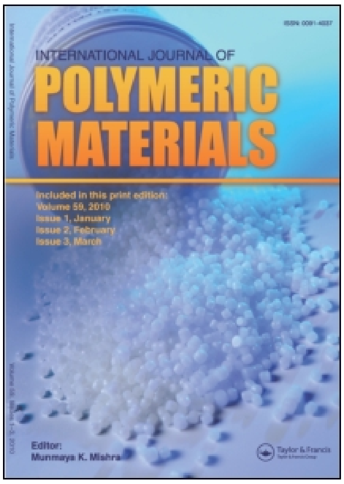

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SHORT COMMUNICATION

The Relationship Between the Microhardness and Glass Transition Temperature of Inorganic Glasses Compared with Polymeric Glasses

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In this article an attempt is undertaken to verify the approach already successfully applied to polymeric glasses for deriving a simple analytic relationship between the glass transition temperature, T_g, *and Vickers microhardness,* H_v, *(for polymers it is* $H_v = 1.57\ T_g - 571$, H_v *in MPa,* T_g *in K). On the basis of previously reported data for* H_v *and* T_g *of 12 inorganic glasses (lead-silicate-, alkali-silicate-, alumosilacate, and quartz glasses) a linear relationship in the form* $H_v = 5.87\ T_g + 1740$ *(*H_v *in MPa,* T_g *in K) is derived. In addition, a critical analysis of the published attempt for theoretical deriving of the relationship between* H_v *and* T_g *is also offered.*

Keywords: microhardness, glass transition temperature, inorganic glasses

In a recent review by Baltá Calleja et al. [1] a profound theoretical analysis of microhardness of non-crystalline materials is offered.

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Defining hardness, H, as a phenomenological measure of resistance of a material to shear stresses under local volume compression, the authors [1] show that this definition may serve as a theoretical basis for existing empirical relationships between the Vickers microhardness, H_v, and the various phenomenological, packing density-sensitive parameters of non-crystalline materials, including among them, the internal pressure, the glass transition temperature, T_g, the excess enthalpy, and the free volume fraction at T_g. It is demonstrated that under the Vickers indenter a local plastic shear deformation should occur in the region of isotropic compression, when the maximum shear stress, τ_m, matches the yield stress, σ_y, of the material. Then, the Vickers microhardness $H_v = \tau_m = \sigma_y$ may be defined as a phenomenological measure of the resistance to shear deformations under conditions of isotropic compression [1]. Moreover, assuming that a small volume element of a glassy material under the indenter is "forced" by a plastic flow mechanism into the state of a hypothetical melt at temperature T' being below its glass transition temperature ($T' \ll T_g$), the authors [1] consider such a transition as equivalent to an exothermal transition from the high-energy glassy state, H_{glass}, into a low-energy melt state, H_{melt}. The heat liberated during this transition, $\Delta H = H_{melt} - H_{glass}$, can be envisioned as a new measure of the strength of a glassy lattice, alternative to the σ_y [1–2]. Further, assuming $\sigma_y = \Delta H$ they derive [1]

$$H_v = C'\Delta H = C'\langle \Delta c_p \rangle (T' - T_g) \tag{1}$$

where C' is a numerical parameter, and $\langle \Delta c_p \rangle = c_{p,melt} - c_{p,glass}$ is the mean difference between the specific heat capacities of a substance in the melt and in the glassy state, respectively, in the temperature interval between the temperature of the measurement T' and the glass transition temperature T_g [1–4].

The authors stress the fact that the predicted linear increase of H_v with T_g (Eq. (1)) is in an excellent agreement with the experimental data for inorganic glasses reported earlier [5], but only when obeying the condition

$$C'\langle \Delta c_p \rangle = const \tag{2}$$

According to their statement [1], the apparent constancy of the product $C'\langle \Delta c_p \rangle$ implies either the constancy of each term, or an inverse proportionality between them. Nevertheless, they note that the observed scatter of experimental data on the typical H_v versus T_g plot for several series of glassy polymers [2,6] suggest that at least one of the earlier assumptions may not be strictly valid. Therefore they looked for other reasons for the observed deviations [2,6] from the expected linear relationship between H_v and T_g.

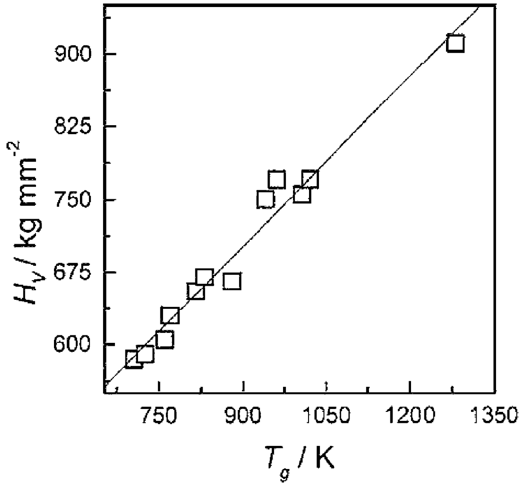

FIGURE 1 Relationship between vickers microhardness, H_v, and glass transition temperature, T_g, for inorganic glasses: lead-silicate glass (first point), alkali-silicate glasses (the next six points), alumosilicate glasses (the group of next four points), and quartz glass (the very last point) [1].

It should be mentioned here that Eq. (1) also has other peculiarities. In addition to the fact that the numerical parameter C' is not further specified, the term $\langle \Delta c_p \rangle = c_{p,melt} - c_{p,glass}$ seems to be substance-specific, that is the suggested Eq. 1 is not applicable for prediction of H_v value of any glass starting only by its T_g. It should be also noted that, as a matter of fact, Eq. (1) also comprises the temperature dependence of H_v because T' assumes various temperatures at which the measurement of H_v can be carried out.

At the same time, the experiment found [5] reported in [1] (also replotted as Figure 1) perfect straight line defined by 12 inorganic glasses reflects the relationship between the microhardness (*measured only at room temperature*) and T_g. For this reason, strictly speaking, the plot H_v *versus* T_g (Figure 1, [1]) does not reflect the relationship between H_v and ($T' - T_g$) as the authors state [1], but only between H_v and T_g, which seems to be a rather different case.

The impressive perfect linear plot shown in Figure 1 [1] demonstrates the linear relationship between Vickers microhardness and glass transition temperature for 12 inorganic glasses, all of them measured at room temperature by Sanditov and Sangadiev [5], allows one to derive an analytical expression in the form

$$H_v = 5.87\,T_g + 1740 \quad (H_v \text{ in MPa},\ T_g \text{ in K}) \tag{3}$$

Equation (3) offers the opportunity to calculate the H_v value of an inorganic glass starting only from its T_g (at least for these particular classes of inorganic glasses).

At this place it seems worth mentioning that the same approach for empirical deriving of an analytical relationship between H and T_g was applied by Fakirov et al. [7–8] to 14 glassy polymers. The expression obtained in the form [7]

$$H = 1.97\,T_g - 571 \quad (H \text{ in MPa},\ T_g \text{ in K}) \tag{4}$$

has been applied also for accounting the contribution of liquid-like (soft at room temperature and thus not capable to display a stable indentation with reliably measurable sizes) phases and/or components to the overall microhardness of multicomponent and/or multiphase systems [8–9]. Before accepting this possibility the microhardness of such soft materiels at room temperature, components and/or phases has been accepted to be zero [10] when describing the microhardness of complex systems by means of the widely used additivity law [11]. Usually, this approach resulted in wrong values of the calculated H (being frequently up to 5 to 10 times larger than the experimentally measured ones) [11].

Some time later [12], Eq. (4) was complemented in such a way that the temperature dependence of H was taken into account

$$H^T = 1.97\,T_g - 0.6T - 395 \quad (\text{MPa}), \quad (T_g \text{ and } T \text{ in K}) \tag{5}$$

where H^T is the microhardness value at the test temperature T.

Equation 5 seriously contradicts the statement disclosed in Ref. [1] that Figure 1 [1,5] is the graphical presentation of Eq. (1), which, as a matter of fact, in addition to the relationship between H and T_g also incorporates the temperature dependence of H.

The next step of the present study will be an attempt to introduce in Eq. (3) the temperature dependence of H_v, that is, to make possible the prediction of H_v of inorganic glasses at any temperature of measurement below T_g similarly to the case done for glassy polymers [12], as well as to check the applicability of Eq. (3) to other classes of inorganic glasses.

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