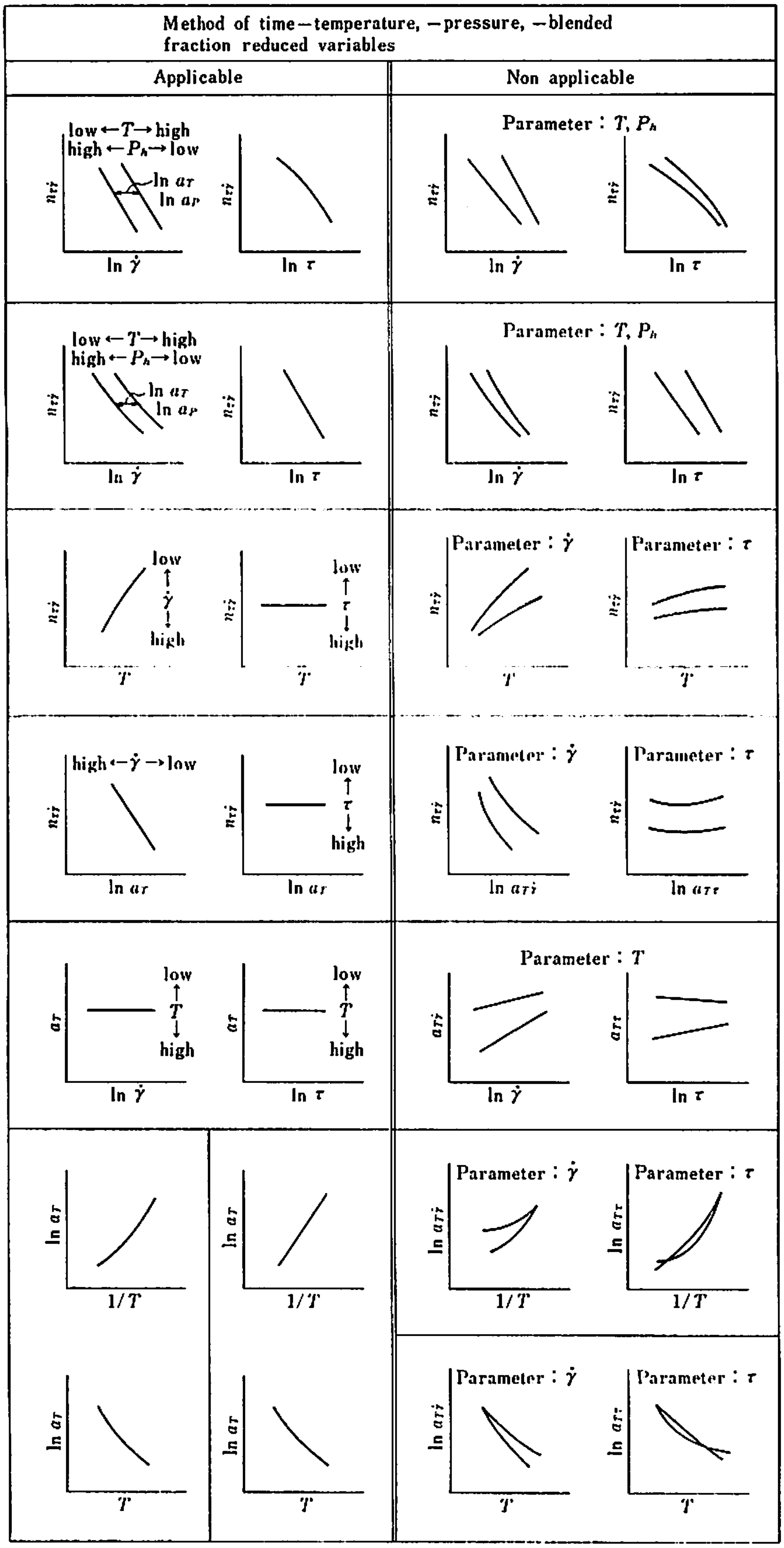

Fig. 10　Schematic illustrations of various curves with respect to flow index, temperature shift factors, pressure shift factors and blended fraction shift factor.

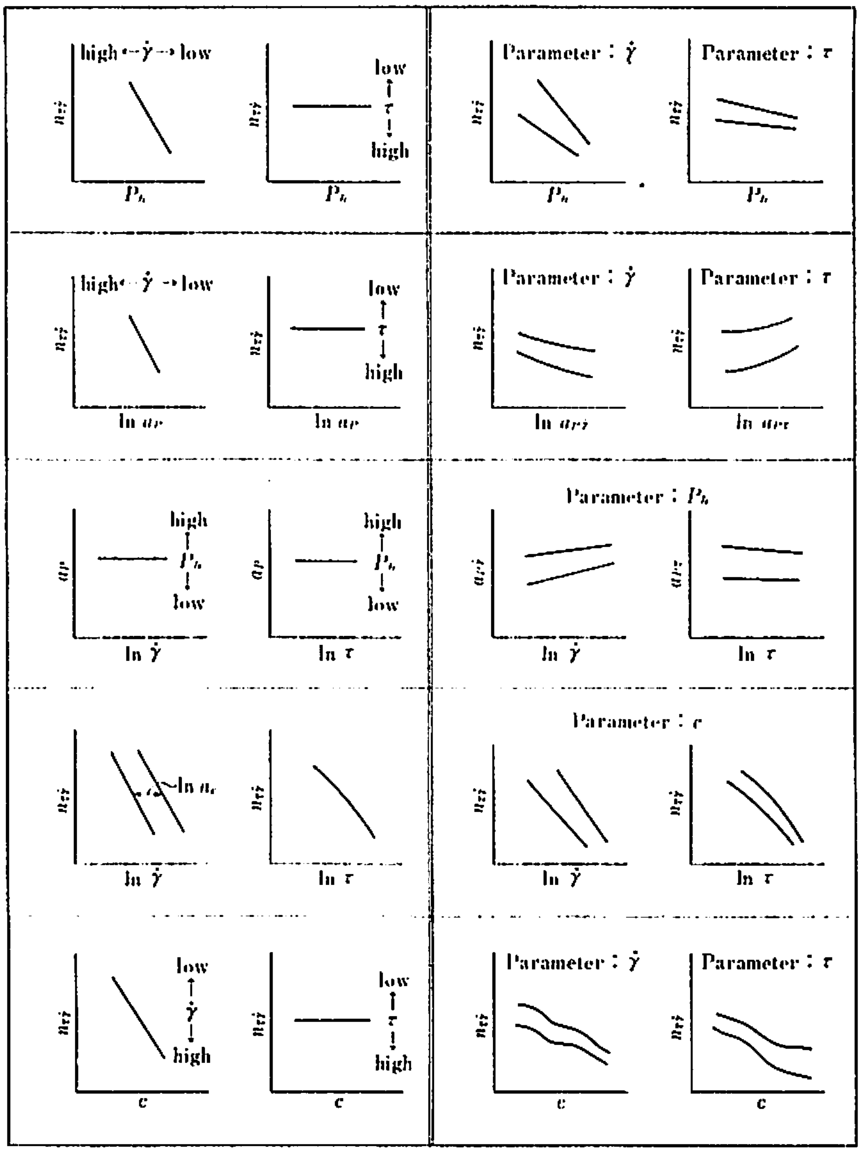

Fig. 10 (continued).

ated in Fig. 4 and Eq. (7), are shown in Fig. 9 using the broken line. Such $n_{\tau\dot\gamma}-\ln a_T$ relation is represented by a straight line. The $n_{\tau\dot\gamma}-\ln a_T$ line agrees substantially with the value of ⊕ mark. Comparing Fig. 4 and Fig. 9, it is seen that inclinations of the $n_{\tau\dot\gamma}-\ln\dot\gamma_w$ line and the $n_{\tau\dot\gamma}-\ln a_T$ line are the same, and this is validated by Eq. (26) obtained from Eq. (7).

$$\frac{\partial n_{\tau\dot\gamma}}{\partial \ln\dot\gamma}=\frac{\partial n_{\tau\dot\gamma}}{\partial \ln a_T} \tag{26}$$

The $m_{\tau\dot\gamma}-\ln a_T$ relations obtained by the $m_{\tau\dot\gamma}-\ln\dot\gamma_w$ lines (indicated by solid line) shown in Fig. 4, Eq. (12) and a_T shown in Fig. 3, are shown in Fig. 9 using the solid line. With increasing $\dot\gamma_w$, these $n_{\tau\dot\gamma}$, $m_{\tau\dot\gamma}-\ln a_T$ lines are located in the direction of decreasing $n_{\tau\dot\gamma}$ or $m_{\tau\dot\gamma}$. The inclination of the $m_{\tau\dot\gamma}-\ln a_T$ line agrees with the inclination of the $m_{\tau\dot\gamma}-\ln\dot\gamma_w$ line. This is validated by Eq. (27) obtained from Eq. (12). Eq. (28) is induced from Eqs. (25)～(27).

$$\frac{\partial m_{\tau\dot{\gamma}}}{\partial \ln \dot{\gamma}}=\frac{\partial m_{\tau\dot{\gamma}}}{\partial \ln a_T} \tag{27}$$

$$\frac{\partial n_{\tau\dot{\gamma}}}{\partial \ln a_T}=2\frac{\partial m_{\tau\dot{\gamma}}}{\partial \ln a_T} \tag{28}$$

The relationship between the $n_{\tau\dot{\gamma}}-\ln a_T$ lines and the $m_{\tau\dot{\gamma}}-\ln a_T$ lines agrees with the relation expressed by Eq. (28).

From the above results and the previous papers[12),24),26),27),35)], curves with respect to various flow indices, the temperature shift factors and the pressure shift factors etc. are shown schematically in **Fig. 10.** In this figure P_h means the hydrostatic pressure, a_P means the pressure shift factor, $a_{P\tau}$ means the pressure shift factor at constant shear stress, $a_{P\dot{\gamma}}$ means the pressure shift factors at constant shear rate, c means the blended fraction, a_c means the blended fraction shift factor. For instance, the indication "parameter: T" expressed in the schematic illustrations of Fig. 10 means that the illustrated curve is influenced by the T. However, the shifting direction of the curve is different depending upon the kind of material and the external operating conditions, and can not be easily decided. Therefore, "parameter: T" indicate that influencing factor with regard to the particular curve is T. The WLF equation[29),34),36),37)] which expresses a relation between a_T and T is well known for amorphous polymer. The formulae induced by combining the WLF equation and the formulae of flow indices have very wide applicability.

5. Conclusion

The investigation of flow characteristics, various temperature shift factors and various flow indices for polymer melts of PMMA lead to the following conclusions:

(1) The η_w dependence of $\dot{\gamma}_w$ differs from the η_w dependence of τ_w. The value of $a_{T\dot{\gamma}}$ is larger than the values of a_T and $a_{T\tau}$. Inclinations of the $a_{T\dot{\gamma}}-T$ lines are less than inclinations of the a_T, $a_{T\tau}-T$ lines.

(2) The various flow indices show relatively great dependence on $\dot{\gamma}_w$ or τ_w. The indices decrease with increase of $\dot{\gamma}_w$ or τ_w. In the measuring region, $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\ln \dot{\gamma}_w$ and $n_{\eta\dot{\gamma}}$, $m_{\eta\dot{\gamma}}-\ln \dot{\gamma}_w$ relations can be represented, respectively, by the straight line. $n_{\eta\tau}$, $m_{\eta\tau}-\ln \dot{\gamma}_w$ and $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\ln \tau_w$ relations are curvilinear, respectively. Inclinations of $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\ln \dot{\gamma}_w$ lines agree with inclinations of $n_{\tau\dot{\gamma}}$, $m_{\tau\dot{\gamma}}-\ln a_T$ lines.

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