THE EFFECTS OF TEMPERATURE AND PRESSURE ON THE LONGITUDINAL VOLUME VISCOS. (U) CONNECTICUT UNIV STORRS INST OF MATERIALS SCIENCE B S HSIAO ET AL. 30 JUL 87
The Effects of Temperature and Pressure on the Longitudinal Volume Viscosity of Two Model Polymers

by

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**Title:** The Effects of Temperature and Pressure on the Longitudinal Volume Viscosity of Two Model Polymers (Unclassified)

**Authors:** B. S. Hsiao, M. T. Shaw and E. T. Samulski

**Abstract:**
A method of studying dynamic longitudinal volume viscosity ($\eta^L$) at high pressure using a modified Instron capillary rheometer is demonstrated. Two model polymers were chosen as examples: an amorphous polysulfone and a semi-crystalline high density polyethylene.

$\eta^L$ was measured at fixed pressure using a continuous temperature sweep. The pressure ranged up to 2000 bar, while temperatures were swept through the liquid to solid transition for each of the materials. The effects of frequency (from 0.0125 to 0.125 Hz) and strain (0.06 to 0.24%) on $\eta^L$ were also investigated in both polymer systems. $\eta^L$ increased as the pressure was increased or the frequency was decreased (continued on reverse side).
19. ABSTRACT

In spite of the small strains employed, the viscosity was found to decrease as the strain was increased. The temperature-dependent $\eta_e$ varied with the nature of the transitions. In polysulfone, $|\eta_e|$ decreased sharply with temperature above the $T_g$. However, in polyethylene, a positive dependence of $|\eta_e|$ on temperature, limited to only a small temperature range above $T_m$, was observed. Under all conditions, $|\eta_e|$ varied over the range $10^2$ to $10^3$ Pa.s, a much smaller change than found in $\eta'$. 
THE EFFECTS OF TEMPERATURE AND PRESSURE ON THE
LONGITUDINAL VOLUME VISCOSITY OF TWO MODEL POLYMERS

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SYNOPSIS

A method of studying dynamic longitudinal volume viscosity ($\eta_v$) at high pressure using a modified Instron capillary rheometer is demonstrated. Two model polymers were chosen as examples: an amorphous polysulfone and a semicrystalline high density polyethylene.

$\eta_v$ was measured at fixed pressure using a continuous temperature sweep. The pressure ranged up to 2000 bar, while temperatures were swept through the liquid to solid transition for each of the materials. The effects of frequency (from 0.01 to 0.125 Hz) and strain (0.06 to 0.24%) on $\eta_v$ were also investigated. In both polymer systems, $\eta_v$ increased as the pressure was increased or the frequency was decreased. In spite of the small strains employed, the viscosity was found to decrease as the strain was increased. The temperature-dependent $\eta_v$ varied with the nature of the transitions. In polysulfone, $\eta_v$ decreased sharply with temperature above the glass transition temperature. However, in polyethylene, a positive dependence of $\eta_v$ on temperature, limited to only a small temperature range above $T_g$, was observed. Under all conditions, $\eta_v$ varied over the range $10^2$ to $10^3$ Pa.s, a much smaller change than found in $\eta'$.
INTRODUCTION

Dynamic longitudinal volume viscosity ($\eta_L^*$) can be expressed by the equation:\)

$$\eta_L^* = \frac{M'}{i\omega}$$  \hspace{1cm} [1]

where $M'$ is the complex bulk longitudinal dynamic modulus, and $\omega$ is the radial frequency. In general, $M'$ is defined as the modulus measured under compression (or tension), where the deformation is one-dimensional. In this study, $M'$ was measured by the axial compression of a cylinder confined by a rigid cylindrical wall.

$M'$ is a combination of shear modulus ($G'$) and bulk modulus ($K'$). It is given by

$$M' = K' + \frac{4}{3} G'$$  \hspace{1cm} [2]

Therefore, $\eta_L^*$ can be expressed by

$$\eta_L^* = \eta_K^* + \frac{4}{3} \eta_v^*$$  \hspace{1cm} [3]

The complex dynamic longitudinal volume viscosity is defined in the usual manner:

$\eta_L = \eta_L' + i \eta_L''$, where $\eta_L'$ is the viscous (in phase) component of $\eta_L^*$ and $\eta_L''$ is the elastic (out of phase) component. One can calculate the dynamic bulk viscosity from $\eta_L^*$ data using eq (1) if shear viscosity of the material is known.

Aleman et al.\textsuperscript{14,5} have recently studied the longitudinal volume viscosity ($\eta_L$) of epoxide prepolymer, poly (vinyl chloride) and poly (butylene terephthalate) with an Instron capillary rheometer. Assuming that polymer melts behaved similarly to a Voigt-Kelvin element, they calculated $\eta_L$ from the viscous component of the bulk volume modulus. They found that $\eta_L$ increased with an increasing compression rate, increasing temperature and decreasing strain.
In this paper, a novel technique will be introduced to measure the dynamic longitudinal volume viscosity; this technique uses a capillary rheometer, an instrument available in most of the polymer laboratories. No assumption of Voigt-Kelvin behavior is necessary. The transient longitudinal volume viscosity measured by Aleman is expected to behave differently than the \( \eta_L \) found in this research.

It was of particular interest to investigate the behavior of \( \eta_L \) through transitions, namely, a second-order and a first-order transition. From a molecular standpoint, longitudinal volume viscosity reflects both local motions as well as motions associated with entanglements and cross-links of the polymer molecules. One would expect to see an inherent distinction of the \( \eta_L \) behavior through different transitions. It is thus conceivable that \( \eta_L \) could be used to identify the transitions at high pressures.
EXPERIMENTAL PROCEDURE

Apparatus

A modified Instron capillary rheometer was used in this study; a detailed description was given previously. An APPLE II plus computer was adapted for system control and data acquisition, serving to collect sample temperature, heater temperature, volume change and pressure response, as well as to control the system temperature and pressure. In addition to measuring longitudinal volume viscosity, software was developed to conduct various other experiments, such as differential thermal analysis (DTA) and pressure-volume-temperature (P-V-T) analysis using temperature or pressure sweeps.

The maximum operating temperature of the modified capillary rheometer was 380°C, while the maximum pressure was 6000 bars (6 GPa). The heating rate of the experiment was programmable from 1°C min to 10°C min and the cooling rate from 1°C min to 3°C min via software. The temperature along the heater barrel would be held to within ±1°C. The accuracy of the pressure measurement was about 0.5% and that of the volume measurement about 0.1%. The data collected on the microcomputer were transferred to an IBM 3054 for further analysis.

Materials and Specimen Preparation

The chosen amorphous system was polysulfone (PSF). This particular polysulfone was purchased directly from Modern Plastics Co., Bridgeport CT, in the shape of a rod; it was identified as similar to Union Carbide's P-1700 polysulfone** by NMR, FTIR, solution viscosity and DSC analysis. This polysulfone is derived from bisphenol A and 4,4'-dichlorodiphenylsulfone. The glass transition temperature ($T_g$) of this PSF, measured via a Perkin Elmer DSC 2 at a heating rate of 5°C min, was about 185°C. $T_g$ was defined as the temperature corresponding to the first change in slope of the heat capacity thermogram. The PSF rods were machined down to the size of the inner diameter of the Instron barrel and vacuum dried at 140°C for 24 hours. Each rod weighed about 20 grams.
Semcrystalline high density polyethylene (HDPE) rods were supplied by AIN Plastics Co, N.Y.; its $M_n$ is about 181,000 g/mole determined by GPC analysis calibrated with the polystyrene standards. The melting temperature ($T_m$) of this HDPE, measured at the heating rate of 5°C/min, was 135°C. $T_m$ was taken as the peak temperature of DSC enthalpy thermogram. The crystallinity of this HDPE is approximately 82%. Specimens were prepared similarly to those made from PSF.

**Rheological Measurements**

Both materials' shear responses were characterized by a Rheometrics System 4. The dynamic shear modulus was measured at a fixed strain (0.24%), fixed frequency (1 Hz) and under negative temperature sweep to mimic the conditions typically used for bulk longitudinal volume viscosity runs. Two test fixtures were used, a parallel plate for the melts and a rectangular bar for the solid specimens.

For the bulk longitudinal viscosity measurements, the materials were first heated to the melt state at a rate of 3°C/min under high pressure. During the heating process, the high pressure DTA thermogram and P-V-T data could be gathered. This information was used to characterize the system at high pressure. After annealing at the first temperature for 30 minutes, data was taken as described below. It was anticipated that the annealing would erase the previous thermal history of the specimen. The specimen was cooled at a rate of 2°C/min to the next temperature, where it was held for 5 minutes before measurements were taken.

To measure $\eta_L$, a constant-frequency sawtooth volume deformation was applied to the specimen. A typical example of this volume deformation and its pressure response is shown in Figure 1. The data rate was typically 4 points per second.

Both pressure and volume responses were normalized by dividing by the average pressure ($P_{av}$) and average volume ($V_{av}$) respectively. $P_{av}$ and $V_{av}$ are the mean values of pressure and volume responses. To these normalized responses, Fourier series were fitted using IMSL subroutine FFTSC. This procedure is illustrated in Figure 2, where the normalized pressure and volume
responses are shown along with the fundamentals of the respective Fourier series. The magnitude of $\eta^*_L$ was then calculated by:

$$|\eta^*_L| = \frac{\Delta P}{\Delta V_v \omega} \frac{1}{\omega} = \frac{P_1}{V_1} \frac{P_{ave}}{\omega}$$

[4]

where $\Delta P$ is the amplitude of the pressure fundamental, $\Delta V$ is the amplitude of the volume fundamental, $P_1$ is the amplitude of the fundamental of the Fourier series of the pressure response, $V_1$ is that for the volume and $\omega$ is the radial frequency. The viscous (in phase) part of $\eta^*_L$ was then determined by:

$$\eta_L' = |\eta^*_L| \sin \delta$$

[5]

where $\delta$ is the phase angle between the pressure and volume fundamentals.

In this study, four frequencies were investigated, namely 0.0125, 0.025, 0.0625 and 0.125 Hz; pressure was ranged from 500 bar to 2000 bar; and three strains were examined (0.06%, 0.12% and 0.24%). The strain referred here was the ratio of the volume change ($\Delta V$) to the average volume ($V_{ave}$). These conditions covered approximately the capabilities of the instrument.
RESULTS AND DISCUSSIONS

Polysulfone

Temperature Effects

An example of the longitudinal volume viscosity vs. temperature response for PSF is shown in Figure 3. The upper curve is the magnitude of $\eta_L' (|\eta_L^2|)$ while the lower one is $\eta_L$. For discussion, this curve can be divided into four regions. In region 1, at high temperature, a positive dependency of $\eta_L'$ on temperature is exhibited. This effect has tentatively been assigned to a failure to achieve thermal or mechanical equilibrium at the beginning of the experiment. In region 2, the melt range, the influence of temperature on $\eta_L^2$ is in the expected direction. A comparison of this dependence and the temperature dependence of steady shear viscosity ($\eta_s$) for PSF, published by Shaw and Miller, is shown in Figure 4. $|\eta_L^2|$ has a smaller temperature dependence than $\eta_s$ and $\eta'$ (compare Figure 5 with Figure 3). In this region, $\eta_L'$ dominates $\eta_L^2$, while the elastic contribution is small. The ratio of $|\eta_L^2|$ to $|\eta'|$ is about $10^6$. In region 3, the material passes through its $T_g$ and $|\eta_L^2|$ approaches a plateau while $\eta_L'$ passes through a maximum, as does $\eta'$ (in Figure 5) or $\eta_s$. In region 4, the glass state, the response is primarily elastic and insensitive to temperature. The peak temperature of $\eta_L'$ in region 3 is assigned logically to the glass transition temperature ($T_g$) during the cooling process. It is observed that, under 2000 bar, this $T_g$ (242 °C) is lower than the $T_g$ (292 °C) determined previously during a positive temperature sweep, which is not unexpected.

Pressure Effects

The effect of pressure on $\eta_L^2$ is shown in Figure 6 ($|\eta_L^2|$ vs. $T$) and Figure 7 ($\eta_L'$ vs. $T$). The pressures range from 500 bar to 2000 bar. According to these figures, $|\eta_L^2|$ increases as the pressure is increased, and the peak temperature of $\eta_L'$ is shifted to higher temperatures. The shift rate was about 22° C/kbar, compared to a $dT_g/dP$ rate of 45° C/kbar found from P-V-T measurements. All the $T_g$ values are listed in Table 1. The glass temperatures, measured from both paths, are dependent on the thermal history and pressure effects on the specimens. These have been discussed before.
Frequency Effects

In spite of the narrow achievable frequency range (0.0125 to 0.125 Hz), the influence of frequency on the components of $\eta_L$ was found to be significantly negative. This can be seen in Figure 5 ($|\eta_L|^2$ vs. $\tau$) and Figure 9 ($\eta_L^\prime$ vs. $\tau$). Again, this behavior is similar to that of the complex shear viscosity. Because the components of $\eta_L$ are approximately dependent on the inverse first power of frequency, the longitudinal modulus ($|\mathcal{M}^1|)$ of the solid is roughly constant. $T_s^\prime$ also increased slightly with frequency, an effect which has been confirmed in other polymers.\textsuperscript{10}

Strain Effects

The influence of strain on $\eta_L$ was determined by crossplotting $\eta_L$ temperature sweeps taken at various fixed strains. The $|\eta_L|^2$ vs. strain response in Figure 10 shows a significant decrease of $|\eta_L|^2$ with strain; $\eta_L^\prime$ exhibited the same behavior. This observation confirms the reports of Aleman et al. that $\eta_L$ increases with a decrease in the compression ratio (same as the strain). In the strain investigated (0.06 to 0.12%), one expects linear behavior for the shear response. It is believed that part of this nonlinearity is due to the inherently nonlinear relations between the pressure and volume, which will be discussed next, while the other part might be purely geometrical.

Intrinsic Nonlinearity

To demonstrate the nonlinear strain dependence of the longitudinal volume viscosity, we start the discussion with a general form of the linear stress-strain relation:\textsuperscript{1}

\[
\sigma_y = \int_{-\infty}^{t^\prime} \left( G(t - t') \gamma(t) - \frac{1}{3} \sum_{k=1}^{k} \gamma_{kk}(t') \delta(t') \right) + \frac{3}{2} K(t - t') \frac{1}{3} \sum_{x=1}^{x} \gamma_x(t') \delta(t') \right) \right)d\tau' \]

Equation 6 can be then reduced to:

\[
\sigma_{T^\prime} = \frac{2}{3} \int_{-\infty}^{t^\prime} G(t - t') \gamma(t') \right)dt' + \frac{1}{2} \int_{-\infty}^{t^\prime} K(t - t') \gamma(t') \right)dt' \]

\[ \text{Equation 7} \]
Since in the melt region, \( K(t) >> G(t) \), the following relation holds.

\[
\sigma_T = \frac{1}{2} \int_{-\infty}^{t'} K(t - t')\dot{\gamma}(t')dt'
\]  

[8]

Assuming that the polymer melt behaves like a single Maxwell element,

\[
K(t) = K_0e^{-\frac{t}{\tau}}
\]  

[9]

Here \( K_0 \) is a constant and \( \tau \) is the relaxation time. Equation 8 and 9 can be combined, giving:

\[
\sigma_T = \frac{1}{2} \int_{-\infty}^{t'} K_0e^{-\frac{t}{\tau}}\dot{\gamma}(t')dt'
\]  

[10]

Additionally, two assumptions were made to simplify the above relations. Firstly, \( \tau \) was assumed to be a linear function of the pressure (P):

\[
\tau = \alpha P + \tau_o
\]  

[11]

and secondly, P was proportional to the strain, \( \gamma (P \propto \gamma) \), so that,

\[
\tau = \alpha'\gamma + \tau_o
\]  

[12]

Where \( \alpha, \alpha' \) and \( \tau_o \) are constants. Equation 10 can be expressed as

\[
\sigma_T = \frac{1}{2} \int_{-\infty}^{t'} K_0e^{-\frac{t}{\alpha'\gamma + \tau_o}}\dot{\gamma}(t')dt'
\]  

[13]

Using equation 13, we integrated numerically over the sawtooth strain history, knowing that the material was underformed at \( t < 0 \). With the suitable constants (\( K_0, \alpha' \) and \( \tau_o \)) chosen, the pressure response was calculated and the reduced pressure was illustrated in Figure 11, where \( \gamma(t) \) was a triangle longitudinal deformation, simulating the typical strain deformation in the experiment. This calculated pressure qualitatively resembled the experimental pressure responses in Figure 1. Utilizing the analytical procedures described previously, \( |\eta_L^*| \) and \( \eta_L^* \) were calculated from equation 13 at various strains. Not surprisingly, the results revealed a nonlinear strain dependence of the longitudinal volume viscosity. Both \( |\eta_L^*| \) and \( \eta_L^* \) decreased rapidly with increasing strain. Only at very low strains (\( < 0.0001 \)) did the viscosity approach an asymptotic value.
In summary, it can be shown by making reasonable assumptions that the dynamic longitudinal volume viscosity will appear to be nonlinear because of the asymmetry of the pressure over the deformation cycle. Linear behavior is expected only at very low strains, whereas convenient experimental strains are beyond this region.

**High Density Polyethylene**

Temperature Effects

An example of the temperature response of the dynamic complex longitudinal volume viscosity of HDPE is shown in Figure 12. The upper curve is $|\eta_L^*|$ while the lower one is $\eta_L'$. From this figure it can be seen that the behavior of both components of $\eta_L^*$ is distinctively different than that of the shear response shown in Figure 13. Again, the magnitude of longitudinal volume viscosity exhibited a much narrower range than the equivalent shear properties.

For the purpose of discussion, Figure 12 can be divided into three regions. In region 1, the melt region, a different behavior is observed compared to that of PSF. As the temperature is lowered, $|\eta_L^*|$ remains almost constant until region 2, the melting transition, is reached. In region 2, the material passes through a minimum near its crystallization temperature and $|\eta_L^*|$ is found to decrease with decreasing temperature. This confirms Aleman et al.'s observation that temperature has a positive effect on the longitudinal volume viscosity. However our data indicate that this effect occurs near the crystallization transition temperature only. In region 3 (solid region), the behavior of $|\eta_L^*|$ is somewhat similar to that of solid PSF, in that the viscous part ($\eta_L^*$) no longer dominates. However, unlike PSF, the elastic contribution increases rapidly as temperature decreases.

Pressure Effects

As with PSF, pressure had a positive effect on the longitudinal volume viscosity of HDPE. This is shown in the Figures 14 and 15, for $|\eta_L^*|$ and $\eta_L'$ respectively. $|\eta_L^*|$ increased with increasing pressure and the minimum was shifted to higher temperature by pressure. This shift rate was about 10°C min, which is lower than the shift rate of the melting point due to pressure. The
crystallization temperatures and the melting temperatures are listed in Table 2. The pressure dependencies of the above transition temperatures again are different.

**Frequency Effects**

Figures 16 and 17 display the effect of frequency on $|\eta_L|$ and $\eta_L'$ respectively. It was observed that both components of $\eta_L$ decreased with increasing frequency. This behavior was similar to that of PSF. The crystallization temperatures appeared to be insensitive to frequency. In the solid-state region, frequency had a negative effect on $|\eta_L|$; again, $|M'|$ (longitudinal bulk volume modulus) remained about constant.

**Strain Effects**

The strain dependence on the longitudinal volume viscosity of HDPE was examined by cross-plotting the $|\eta_L|$ vs. temperature diagrams at various fixed strains. The result is shown in Figure 18. From this figure, it can be seen that a negative correlation exists between strain and both components of $\eta_L$. This once more indicated that a intrinsic nonlinearity exists in the longitudinal volume viscosity. Aleman and his coworkers have reported a similar strain effect.\(^\text{3,45}\)
CONCLUSIONS

In this paper, a modified Instron capillary rheometer was used to measure the complex dynamic longitudinal volume viscosity ($\eta_L$) of polymers. Two model polymer systems were investigated: an amorphous polysulfone and a semi-crystalline high density polyethylene. In both systems, all components of $\eta_L$ increased with pressure, and decreased with frequency and strain. The negative strain dependence of $\eta_L$ at very low strains could be explained as an artificial consequence of the geometry. The two materials exhibited different behavior near their transitions. In PSF, temperature had a negative effect on both components of $\eta_L$, resembling the behavior of the complex dynamic shear viscosity ($\eta'$) in polymer melts. A maximum of $\eta_L$ corresponded to the glass temperature. In HDPE, a positive temperature effect was observed just above the transition temperature region. A minimum in $\eta_L$ was observed, corresponding to the crystallization temperature of HDPE.

ACKNOWLEDGEMENT

Financial support for this research by the DARPA ONR Contract N00014-86-K-0772 is greatly acknowledged.
FIGURE CAPTIONS

Figure 1. Volume deformation and the corresponding pressure response of HDPE at of 150°C.

Figure 2. The normalized volume and pressure responses along with their Fourier series' fundamentals.

Figure 3. The longitudinal volume viscosity vs. temperature diagram of PSF. The pressure is 2000 bar, frequency is 0.0625 Hz and strain is 0.24%. The upper curve is $|\eta_L|$ and the lower one is $\eta_L'$.

Figure 4. Temperature dependence of $|\eta_L|$ in Figure 3, compared with that of $\eta_\alpha$, calculated from the Arrhenius relationship for PSF published by Shaw and Miller.

Figure 5. Shear modulus against temperature diagram for PSF. The strain is 0.24%, frequency is 1 Hz. The upper curve is $|\eta'|$ and the lower one is $\eta'$.

Figure 6. The pressure dependence of $|\eta_L|$ for PSF. The strain is 0.24% and frequency is 0.0625 Hz.

Figure 7. The pressure dependence of $\eta_L'$ for PSF. The strain is 0.24% and frequency is 0.0625 Hz.

Figure 8. The effect of frequency on $|\eta_L|$ for PSF. The pressure is 2000 bar and strain is 0.12%.

Figure 9. The effect of frequency on $\eta_L'$ for PSF. The pressure is 2000 bar and strain is 0.12%.

Figure 10. The effect of strain on $|\eta_L|$ for PSF. The pressure is 1500 bar and frequency is 0.0625 Hz.
Figure 11. Reduced pressure responses calculated by equation 14, where \( \gamma(t) \) is a triangle deformation, and frequency = 0.625 s\(^{-1} \), strain = 0.0012. \( K_s = 1 \times 10^6 \) Pa, \( \omega' = 0.125 \times 10^4 \) s, \( \rho_m = 1 \times 10^4 \) Pa, \( \tau_s = 5s \)

Figure 12. The longitudinal volume viscosity vs. temperature diagram of HDPE. The pressure is 1000 bar, frequency is 0.0625 Hz and strain is 0.24%. The upper curve is \( |\eta'_L| \) and the lower one is \( \eta'_L \).

Figure 13. Shear modulus vs. temperature diagram for HDPE. The strain is 0.24%, frequency is 1 Hz. The upper curve is \( |\eta'_L| \) and the lower one is \( \eta'_L \).

Figure 14. The pressure dependence of \( |\eta'_L| \) for HDPE. The strain is 0.24% and frequency is 0.0625 Hz.

Figure 15. The pressure dependence of \( \eta'_L \) for HDPE. The strain is 0.24% and frequency is 0.0625 Hz.

Figure 16. The effect of frequency on \( |\eta'_L| \) for HDPE. The pressure is 1000 bar and strain is 0.06%.

Figure 17. The effect of frequency on \( \eta'_L \) for HDPE. The pressure is 1000 bar and strain is 0.06%.

Figure 18. The effect of strain on \( |\eta'_L| \) for HDPE. The pressure is 1000 bar and frequency is 0.0625 Hz.
REFERENCES


Table 1. $T_s$'s measured in PSF

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1. $T_s$(HPDTA): $T_s$ measured from high pressure differential thermal analysis
2. $T_s'$(ηl): $T_s$ measured from longitudinal volume viscosity
Table 1. $T_a$ and $T_e$ measured in HDPE

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1. $T_a$ (HPDFA): $T_a$ measured from high pressure thermal analysis
2. $T_e$ ($\eta_L$): $T_e$ measured from longitudinal volume viscosity
Longitudinal deformation

Pressure response

Fundamentals of Fourier series

Volume

Pressure
The diagram shows the relationship between flow behavior index (n) and shear rate (\dot{\gamma}) at different temperatures: 250°C, 275°C, 300°C, and 325°C. The x-axis represents \log(\dot{\gamma}) and the y-axis represents the strain (%). The data points indicate a decrease in flow behavior index as the shear rate increases, with higher temperatures showing a more pronounced effect on the flow behavior index.
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