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KINETICS OF THE THERMAL POLISHING OF THE ROUGH GLASS SURFACE

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Abstract

A simple mathematical model of thermal polishing of rough glass surface as observed by light beam thermal analysis (LBTA) is presented. The rough surface is represented by a triangular profile used for calculation of the light beam intensity attenuation and an equivalent rectangular profile is used for the modeling of the time course of the thermal polishing. Computational results obtained for the NBS 711 viscosity standard glass showed that the characteristic temperature, obtained from the series of LBTA experiments after extrapolation to zero starting surface roughness, does not represent the glass transition temperature, but it corresponds to the viscosity value of about 10^9 dPa.s. The validity of the proposed model was confirmed by the comparison of simultaneous LBTA and viscosity measurements of $CaO–Y_2O_3–Al_2O_3–SiO_2$ glasses.

Keywords: glass, glass transition, ligth beam thermal analysis, softening point, structural relaxation, thermal glass polishing

Introduction

In the works of Lichvár *et al*. [1, 2], the application of the light beam thermal analysis (LBTA) [3, 4] was proposed as a tool for determination of the glass transition temperature, T_g (LBTA). However, some doubts about the interpretation of the results arose, mainly due to a significant difference between the T_g (LBTA) and the T_g (DTA) values (i.e. the T_g values measured by differential thermal analysis, DTA [5]). Moreover, the dependence of T_g (LBTA) values on the heating rate applied during the thermo-optical experiment was not satisfactorily explained. The present paper deals therefore with a very simple model based on the regular geometrical shape of rough glass surface in combination with the Narayanaswamy–Tool model of the structural relaxation, in order to explain the phenomena observed during the LBTA experiments.

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Computational method

According to Tool and Narayanaswamy [6–8], the fictive temperature, $T_{\mathrm{f,l}}(t)$, can be calculated for an arbitrary temperature–time schedule $T(t)$:

$$T_{\mathrm{f,l}}(t) = T(t) - \int_0^{t} \mathrm{d}t' \left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_{t'} M_1[\xi(t)-\xi(t')] \tag{1}$$

where M_l is the Kohlrausch–William–Watts (KWW) relaxation function [6, 9]:

$$M_l(\quad \exp(- \quad ^{b}) \tag{2}$$

where b is the non-exponentiality parameter $(0<b \quad 1)$ and   is the dimensionless relaxation time [6, 10, 11]:

$$\xi(t) = \int_0^{t} \frac{\mathrm{d}t'}{\tau_1(t')} = \int_0^{t} \frac{K_1}{\eta(t')}\mathrm{d}t' \tag{3}$$

where   is the viscosity, which depends both on the fictive and thermodynamic temperatures, $\eta=\eta(T,T_{\mathrm{fl}})$. According to Mazurin [10, 11] this dependence is described by:

$$\lg\{\eta(T,T_{\mathrm{f,l}})\} = \lg\{\eta(T_{\mathrm{f,l}},T_{\mathrm{f,l}})\}\frac{T_{\mathrm{f,l}}}{T} - \lg\{\eta_0\}\left(\frac{T_{\mathrm{f,l}}}{T}-1\right) \tag{4}$$

where η_0 is constant and the meta-stable equilibrium viscosity is given by Vogel–Fulcher–Tammann equation:

$$\lg\{\eta(T=T_{\mathrm{f,l}},T_{\mathrm{f,l}})\} = A + \frac{B}{T-T_0} \tag{5}$$

The rough glass surface is represented by a periodic rectangular profile with the rectangles of width h and height l above the base level (Fig. 1). The change of the rectangle height with time can be calculated by numerical integration of the equation:

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = \frac{1}{\mathrm{d}t}\left(\frac{\mathrm{d}l}{l}\right) = \frac{\sigma(h,l)}{3\eta} = \frac{1}{3\eta}\left(\frac{1}{2}\rho g h + \frac{2\gamma}{h}\right) \tag{6}$$

where σ is the combined gravity and surface tension load, ρ is the density of glass, and γ is the surface tension.

Glass of the identical volume was then rearranged into the form of equivalent triangular profile (Fig. 1) in order to calculate the optical transmittance, T_{opt}, according to the Fresnel's equations:

$$T_{\mathrm{p}} = \frac{\sin 2\alpha \sin 2\beta}{\sin^2(\alpha+\beta)\cos^2(\alpha-\beta)} \quad T_{\mathrm{s}} = \frac{\sin 2\alpha \sin 2\beta}{\sin^2(\alpha+\beta)} \quad T_{\mathrm{opt}} = \frac{1}{2}(T_{\mathrm{s}}+T_{\mathrm{p}}) \qquad (7)\text{–}(9)$$

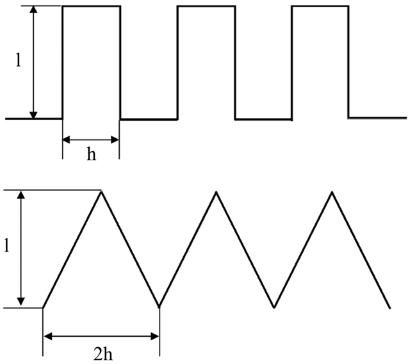

Fig. 1 Schematic representations of the rectangular and triangular profiles of the rough surface used for the calculation of optical transmittance and time course of thermal polishing, respectively

where α is the angle of light beam incidence on the planes of triangular profile and β is the angle of refraction given by the Snell's law:

$$\alpha=\frac{\pi}{2}-\mathrm{arctg}\left(\frac{h}{l}\right)\quad n=\frac{\sin\alpha}{\sin\beta} \tag{10}$$

where n is the refractive index. The value of n=1.52 was used throughout all presented calculations.

The relative transmittance, T_r, was defined as a relative measure of the transmittance change from the initial (minimal) value of $T_{\text{opt},0}$ to the maximum value of $T_{\text{opt,}}$ corresponding to the flat (i.e. h=0, α=0) glass surface.

$$T_r=\left(\frac{T_{\text{opt}}-T_{\text{opt},0}}{T_{\text{opt},\infty}-T_{\text{opt},0}}\right) \tag{11}$$

Results and discussion

The NIST viscosity standard glass NBS 711 was used in the presented calculations. The values of physical quantities needed for the model calculation are given in Table 1.

Figure 2 summarizes the temperature dependences of the relative transmittance calculated for the heating rate of 5°C min^{-1} and for the starting roughness l_0=(0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00) m, respectively. As the various roughness of the glass surface was obtained by using abrasive agents with different grain size, the width of the rectangular profile was considered to be equal to the starting roughness, i.e. h=l_0. This way the stress caused by the glass surface tension decreases with increasing l_0 values. The relative transmittance curves are therefore shifted with increasing l_0 values towards higher temperatures. Moreover, larger l_0 value alone requires longer time in order to reach the final stage where the surface is flat, even in case the acting stresses are identical.

Table 1 The values of physical quantities of NBS 711 viscosity standard glass used in the calculation

Quantity	Value	Equation
A	–1.621	5
B/°C	4254.64	5
T_0/°C	152.100	5
n_{20}	1.520	10
/kg m^{-3}	2500.00	6
lg$K$/dPa. s	10.024	3
b	0.571	2
lg $_0$/dPa.s	2.817	4
/N m^{-1}	0.333	6

Figure 3 compares the relative transmittance curves obtained for the values $h=l_0=1.00$ m and for various heating rates (5.0, 10.0, 20.0)°C min^{-1}. It can be concluded that the heating rate does not affect the obtained results in the frame of the proposed model.

Three significant temperature points can be identified on each T_r curve: the starting temperature, T_l, the temperature of the inflex point, T_i, (i.e. the temperature of the maximum velocity of increase of T_r), and the temperature T_h, where the T_r value approaches the final maximum value. These characteristic temperatures may be simply obtained from the derivative of the T_r – temperature dependence (Fig. 4).

Table 2 summarizes these quantities together with the corresponding viscosity values for various starting roughness and the heating rate of 5°C min^{-1}.

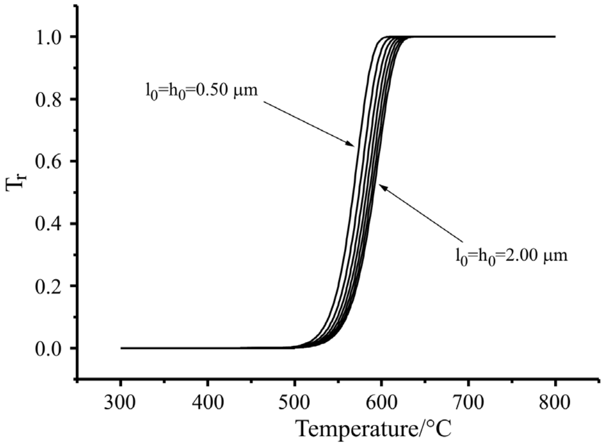

Fig. 2 T_r *vs*. temperature for the heating rate of 5°C min^{-1}, $h= l_0$=(0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00) m

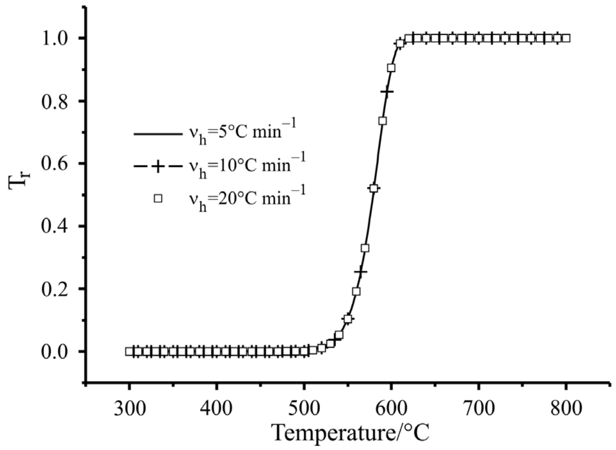

Fig. 3 T_r *vs*. temperature for $h=l_0$=1.00 m and for the heating rate of (5.0, 10.0, 20.0)°C min^{-1}

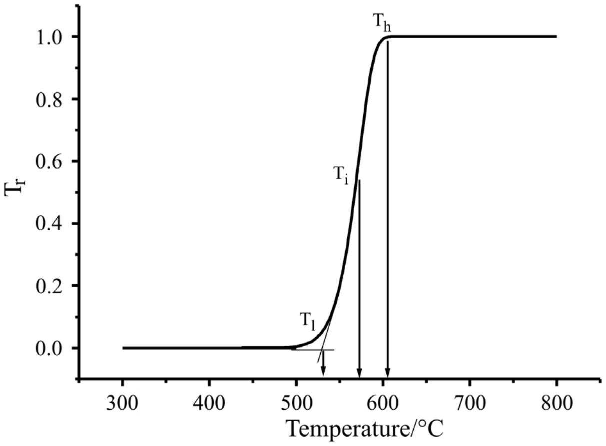

Fig. 4 The determination of characteristic temperatures T_l, T_i and T_h

The values extrapolated to zero starting roughness (i.e. l_0=0) are presented in the last row of the Table 2. In all cases, the values of characteristic temperatures correspond to the viscosity values significantly lower than the viscosity at glass transition temperature (approx. $10^{13.3}$ dPa.s), and higher than the Littleton's softening point (i.e. $10^{7.65}$ dPa.s). Thus the proposed [1, 2] unambiguous attribution of the LBTA experimental results to the specific viscosity point or to the glass transition temperature seems to be questionable, at least in the frame of the simple model used in the present work.

To compare the obtained model results with the experiment, the temperature–viscosity curves were measured [12, 13] for the glass samples in the $CaO–Y_2O_3–Al_2O_3–SiO_2$ system, as reported in the work of Lichvár *et al*. [1, 2]. Table 3 summarizes the viscosities of these glasses at the temperature T_l reported in the work [1]. It can be seen that the difference between the viscosity at T_l predicted by the model ($10^{9.25}$ dPa.s) and its experimental value (Table 3) ranges from 1.05 to 1.75 in the logarithmic scale. This discrepancy can be simply rationalized as a consequence of an underestimation of the glass surface tension influence. The surface of the real glass sample is more complex than our model, namely its mean curvature is larger due to the presence of numerous sharp peaks and edges where the surface tension predominantly determines the onset temperature of the polishing process.

Table 2 Characteristic temperatures of normalized transmittance curves calculated for various starting roughness l_0 and corresponding viscosity values of NBS 711 glass

l_0/ m	T_l/°C	lg /dPa.s	T_i/°C	lg /dPa.s	T_h/°C	lg /dPa.s
0.50	549	9.10	573	8.49	589	8.12
0.75	555	8.94	579	8.35	596	7.96
1.00	559	8.84	585	8.21	602	7.84
1.25	563	8.73	590	8.10	606	7.75
1.50	566	8.66	592	8.05	609	7.69
1.75	568	8.61	595	7.99	612	7.63
2.00	572	8.51	597	7.94	615	7.57
0.00*	544	9.25	568	8.62	583	8.25

*Values extrapolated to zero starting roughness

Table 3 Viscosity at the characteristic temperature T_l for $CaO–Y_2O_3–Al_2O_3–SiO_2$ glasses (glass compositions and experimental details are given in the work [3])

Glass	T_l/°C	lg /dPa.s
YAGSiO2	970	10.3
YASICa01	948	10.5
YASICa02	923	10.9
YASICa03	913	10.8

Nevertheless, both the experiment and the present model confirm that the optical polishing process takes place at temperatures well below the T_g. Thus no relaxation process can take place at normal heating rate, as can be seen from Fig. 3.

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References

1 P. Lichvár, D. Galusek and M. Liška, Ceramics, 46 (2002) 74.
2 P. Lichvár, Ph.D. thesis, Institute of Inorganic Chemistry of Slovak Academy of Sciences, Bratislava 2003.
3 J. Majling, Š. Svetík, J. Annus, J. Krištín and P. M. Marquis, Chem. Pap., 51 (1997) 268.
4 J. Majling, V. Kremničan, R. Ďurovčíková and Š. Svetík, J. Therm. Anal. Cal., 57 (1999) 587.
5 J. M. Hutchinson, J. Therm. Anal. Cal., 72 (2003) 619.
6 G. W. Scherer, J. Non-Crystalline Solids, 123 (1990) 75.
7 A. Q. Tool, J. Amer. Ceram. Soc., 29 (1946) 240.
8 O. S. Narayanaswamy, J. Amer. Ceram. Soc., 54 (1971) 491.
9 G. Williams, D. C. Watts, B. S. Dev and A. M. North, Trans. Faraday Soc., 67 (1971) 1323.
10 S. M. Rekhson, A. V. Bulaeva and O. V. Mazurin, Sov. J. Inorg. Mater., 7 (1971) 622.
11 O. V. Mazurin, Steklovanie. Nauka, Leningrad 1986 (In Russian).
12 F. Lofaj and F. Dorčáková, Metallurgy, 42 (2003) 229.
13 F. Dorčáková, Unpublished results.