EFFECT OF AGING TIME ON A GLASS TRANSITION OF AMORPHOUS POLYMERS AT HEATING

JIŘÍ HADAC\textsuperscript{a}, PAVEL RIHA\textsuperscript{b}, PETR SLOBODIAN\textsuperscript{c}, PETR SAHA\textsuperscript{c}, and JOSEF KUBÁT\textsuperscript{d,e}

\textsuperscript{a} University Institute, Tomas Bata University in Zlín, Nad Ovcirnou 3685, 760 01 Zlín, \textsuperscript{b} Institute of Hydrodynamics, Academy of Sciences of the Czech Republic, 166 12 Prague, \textsuperscript{c} Centre of Polymer Systems, University Institute, Tomas Bata University in Zlín, Nad Ovcirnou 3685, 760 01 Zlín, Czech Republic, \textsuperscript{d} Chalmers University of Technology, Polymeric Materials and Composites, 412 96 Gothenburg, Sweden, \textsuperscript{e} Polymer Centre, Faculty of Technology, Tomas Bata University in Zlín, nám. T.G. Masaryka 275, 762 72 Zlín, Czech Republic slobodian@fi.utb.cz

Abstract

The relaxation and consolidation processes accompanied the glass transition are linked in this paper with an induction mechanism introducing a cooperative character of relaxation into those processes. The induction mechanism supplements the proposition underlying the internal energy material clock used in a recently developed thermodynamically consistent non-linear viscoelastic theory modeling thermal and mechanical behavior of amorphous polymers in the glass transition range\textsuperscript{1,2}. The mechanism is introduced into the constitutive theory framework where it replaces the stretched exponential relaxation functions. The proposed modification is used to describe the dilatometric behavior of PMMA during heating from the glassy state after varying aging times. The modified theoretical approach is found to produce a fairly good description of the peaks in thermal expansivity, both with regard to their intensity and position along the temperature axis. The length of the aging period in the glassy state is found to affect the material time scale while the relaxation functions are unchanged.

Introduction

During cooling below the glass transition region amorphous polymers undergo complex time-dependent changes of volume, enthalpy and stress reaching a glassy non-equilibrium state. Owing to this complexity, the glass transition is difficult to deal both experimentally and theoretically. The investigation is thus mostly limited to independent tests specifying, e.g., the stress response to strain, the volume change with temperature, etc. Recently a thermodynamically consistent non-linear viscoelastic formalism has been proposed to describe the behavior of amorphous polymers in terms of parameters determined in such independent tests\textsuperscript{1,2}. According to this theory the nonlinearities associated with the glass transition are not a result of using of nonlinear parameters, but rather they are a consequence of the developed thermodynamic constitutive framework. The transition employs a material clock based upon the potential energy and the stretched exponential representation of relaxation functions.

In contrast to the initial equilibrium of a rubbery polymer, the non-equilibrium glassy state is associated with time dependent processes known as physical aging. Basically, aging is the approach to equilibrium of a disturbed system accompanied by changes in thermodynamic, mechanical and other physical properties. Changes in volume, enthalpy and the time dependent response to mechanical stresses at different stages of the aging process are important for all users of polymeric materials. The time dependence of the glass transition appears to provide a natural link to aging processes, a circumstance often reflected in the models used to describe such phenomena. A natural consequence of this is a pronounced dependence of the melting process (solid to liquid transition) on the degree of structural consolidation reached during the aging process.

During aging following a simple cooling or quenching step the volume of the sample decreases in a monotonic fashion, reflecting the change in molecular mobility due to closer molecular packing\textsuperscript{3}. Dilatometric measurements thus appear to represent a suitable tool to follow the extent of the consolidation process. In the present paper we use this method to study the glass-liquid transition in atactic poly(methyl methacrylate), \textit{\alpha}-PMMA, during constant rate heating of glassy samples aged for various periods of time. The influence of aging is reflected in the intensity and position along the temperature axis (t-axis) of the peaks in thermal expansivity appearing at glass transition. For quantifying the melting process, the thermodynamic formalism proposed in ref.\textsuperscript{1,2} is used. The stretched exponential function applied in ref.\textsuperscript{1,2} in connection with the material clock mechanism is in our calculations replaced by a relaxation function based on a simple cooperative mechanism\textsuperscript{4–6}. 

Keywords: Physical aging, glass transition, PMMA, relaxation function
Thermodynamic formalism

Nonlinear viscoelastic model

The set of thermodynamic constitutive equations, which has been proposed recently to capture the wide range of behavior observed in amorphous polymers, are determined from the Helmholtz free energy using the rational mechanics and the material time scale\(^1,2\). The Helmholtz free energy is approximated by a Frechet expansion in the temperature and strain histories about the equilibrated state at the current temperature and strain. The resulting Piola-Kirchhoff stress is given by

\[
S_{ij} = S_{ij0} + \rho_v \left\{ \frac{d}{ds} \left( t' - s', 0 \right) \right\} I + 2 \rho_v \left( \frac{d}{ds} \psi_v(T) \right) \left\{ \frac{d}{ds} \left( t' - s', 0 \right) \right\} I + \rho_v \left( \frac{d}{ds} \psi_v(T, I) \right) \left\{ \frac{d}{ds} \left( t' - s', 0 \right) \right\} I,
\]

where

The specific total entropy is given by

\[
\eta = \eta_{\omega} - \psi_v(T, I_u) \left\{ \frac{d}{ds} \left( t' - s', 0 \right) \right\} I = \left( \frac{d}{ds} \psi_v(T) \right) \left\{ \frac{d}{ds} \left( t' - s', 0 \right) \right\} I - \frac{1}{2} \left( \frac{d}{ds} \psi_v(T) \right) \left\{ \frac{d}{ds} \left( t' - s', 0 \right) \right\} I - \frac{1}{2} \left( \frac{d}{ds} \psi_v(T, I) \right) \left\{ \frac{d}{ds} \left( t' - s', 0 \right) \right\} I - \frac{1}{2} \left( \frac{d}{ds} \psi_v(T, I, I_u) \right) \left\{ \frac{d}{ds} \left( t' - s', 0 \right) \right\} I,
\]

where

\[
\eta_{\omega} = \eta_1^\rho - \psi_v(T) I_{\omega} - \frac{1}{2} \psi_v(T) I_{\omega}^2 - \psi_v(T) \Delta T I_{\omega} - \psi_v(T) \Delta T
\]

The details of the constitutive theory as well as all symbols are introduced in the cited papers. The basic features of the above constitutive equations represent the Hencky strain measure \( H \), \( I_u \) the first invariant of \( H \), the material time \( t' \) and the prefactors \( \psi_k \) (k=1,2,3,4). The Taylor series coefficients of the equilibrated stress \( S_{eq} \) and entropy \( \eta_{\omega} \) as well as the prefactors \( \psi_k \) define a relationship to the glassy bulk modulus \( K_{eq}^\rho \), the equilibrium bulk modulus \( K_{eq}^\rho \), the glassy shear modulus \( G_{eq}^\rho \), the equilibrium shear modulus \( G_{eq}^\rho \), the glassy coefficient of thermal expansion (CTE) \( \alpha_{eq}^G \), the equilibrium CTE \( \alpha_{eq}^G \), the glassy heat capacity \( C_{eq}^\rho \) and the equilibrium heat capacity \( C_{eq}^\rho \) at the reference temperature \( T_{ref} \) and temperature change \( \Delta T = T - T_{ref} \) (ref.\(^2\)). The Taylor series coefficients used in the calculations are,

\[
\psi_{\omega}^H = \left( K_{eq}^\rho - 2 G_{eq}^\rho / 3 \right) \rho_{\omega} - K_{eq}^\rho \alpha_{eq}^G \rho_{\omega},
\]

\[
\psi_{\omega}^T = - \frac{\partial}{\partial \rho_{\omega}} \left( \frac{\partial K_{eq}^\rho}{\partial \tau} \right),
\]

\[
\psi_{\omega}^TT = \left( \frac{1}{\rho_{\omega}} \frac{\partial K_{eq}^\rho}{\partial \tau} \right) \rho_{\omega},
\]

\[
\psi_{\omega}^{TT} = \psi_{\omega}^{TT},
\]

The used prefactors are given by,

\[
\eta_{\omega} = \eta_1^\rho = \frac{1}{\rho_{\omega}} \left( K_{eq}^\rho - 2 G_{eq}^\rho / 3 \right) - K_{eq}^\rho \alpha_{eq}^G\rho_{\omega},
\]

\[
\psi_{\omega}^H = \left( \frac{1}{\rho_{\omega}} \frac{\partial K_{eq}^\rho}{\partial \tau} \right) \rho_{\omega},
\]

\[
\psi_{\omega}^{TT} = \left( \frac{1}{\rho_{\omega}} \frac{\partial K_{eq}^\rho}{\partial \tau} \right) \rho_{\omega},
\]

\[
\psi_{\omega}^{TT} = \psi_{\omega}^{TT},
\]

\[
\eta_{\omega} = \eta_1^\rho = \frac{1}{\rho_{\omega}} \left( K_{eq}^\rho - 2 G_{eq}^\rho / 3 \right) - K_{eq}^\rho \alpha_{eq}^G\rho_{\omega},
\]

\[
\psi_{\omega}^H = \left( \frac{1}{\rho_{\omega}} \frac{\partial K_{eq}^\rho}{\partial \tau} \right) \rho_{\omega},
\]

\[
\psi_{\omega}^{TT} = \left( \frac{1}{\rho_{\omega}} \frac{\partial K_{eq}^\rho}{\partial \tau} \right) \rho_{\omega},
\]

\[
\psi_{\omega}^{TT} = \psi_{\omega}^{TT},
\]

The normalized relaxation functions \( f_k(t' - s', t' - u') \) (k=1,2,3,4) depend upon two backward looking material times and decay from one in the relaxed stay at \( t' - s' = t' - u' = 0 \) to zero in the fully relaxed state when either argument goes to infinity. After the separation of the dependence on two material times, the relaxation functions are represented by a stretched exponential (Kohlrausch-Watt-Williams, KWW) function

\[
f_k(t' - s') = \exp \left[ - \frac{(t' - s')^{\rho_k}}{\tau_k} \right],
\]
where $\tau_k$ denotes the relaxation time and $\beta_k$ the stretched exponential.

The material time

The introduction of the material time $t'$ into the rational mechanics framework postulates that the polymers in the course of phase transition relax on this scale. Contrary to the normal laboratory time, the material time scale incorporates the effect of temperature and density on the rate of polymer transition. The material time is defined as

$$t' = \int_0^t dx / a(x),$$

where the viscoelastic shift factor $a$ acts to compress or expand the apparent timescale as compared to the actual time interval measured in the reference state. The factor for the equilibrated system reduces to a form similar to the WLF equation and is less than its equilibrium value as the temperature decreases below $T_g$.

The shift factor is expressed by means of the potential energy that is used to define the configurational energy $U_c$:

$$a = C_1 a_{eq} (a_{eq})^{-1}.$$ (9)

The definition is associated with the physical picture that the relaxation rates slow due to an increase in the number of monomers in the smallest cooperative region required to produce a transition. Thus as the configurational energy decreases, the number of monomers involved in the transition increases. At low temperature where the configurational energy is small, an extremely large cooperative motion of many monomers is required.

The above relaxation mechanism is associated by way of the material time with the relaxation functions (Eq. (9)). Those functions themselves reflect a kind of inner units cooperativity. The distribution of relaxation times, $\tau$, describing various types of time-dependent behavior of solids or semi-solids are known to cover range of several decades of logarithmic scale. Cooperative effects are usually assumed to play a key role in this context. The stretched exponential (KWW) functions are frequently used to describe the observed time variation. Such a description is basically a formal approach, since the connection between the exponent of this function, defining the extent of stretching along the log $t$-axis, and the cooperativity of the underlying elementary processes has not been clarified.

In the present paper we make an attempt to replace the KWW function in the normalized relaxation functions in Eqs. (1) and (2) by an expression formally representing the time domain equivalent of a Bose-Einstein (B-E) distribution. This expression, to be used for $f_k(t) = \sigma_k(t,0) = \frac{dn_k(t,0)}{dt}$, $k=1,2,3,4$, reads as follows

$$\sigma_k = \frac{b_k}{b_0} \left(1 + \frac{1}{b_0 \sigma_k} \right) \exp(\sigma_k / b_0) - 1,$$ (9)

where $\lambda_k$ denotes the rate of the relaxation, $\lambda_k = 1/\tau_k$, and $b_k$ is related to the degree of cooperativity of the elementary events. In contrast to the KWW function, which stretches the $\tau$ spectrum to both sides of the $\tau$ value entering the exponential, Eq. (9) yields a spectrum extending towards times shorter then $\tau = 1/\lambda_k$. This is a consequence of the mechanism underlying B-E statistics, implying that apart from single elementary transitions, involving only one relaxing unit, also double, triple, etc. transitions can take place, leading to correspondingly shortened $\tau$ values. For double transitions the relaxation time is $\tau/2$, for triple $\tau/3$, etc. Eq. (9) thus leads to a discrete $\tau$ – spectrum with a limiting $\tau_{max}$ value related to the parameter $b$ in this equation. To a high degree of approximation, such a discrete $\tau$ – distribution is equivalent to a box-type spectrum of $\tau$ as used in describing various viscoelastic responses.

Eq. (9) is the integral of the following relation

$$\frac{dn_k}{dt} = -\lambda_k \sigma_k \left(1 + \frac{b_k}{b_0} \sigma_k \right),$$ (10)

where the parenthesis contains the enhancement factor appearing in the same way in a B-E energy distribution.

The notion that a similar mechanism can be applied to the time evolution of a system of discrete relaxing units may need some comments. It may suffice here to note that the basic idea behind statistical distributions of B-E or Fermi-Dirac (F-D) is of a rather general type and not limited to phenomena involving quantum mechanics. For instance, when analyzing sorption phenomena the exclusion principle of F-D statistics appears to be a useful tool taking into account the effect of occupational sorption sites. In contrast to this there appears to be no attempts to exploit the equally plausible inclusion mechanism of B-E statistics in modeling time dependent phenomena in solids, where independent processes are unlikely to occur and where such a mechanism seems to offer an appropriate statistical picture of the cooperative motion of the relaxing units about which there is a general agreement. Considering the limitations imposed on the motion of these units by the free volume, it certainly is not unreasonable to assume that a successful activation of a unit leads not only to single transition, but facilitates

s61
simultaneous transitions of other units in its vicinity. This is a basic idea behind Eq. (10) leading in a natural way to the formation of multiple elementary transitions (relaxational clusters regions). The size distribution of the clusters emerging from Eqs. (9) and (10) has been calculated in ref. 8, where it has been shown that simple transitions are still the most numerous ones, and that the frequency of larger clusters decreases as 1/size. If \( n \) denotes the total number of units in a relaxing system, then the relaxation rate expressed in terms of the decreasing number of clusters, \( m \), is simply \( m = -\lambda n \), implying that the total number of relaxing units, \( n \), is partitioned among a smaller number of successful activations. From ref. 9 further follows the expected result that the clustering tendency decreases with time.

A stochastic treatment of the evolution of a macroscopic ensemble in terms of the master equation accounting for the B-E enhancement has been presented in ref. 6.

For stress relaxations in solids, including both polymers and metals, the relation \( b_{n0} \approx 10 \) was found (\( b \) determined from the inflexion slope of the stress-log time plots, \( n_0 \) the initial effective stress). This corresponds to an average cluster size taken over the entire process of \( 6 \), that is \( m_0/n_0 \approx 6 \). By translating this into the formalism of the stretched exponential one obtains \( \beta = 0.27 (= e/10) \) as the value of the stretching exponent.

Introducing \( dn/dn = \dot{n}/\dot{n} \) into Eq. (10), the integration gives

\[
\dot{n} = \frac{2}{b} \left[ \exp(bn) - 1 \right],
\]

where \( n \) denotes the number of unrelaxed units at a given time, relaxing one by one or in clusters of varying size. This is largely equivalent to the expressions obtained for thermally activated processes where the activation energy is assumed to depend in a linear manner on the relaxing quantity.

With regard to the expectancy of clusters of differential size a similarity can also be found with the approach of Adam and Gibbs\(^9\) starting from the assumption that the rate \( R \) depends on the size \( z \) as

\[
R \sim \exp\left(-z\Delta\mu/kT\right),
\]

where \( \Delta\mu \) is the energy barrier and \( z \) denotes the number of units in a “cooperatively rearranging region”.

**Experimental**

The polymer used is Poly(methyl methacrylate), \( a \)-PMMA, Plexiglas 6N, Rohm GmbH, density \( \rho = 1.190 \) kg m\(^{-3} \), \( M_n = 90 \) kg mol\(^{-1} \), \( M_d/M_n = 1.97 \). The polymer contains 6 mol.% of methyl acrylate distributed at random as determined by \(^{13}\)C NMR (ref. 16).

The dilatometric measurements were done with help of Mercury-in-Glass Dilatometry (MIG) constructed according to ASTM Standard D 864-52. The PMMA specimen was prepared by compression molding and grinded to form of bar with the cross-section approximately 6x6 mm. The volume of the specimen was 3.24 cm\(^3\). Before inserting of specimen into dilatometer the specimen was annealed in the furnace at temperature close above \( T_g \) to erase internal stress build up during preparation procedure. Then it was inserted into the dilatometer, dilatometer was sealed and filled with filtrated high purity (> 99.999 %) mercury under vacuum of about 2 Pa. During filing procedure temperature of the specimen was kept close above its \( T_g \). The accuracy of volume change measurement by this method in respect to the amount of PMMA, mercury and dilatometer capillary bore achieve value of about 1.2x10\(^{-7}\) cm\(^3\)/cm\(^2\). The temperature programs were done with help of precision thermostat baths (HUBER CC-130A Visco 3, and GRAND W14, Grand Instrument, Shepreth, UK). The bath was filled with silicon oil where the dilatometer was immersed into. The temperature fluctuations of the bath reported by the manufacturer are ±0.004 °C. Experiments like temperature scans and isothermal annealing were done. Cooling rates was selected to be 0.3 °C/min and heating rates 3.0 °C/min. Erasing of thermal histories of the PMMA was done by isothermal annealing at temperature well above \( T_g \) till equilibrium. Temperature up-scans were performed after cooling from equilibrium state above \( T_g \) to temperature 75 °C where PMMA was allowed to isothermally relaxed for different period of time, that is, 0 and 14 hours.

The calorimetric measurements were carried out using Perkin-Elmer DSC 1 Pyris analyzer. Temperature and heat flow were calibrated using indium standard. The value of specific heat was calibrated on sapphire standard. Temperature program, cooling and isothermal stages, of PMMA were done in the thermostatic bath together with dilatometer so at the same thermal conditions. For this case a set of specimens for DSC was prepared, each sample of the mass of cca 6 mg. The samples were covered in aluminum foil and placed into thermostatic bath in a strainer. Final calorimetric temperature up-scans of annealed samples were performed in DSC apparatus again as in volumetric measurements by rate 3 °C/min.

The values of bulk modulus were extracted from cooling volume-temperature isobars recorded at 20–120 MPa using piston-die type of pvT instrument (PVT 100 analyzer, SWO Polymertechnik GmbH, Krefeld, Germany) extrapolated on atmospheric pressure. The temperature range was from 150 to 60 °C, the isobaric cooling rate 5 °C/min.

**Results**

The effect of the physical aging time on the physical properties of PMMA represented here by CTE in the
course of the isobaric heating at the rate 3 °C/min and zero-pressure is shown in Fig. 1. The symbols denote the computed values from the corresponding temperature dependence of the specific volume and the solid lines only connect them. The aging time increases a diverseness of CTE manifested by characteristic peaks corresponding presumably to conformation changes of polymer chains.

The evaluated values of glassy CTE \( \alpha_g \) and equilibrium CTE \( \alpha_\infty \) (Table I) are in good agreement with values published in literature. Greiner and Schwarzl \(^{11} \) found in the range 2.25–2.72 \( \times 10^{-4} \) K\(^{-1} \) and the rate dependent glassy CTE values below \( T_g \) \( \alpha_g = 2.46–2.35 \times 10^{-4} \) K\(^{-1} \). The published CTE values for the identical type of PMMA as used in the present work are, \( \alpha_g = 2.17 \times 10^{-4} \) K\(^{-1} \) and \( \alpha_\infty = 6.14 \times 10^{-4} \) K\(^{-1} \) (ref. \(^{12} \)) and \( \alpha_g = 2.04 \times 10^{-4} \) K\(^{-1} \), \( \alpha_\infty = 6.07 \times 10^{-4} \) K\(^{-1} \) (ref. \(^{13} \)). Finally, CTE values for glassy PMMA at \( T < T_g \) were found in the range 2.25–2.72 \( \times 10^{-4} \) K\(^{-1} \) and the equilibrium CTE at \( T > T_g \) in the range 5.60–5.80 \( \times 10^{-4} \) K\(^{-1} \) (ref. \(^{14} \)).

Isobaric variation of volume during heating of the sample and its consequent conversion into the temperature dependence of CTE are very rarely presented in literature and only some works done by Hutchinson et al. can be found\(^{15-17} \). These mainly theoretical papers present results of the heating scan of annealed PS sample at 80 °C for 256 hours and the heating rate \( \approx 1 \) °C/min which shows an abrupt volume increase in the glass transition region. The evaluated CTE peak value was about 3.4 times higher than equilibrium CTE value measured at temperatures well above \( T_g \).

The Table I summarizes the measured physical properties and the model parameters in Eqs. (1) and (2) used to predict CTE. The reference temperatures \( T_{ref} \) are chosen to correspond to the CTE peak temperatures of corresponding samples aging for different times. That choice is made to find the optimal representation of CTE data. Consequently, the glassy values and parameters are identified for each scan corresponding to the aging time history.

The computation is done with Mathematica Version 4. The iterative solution of Eq. (1) when setting the stress to zero follows the same procedure as used in ref.\(^{2} \) with an exception that the relaxation functions are not represented by the KWW functions (8). Instead of that, there is used the function emerging from the cooperative model of relaxation discussed in section The cooperative mechanism (Eq. (9))

\[
\psi(s) = \sum_{k=1}^{4} \lambda_k b_k \left( 1 + \lambda_k / b_k \right) \exp \left[ \lambda_k \left( s - s' \right) \right] - 1 ,
\]

for \( k = 1, 2, 3, 4 \) where \( b_k \) and \( \lambda_k \) are positive constants and

\[
t' - s' = \int_{s}^{t} \frac{dx}{a(x)} \quad \text{and} \quad \log a = C_1 \left( \frac{U_c^\infty}{U_c} - 1 \right)
\]

where \( C_1, U_c^\infty \) denotes the first and second WLF coefficient, respectively, and \( U_c \) the configurational energy \( U_c = U_{c,\infty} + (\psi - \varphi_{\infty}) + T(\eta - \eta_{\infty}) \) (ref.\(^{1,2} \)). The double integral terms associated with the Helmholtz free energy \( \psi \) contribution to \( U_c \) are negligible for isobaric tests\(^{1} \). Thus in our case \( U_c \) very nearly equals to the configurational entropy \( U_c \approx U_{c,\infty} + T(\eta - \eta_{\infty}) \). The “glassy” limit for the configurational energy \( U_{c,\infty} \) (Eq. 66 in ref.\(^{1} \)) is used in computation.

The results of iterative evaluation of CTE are presented in Fig. 1 together with the experimental data. The relaxation parameters which were optimized in order to provide the best data representation are listed in Table I. The reference state temperature \( T_{ref} \) is above the glass transition temperature \( T_g \). Its chosen value is close to the CTE peak temperature.

**Conclusion**

The purpose of this paper is to examine the effect of the aging time on the glass transition. The polymer consolidation proceeds for various lengths of time before the heating. For quantifying the transition process, the thermodynamic formalism\(^{1,2} \) is used. The formalism is modified by introduction of the relaxation functions (Eq. (13)), which represent the assumed cooperative character of relaxation. The material parameters used in the computation are physically defined and determined from the independent experimental measurements. The
### Table I
Material and relaxation parameters

<table>
<thead>
<tr>
<th>Constant</th>
<th>Units</th>
<th>All samples</th>
<th>Relaxation aging times [hours]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_g )</td>
<td>°C</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>( T_{ref} )</td>
<td>°C</td>
<td>97</td>
<td>97</td>
</tr>
<tr>
<td>( \alpha_{ref} )</td>
<td>K(^{-1})</td>
<td>7.6</td>
<td>9.3</td>
</tr>
<tr>
<td>( C_{pe} )</td>
<td>J kg(^{-1}) K</td>
<td>2400</td>
<td></td>
</tr>
<tr>
<td>( \rho_{ref} )</td>
<td>kg m(^{-3})</td>
<td>1128</td>
<td></td>
</tr>
<tr>
<td>( \alpha^{\infty}_{g} )</td>
<td>K(^{-1})</td>
<td>0.00032</td>
<td></td>
</tr>
<tr>
<td>( \alpha^{\infty}_{w} )</td>
<td>K(^{-1})</td>
<td>0.0006</td>
<td></td>
</tr>
<tr>
<td>( K^{g}_{ref} )</td>
<td>Gpa</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>( K^{w}_{ref} )</td>
<td>Gpa</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>( C^{g}_{ref}^{\infty} )</td>
<td>J kg(^{-1}) K</td>
<td>2200</td>
<td></td>
</tr>
<tr>
<td>( C^{w}_{ref}^{\infty} )</td>
<td>J kg(^{-1}) K</td>
<td>2.300</td>
<td></td>
</tr>
<tr>
<td>( C_{1} )</td>
<td>unitless</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>( U_{C}^{\infty} )</td>
<td>J kg(^{-1})</td>
<td>8000</td>
<td>8000</td>
</tr>
<tr>
<td>( \psi_{II} )</td>
<td>J kg(^{-1})</td>
<td>1.83×10(^{6})</td>
<td></td>
</tr>
<tr>
<td>( \psi_{IT} )</td>
<td>J K kg(^{-1})</td>
<td>−1.01×10(^{3})</td>
<td></td>
</tr>
<tr>
<td>( \psi_{TT} )</td>
<td>J K(^{2}) kg(^{-1})</td>
<td>−5.82</td>
<td></td>
</tr>
<tr>
<td>( \psi_{ITT} )</td>
<td>J K(^{3}) kg(^{-1})</td>
<td>−5.05×10(^{3})</td>
<td></td>
</tr>
<tr>
<td>( \psi_{IIT} )</td>
<td>J K(^{2}) kg(^{-1})</td>
<td>6.03</td>
<td></td>
</tr>
<tr>
<td>( \psi^{\infty}_{II} )</td>
<td>J kg(^{-1})</td>
<td>3×10(^{5})</td>
<td>5.05×10(^{5})</td>
</tr>
<tr>
<td>( \psi^{\infty}_{II} )</td>
<td>J K kg(^{-1})</td>
<td>279</td>
<td>349</td>
</tr>
<tr>
<td>( \psi^{\infty}_{III} )</td>
<td>J K(^{2}) kg(^{-1})</td>
<td>0.6</td>
<td>0.69</td>
</tr>
<tr>
<td>( \left( \frac{\partial \psi_{III}}{\partial T} \right)^{\infty}<em>{T</em>{ref}} )</td>
<td>J K(^{3}) kg(^{-1})</td>
<td>−7.5</td>
<td>−9.04</td>
</tr>
<tr>
<td>( \left( \frac{\partial \psi_{III}}{\partial H} \right)^{\infty}_{T} )</td>
<td>J K(^{2}) kg(^{-1})</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( b_{1} )</td>
<td>unitless</td>
<td>0.0002</td>
<td>0.0003</td>
</tr>
<tr>
<td>( \lambda_{1} )</td>
<td>s(^{-1})</td>
<td>15000</td>
<td>15000</td>
</tr>
<tr>
<td>( b_{3} )</td>
<td>unitless</td>
<td>0.0003</td>
<td>0.0003</td>
</tr>
<tr>
<td>( \lambda_{3} )</td>
<td>s(^{-1})</td>
<td>50000</td>
<td>50000</td>
</tr>
<tr>
<td>( b_{4} )</td>
<td>unitless</td>
<td>0.0001</td>
<td>0.0001</td>
</tr>
<tr>
<td>( \lambda_{4} )</td>
<td>s(^{-1})</td>
<td>50000</td>
<td>50000</td>
</tr>
</tbody>
</table>
agreement between the predictions and experiments is reasonably good what indicates that the constitutive theory captures the glass transition changes of the coefficient of thermal expansion of PMMA.  

This contribution was written with the support of the ’Operational Program Education for Competitiveness’ co-funded by the European Social Fund (ESF) and the national budget of the Czech Republic, within the project ’Advanced Theoretical and Experimental Studies of Polymer Systems’ (reg. number: CZ.1.07/2.3.00/20.0104) and with the support of the ’Research and Development for Innovations’ Operational Program co-funded by the European Regional Development Fund (ERDF) and the national budget of the Czech Republic, within the project entitled ’Centre of Polymer Systems’ (reg. number: CZ.1.05/2.1.00/03.0111)  

The authors acknowledge the Fund of Institute of Hydrodynamics AV0Z20600510 for the support also.

REFERENCES