

Nonlinear Maxwell behavior of sodium silicate glass in the surroundings of glass transition temperature

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Presented are results from uniaxial cylinder upsetting tests of sodium silicate glass at different constant deformation rates each combined with relaxation experiments in the temperature range 480 to 580°C. Due to the complete stress relaxation to final load zero (vanished carrying capacity) also below glass transition temperature T_g , it follows Maxwell behavior in principle. But the rheological analyses of loading and unloading experiments together show that only nonlinear Maxwell model approaches can adequately describe the deformation behavior of the glass in the surroundings of T_g .

1. Introduction

It is a well-known fact that glass is brittle below T_g . That means in a macroscopic deformation experiment, e.g. at room temperature, the deformation behavior shows either absolute elasticity up to the fracture limit in uniaxial tension or compression tests or the well-known cone fissurations typical of Hertzian contact experiments. Moreover, with respect to the Vogel-Fulcher-Tammann equation the viscosity reaches infinity already at $T_0 \approx 285^\circ\text{C}$ for sodium silicate glasses [1 to 3]. But for all that there exist empirically based proposals for the viscosity number at room temperature from 10^{20} up to 10^{40} Pa s [4 to 5]. Permanent imprints without cracks in glass will be found by indentation test with sharp indenters, indicating a T_g -viscosity number of $\eta = 10^{12.3}$ Pa s according to the definition of the viscosity limit given by Tammann [6]. One possible explanation of this exceptional behavior is the reduction in viscosity under high contact pressure, which is realizable due to the high strength of glass [7].

The aim of this work is to investigate the temperature dependence of the deformation behavior of sodium silicate glass with respect to viscoelastic analysis by a pressure deformation of cylinder samples or a test working like a parallel plate viscometer described in the literature [8] within a temperature range of 480 to 580°C ($T_{\text{exp}} \approx (1 \pm 0.1) \cdot T_g$). To secure the viscoelastic analysis the experimental setup of Brückner et al. [9 to 12] was improved by an electronic control of the deformation velocity of the sample itself. Moreover a stress relaxation experiment with an abrupt stop of the deformation velocity was added after the loading part with a constant deformation velocity.

The analysis of the behavior of viscosity is based on rheological models of the visco-elastic solid states and the viscoelastic liquid state.

2. Theoretical

The method of the pressure deformation of compact cylindrical glass samples corresponds to the parallel plate viscometry. For the latter, Gent [13] has derived a relation for calculating the viscosity η_G (Gent viscosity):

$$\eta_G = \frac{F}{3\dot{h}V \left(\frac{1}{h^2(t)} + \frac{V}{2\pi h^5(t)} \right)}, \quad (1)$$

where F is the force, \dot{h} the deformation rate, V the volume of the sample, and $h(t)$ the actual length of the sample at time t . It is assumed that during deformation the volume of the sample

$$V = A_0 h_0 = 2\pi \cdot r^2(t) \cdot h(t), \quad (2)$$

where A_0 is the cross section of the sample, h_0 the length at time $t = 0$ and $r(t)$ the actual radius, will not be changed, as it would be in the case of plastic deformation behavior found on the dislocation model. Only if the glass deformation is purely viscous, equation (1) can be used to calculate the viscosity η . Note that elastic parts of the deformation are not taken into account.

Therefore viscoelastic material behavior was simulated using rheological modeling technique. The arrangement of rheological bodies leads to the following differential equation for the stress σ , the deformation ε and their time derivatives [14 to 16]:

$$\sigma + a_1 \cdot \dot{\sigma} + a_2 \cdot \ddot{\sigma} = b_0 \cdot \varepsilon + b_1 \cdot \dot{\varepsilon} + b_2 \cdot \ddot{\varepsilon}. \quad (3)$$

Table 1. Coefficients of the differential equation (3) of the rheological models investigated

model	a_1	a_2	b_1	b_2	b_3
viscoelastic solid state					
Maxwell	$\frac{\eta}{E}$	0	0	η	0
Double Maxwell	$\frac{\eta_1}{E_1} + \frac{\eta_2}{E_2}$	$\frac{\eta_1 \eta_2}{E_1 E_2}$	0	$\eta_1 + \eta_2$	$\frac{\eta_1 \eta_2}{E_1} + \frac{\eta_1 \eta_2}{E_2}$
Double Maxwell and spring	$\frac{\eta_1}{E_1} + \frac{\eta_2}{E_2}$	$\frac{\eta_1 \eta_2}{E_1 E_2}$	E_3	$\eta_1 + \frac{n_1 E_3}{E_1} + \eta_2 + \frac{n_2 E_3}{E_2}$	$\frac{\eta_1 \eta_2}{E_1} + \frac{\eta_1 \eta_2}{E_2} + \frac{\eta_1 \eta_2 E_3}{E_1 E_2}$
Zener-Kelvin	$\frac{\eta}{E_1 + E_2}$	0	$\frac{E_1 E_2}{E_1 + E_2}$	$\frac{E_2 \eta}{E_1 + E_2}$	0
Zener-Maxwell	$\frac{\eta_1}{E_1}$	0	E_2	$(E_1 + E_2) \frac{\eta_1}{E_1}$	0
viscoelastic liquid state					
Jeffreys	$\frac{\eta_1}{E_1}$	0	0	$\eta_1 + \eta_2$	$\frac{\eta_1 \eta_2}{E_1}$

The meaning of the parameters a_i and b_i for the rheological models of viscoelastic solid states (Maxwell, Double Maxwell, Double Maxwell and spring, Zener-Kelvin, Zener-Maxwell) and the viscoelastic liquid state (Jeffreys) is summarized in table 1.

The point is that we analyze the experimental data of the loading and the relaxation part combined together: in the loading part with $\dot{\varepsilon} = \dot{\varepsilon}_0$ const. and $\varepsilon = \dot{\varepsilon}_0 \cdot t$ for $t \leq t_f$, and in the relaxation part with $\varepsilon = \varepsilon(t = t_f) = \varepsilon_f$ const. for $t \geq t_f$, where t_f is the time of the end of the loading part. A combination of the several solutions with $\varepsilon_0 = \dot{\varepsilon}_0 \cdot t_f$ and $\sigma_0 = \sigma_f$ for $t = t_f$ yields a relation that allows a complete characterization of the whole experiment, loading and relaxation. For instance in the case of the Zener-Maxwell model, one obtains the relation

$$\sigma(t) = E_2 \varepsilon_0 + \eta \dot{\varepsilon}_0 \left(1 - e^{-\frac{E_1 t_f}{\eta}} \right) e^{-\frac{E_1 (t-t_f)}{\eta}}. \quad (4)$$

3. Experimental

The pressure deformation of cylinder samples was performed in the material testing machine MTS 810 (MTS Systems Corporation, Minneapolis, MN (USA)). To realize our claim of a temperature and deformation rate controlled experiment, we developed a high temperature unit integrated in the deformation system which guarantees constancy of deformation temperature better than 1 K. The piston is coupled with a ceramic compression bar at the lower compression plate, which is introduced into the temperature chamber. The upper compression bar is coupled with the load cell and modified for using an inductive displacement transducer. This experimental configuration allows, with a special arrangement of ceramic sensing devices, the measurement of sample length h directly and therefore permits a controlling sensitivity better than 1 μm . This is the main advantage for feedback control of the sample deformation with defined deformation rate \dot{h} .

The deformation of the glass cylinders was performed at various temperatures within the range of 480 to 580 °C. Principally the test can be carried out with various deformation rates in the range of $4 \cdot 10^{-3}$ to $4 \cdot 10^{-8} \text{ s}^{-1}$. To avoid crack formation, the deformation rate must be limited up to a critical value which increases with increasing test temperature.

In this configuration, just as in a parallel plate viscometer, cylindrical samples of sodium silicate glass in the composition (in wt%) 73 SiO₂, 15.5 Na₂O, 6.2 CaO, 4.1 MgO, 0.7 Al₂O₃, 0.2 SO₃, 0.2 K₂O, and 0.1 Fe₂O₃ were investigated. The samples were cut from glass plates using a diamond core drill. The geometrical parameters of these glass cylinders are (5.6 ± 0.2) mm in diameter and (7.5 ± 0.2) mm in height. All samples were cleaned with alcohol, ground and tempered for 4 h at 530 °C for homogenization. The samples were cooled down to room temperature at 1 K/min. Then they were transferred into the parallel plate viscometer and heated-up to test temperature in thermal contact with the compression plates using a small preload of 5 N. The test was started after 1 h waiting time for thermal homogenization.

4. Results and discussion

Compression tests free of cracks should be conducted in the range of linear Newtonian viscosity η_0 . Here the stress is directly proportional to the deformation rate $\dot{\varepsilon}$. Tests in the non-Newtonian range of viscosity lead to enhanced cracking-fissuration and therefore the given deformation rate has to be adjusted to each temperature. On the other hand the sample deformation rates must not be too small for a given temperature; so that the associated viscosity induces a flow velocity which will be high enough for the adequate carrying capacity.

Figure 1 shows exemplarily in a stress-time diagram the deformation of glass cylinders at 540 °C for several sample deformation rates \dot{h} followed by a relaxation part. For rea-

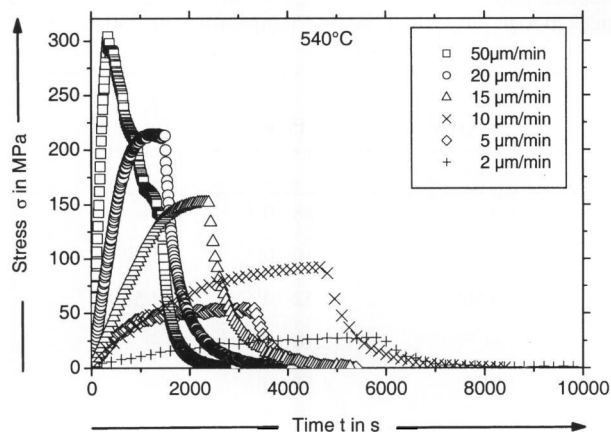


Figure 1. Measured stress-time dependence of cylinder compression experiments for different deformation rates at a temperature of 540°C. In reality the recorded point density is much higher.

sions of clarity, the error bar recordings amounting to 5% are ignored. After an initial increase in linear stress no further changes in stress are found, indicating equilibrium of the viscoelastic deformation processes in the glass; i. e. a quasi-stationary flow is established. For small deformation rates (2, 5, 10 μm/min) the condition of linear viscous equilibrium will be reached only after a very long time (not shown in figure 1). At the highest deformation rates (here 50 μm/min) the crack begins formation coupled with abrupt stepwise stress drop down. Sometimes the samples are partly destroyed by spalling of pieces of glass.

This critical velocity range of beginning brittle deformation behavior characterizes the transition from a Newtonian to a non-Newtonian behavior. This is also indicated by a striking effect: at 50 μm/min and $T = 550^\circ\text{C}$ the stress is linearly increasing up to a stress maximum and then is reduced to a nearly equilibrium stress state. This overshoot of the stress is really an indication of stress reduction due to non-Newtonian flow behavior [9]. The non-Newtonian behavior will probably be accompanied with first crack formation. As a consequence, this fact is used to restrict the upper deformation rate.

To calculate the Gent viscosity η_G corresponding to equation (1) all experimental data sets of the measurements that have a marked equilibrium course are used. It is remarkable that only in this range, when the viscoelastic process in the glass is obviously in equilibrium state, Gent's equation (1) is suitable. However, this equation is not suitable during the initial deformation process from the starting point to the achievement of the equilibrium state. Due to the limitation on the range of quasi-stationary flow, the Gent viscosity η_G is in accordance with the Newtonian viscosity η_0 . Figure 2 shows the viscosity numbers η_G , calculated with respect to equation (1), depending on temperature T . The values show a close match with the values obtained independently by standard bending tests of glass bars¹⁾.

To describe the temperature dependence of the viscosity, the Arrhenius equation

¹⁾ Measured by INM Saarbrücken.

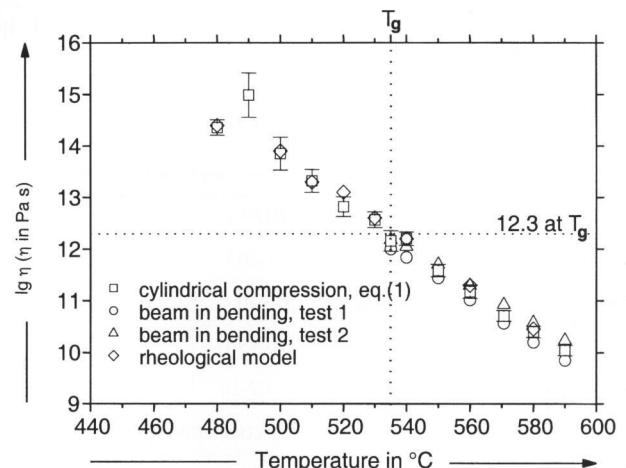


Figure 2. Viscosity parameters of beam bending experiments in comparison to those of the cylinder compression experiments analyzed by equation (1). Additionally plotted are the values of the viscosity received from the Maxwell model.

$$\eta = f(T) = \eta_L \cdot \exp[-E_\eta / (RT)] \quad (5)$$

is used. E_η is the activation energy of the rate controlling process for the movement of the elementary glass units determining the viscosity by the temperature T . The η_L describes the viscosity at infinite temperature and leads by extrapolation to room temperature, and thus to $\eta_L = 10^{25.3}$ Pa s. This value is formally equivalent to the empirical proposal for the viscosity number, see [4]. For the cylinder compression of the glass $E_\eta = 6.05$ eV (= 581 kJ/mol) is obtained. The value corresponds to the literature [1].

Using for the analysis the VFT equation, the Vogel temperature T_0 results in $T_0 = 286^\circ\text{C}$ and parameters of $A = 0.653$ and $B = 2869$ are obtained.

The analysis of the experimental results on the basis of the rheology starts with the assumption that the same elementary units contribute to flow processes as in loading and relaxation processes. Therefore, for the description of the mechanical behavior of the glass cylinders the complete information of both, the compression part and the relaxation part [8], is used. It is remarkable that our experimental conditions prevent the difficulties connected with the step load increment for the perfect relaxation experiment. As listed in table 1, the treated rheological models of the viscoelastic solid states and the viscoelastic liquid state, respectively, describe the results of our viscosimeter experiments in a good manner.

However, we also find that the nonlinear fitting procedure leads to simple values of the model parameter elasticity and viscosity. That means in the rheological models with more than one element of elasticity and/or viscosity, one value from the elastic and one from the viscous parameter trends towards zero. Or, in the case of the "Double Maxwell and spring" model the same amount is partly divided up into the elastic terms and the viscosities, respectively (see table 2). Consequently, only the standard Maxwell model seems justifiable from the rheological point of view. Besides others, there are obtained small but systematic deviations. In detail one observes for the rheological analysis of the load displacement curves below T_g an excellent agreement of the loading curve and in the beginning

Table 2. Calculated coefficient data sets of the investigated rheological models of table 1 for the temperature of 540°C and a deformation rate of 5 μm/min

model	E_1 in GPa	E_2 in GPa	E_3 in GPa	η_1 in Pa s	η_2 in Pa s
viscoelastic solid state					
Maxwell	10.013	—	—	$4.58 \cdot 10^{12}$	—
Double Maxwell	11.203	$1.49 \cdot 10^{-6}$	—	$5.10 \cdot 10^{12}$	$5.60 \cdot 10^{-6}$
Double Maxwell and spring	0.140	5.494	5.508	$2.52 \cdot 10^{12}$	$2.53 \cdot 10^{12}$
Zener-Kelvin	10.790	$1.00 \cdot 10^{-10}$	—	$5.10 \cdot 10^{12}$	—
Zener-Maxwell	$1.02 \cdot 10^{-11}$	10.015	—	$4.58 \cdot 10^{12}$	—
viscoelastic liquid state					
Jeffreys	10.010	—	—	$4.58 \cdot 10^{12}$	$4.94 \cdot 10^{-11}$

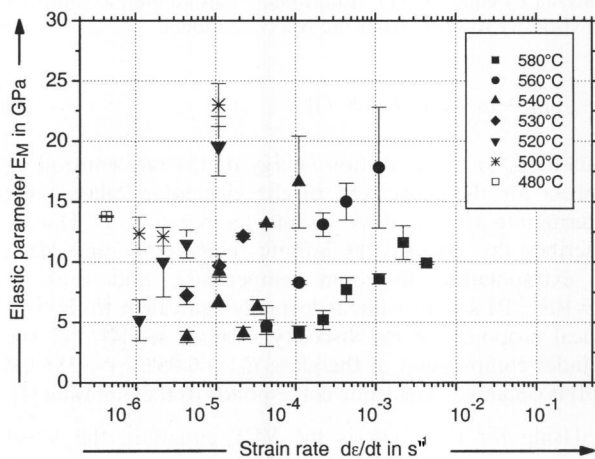


Figure 3. Increase of elastic parameters of the Maxwell model in dependence on strain rates in the investigated temperature range $T_{exp} \approx (1 \pm 0.1) \cdot T_g$.

region of the relaxation a negligible worse adjustment. Above T_g it is contrary; the relaxation part is in better agreement than the loading part.

For different deformation rates in the temperature range 480 to 580°C, the obtained elastic Maxwell parameters E_M are plotted in figure 3. These values are not comparable with Young's modulus found by Bornhöft and Brückner [17] who have determined them by ultrasonic method for which naturally glass melts show absolute rigidity. At the moment of loading in the glass cylinder compression test the deformation is determined by the simultaneous action of both, elasticity and viscosity. The slope of the loading rise decreases at constant deformation rate with decreasing viscosity. Within a temperature state a reduction in the elastic parameter by decreasing the deformation rate is obtained. This effect occurs when the inherent velocity of relaxation is greater than the deformation rate. Otherwise, the sample appears stiffer.

The viscosity parameters from the rheological description of the experimental curves obtained by the Maxwell model are plotted in figure 2 additionally. These values are in very good agreement with the viscosity numbers determined by Gent's equation (1).

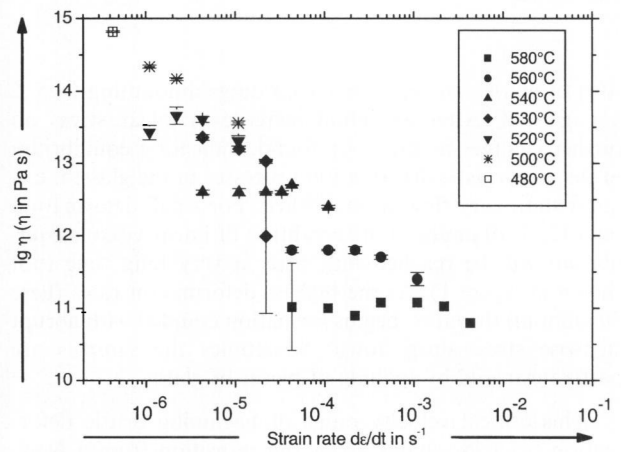
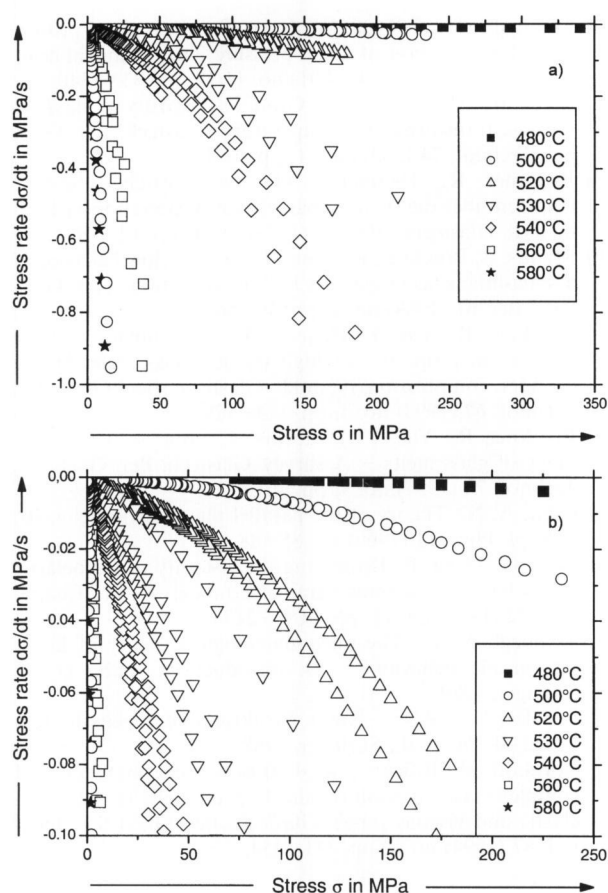


Figure 4. Viscosity parameters of the Maxwell model are shown in dependence on strain rates in the investigated temperature range $T_{exp} \approx (1 \pm 0.1) \cdot T_g$.

Figure 4 shows the dependence of the calculated viscosity numbers on the deformation rate in detail. As it has been expected, the viscosity number is a function of the temperature only. Deviation from the equilibrium values takes place at a critical upper limit for the deformation rate (figure 1) after which an increase of the deformation rate leads to a noticeable reduction in the viscosity of the glass. The reaction time of the glass units on the outer mechanical loading is too long and makes shaping difficult, as the increasing elasticity shows at the same deformation rates (figure 3). It causes an additional internal friction associated with an increase in the inside temperature. However, it is obvious that it is a local difference because cracks and glass melt flaws are detectable, respectively. It changes the equilibrium state of flow into an inhomogeneous metastable flow state. In dependence on temperature a boundary is obtained which appears insensitive to a rising of the deformation rate.

For reasons of the detected dependence of the elastic Maxwell parameter on the deformation rate, such as in the case of the loading rate, we investigated the relaxation behavior in the primary version. That means, the time derivative of the Maxwell approach is written

$$\sigma = \sigma_0 \cdot e^{-t/\tau} \quad (6)$$



Figures 5a and b. Stress rate versus stress yielding nonlinear aspects in the investigated temperature region at all stress rates (figure a) and at lowest stress rates (figure b).

and yields

$$\dot{\sigma} = -\frac{\sigma}{\tau} \quad (7)$$

The graphical plots of the data (figures 5a and b) show a definitely nonlinear correlation in the whole investigated temperature region for all stress rates. That means, the relaxation time $\tau = \eta/E$ itself is dependent on velocity. This is in contradiction to the expected Maxwell behavior.

Since all the models are reduced to the Maxwell behavior, a nonlinear Maxwell model is needed, which is given in a first approximation by the well-known approach of Kohlrausch-Williams-Watts (KWW). Figure 6 compares the relaxation dataset at a temperature where Maxwell behavior seems a good description, and the fit by KWW. The latter yields a better adjustment, mainly due to an additional exponent. So all we obtain is an additional term which is itself dependent on the deformation rate, i.e. the stress rate. And it does not change anything concerning the dependence of the elastic parameters or respective relaxation time on the velocity.

5. Summary

The investigation of glass was carried out using a parallel plate viscometer at temperatures from 480 to 580 °C. Rheol-

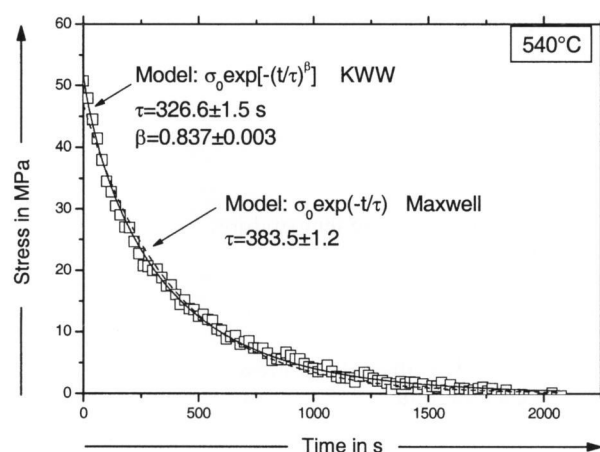


Figure 6. Comparison of the fitting curves of the Maxwell model (dashed line) and of the Kohlrausch-Williams-Watts model (full line) to the measured curve.

ogical analyses confirm a Maxwell behavior in the whole temperature region and the parameters of the viscosity are according to the measured ones. The conventional analysis for the evaluation of the Maxwell parameters, elasticity and viscosity, shows small systematical deviations between the loading and relaxation experiments. Obviously, one reason is the dependence of the Maxwell parameters on the loading rate. This assumption can be shown in a demonstrative manner by unconventional analysis $\dot{\sigma}$ versus σ . It yields a definitely nonlinear correlation – a nonlinear Maxwell behavior. Thus the relaxation time itself is dependent on the velocity and this behavior is not in correspondence with the Maxwell model approach and trends towards the Kohlrausch-Williams-Watts model primarily.

6. List of symbols

a_i	coefficients of differential equation (3), $i = 1, 2$
A	parameter (VFT equation)
A_0	cross section of the sample at $t = 0$
b_i	coefficients of differential equation (3), $i = 1, 2$
B	parameter (VFT equation)
E	elastic modulus
E_M	elastic parameter of the Hookean element of the Maxwell model
E_1, E_2	elastic parameter in rheological model
E_η	activation energy
F	force
h_0	length of sample at time $t = 0$
$h(t)$	length of sample at time t
\dot{h}	deformation rate
r	radius of cylindrical sample
R	universal gas constant
t	time
t_f	duration time of loading process
T	temperature in °C
T_{exp}	experimental temperature
T_g	transformation temperature
V	volume of the sample
β	Kohlrausch exponent
ε	strain

ε_0	strain at time $t = 0$
$\dot{\varepsilon}$	strain rate ($=d\varepsilon/dt$)
$\dot{\varepsilon}_0$	strain rate at time $t = 0$
ε_f	strain at $t = t_f$
$\ddot{\varepsilon}$	second derivative of the strain
η, η_i	viscosity, $i = 0, 1, 2$
η_G	Gent's viscosity
η_L	viscosity at infinite temperature
σ	stress
σ_0	stress at time $t = 0$
σ_f	stress at time $t = t_f$
$\dot{\sigma}$	stress rate ($=d\sigma/dt$)
$\ddot{\sigma}$	second derivative of the stress
τ	relaxation time

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