JOURNAL OF MATERIALS SCIENCE **32** (1997) 5405–5411

Crystallization of glass forming melts under hydrostatic pressure and shear stress

Part II *Flow induced melt crystallization: a new method of nucleation catalysis*

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In this second part of a thorough investigation into the influence of external pressure and shear stress on melt crystallization the effect of shear stress is analysed. Both pseudoplastic and dilatant liquids are examined, and possible effects of the respective rheological behaviour are discussed. It is shown that the very nature of pseudoplastic liquids leads to a reduction of their viscosity, which results in increased nucleation and crystal growth rates, whilst the non-steady-state time lag is, on the contrary, reduced. Experimental evidence supporting the above idea is discussed.

1. Introduction

Part I of the present contribution gave a detailed analysis of the influence of increased hydrostatic pressure on melt crystallization [1]. It was shown that, generally speaking, the effect of hydrostatic pressure in cases where crystallization is accompanied by a positive volume dilatation (for a change in molar volumes $\Delta V > 0$) and in normal liquids (i.e., for a relative volume dilatation of $< 5\%$) can be described mainly as a transition of nucleation and crystal growth processes to higher temperatures, T. This transfer is described in Part I in terms of a shift of the maximum of the nucleation and growth rate curves, following, generally speaking the thermodynamically predicted change of the melting point, $T_m(P)$, of the system under pressure.

Only in cases where crystallization is associated with an abnormally high positive relative dilatation (e.g., about 20% for B_2O_3 melts), can the pressure induced shift of the nucleation or growth versus temperature curves under hydrostatic pressure be associated with a significant increase in nucleation and growth rates. At negative dilatation values ($\Delta V < 0$, as is the case with crystallization of water), no nucleation catalytic effect due to increased pressure is to be expected for melt crystallization under pressure.

Significant nucleation rate increases in melt crystallization are to be expected (even for the optimum ΔV values mentioned) only at relatively high hydrostatic pressures (e.g., in the case of B_2O_3 above 1 GPa). Such conditions pose, however, substantial experimental problems.

On the other hand it has been experimentally found that in undercooled melts flowing under applied tangential stress (e.g., in a rotational viscosimeter, as observed by Pennings *et al.* [2] for undercooled polymer melts) with no hydrostatic pressure applied, or under the combined effect of both relatively low hydrostatic pressure and shear stress (as is the case with melt crystallization in high temperature extrusion pressure experiments [3]), crystallization is readily initiated. A detailed examination of the conventional extrusion pressure techniques applied for silicate melt processing shows that the pressure does not exceed 0.05 GPa at any point in the experimental apparatus [4, 5]. Moreover, this new technique for glass–ceramic processing uses glassforming melts, where (as in $Li_2O \cdot 2SiO_2$ or in phlogopite glass–ceramic crystallization experiments), the relative dilatation is below 3%. Under such conditions (as discussed in reference [1]) the effect of hydrostatic pressure on crystallization can be completely neglected.

That is why in the present investigation we examine another possible cause for induced crystallization: the reduction of viscosity (and thus of the kinetic factors) governing both nucleation and crystal growth in melt crystallization. Such a reduction of viscosity, as shown in the discussion below, is to be expected in the shear stress induced flow of any pseudoplastic liquid, and it is known, that as a rule, both organic polymer liquids and oxide glass forming melts are typical representatives of this type of non-Newtonian rheological behaviour (see references [6–8] and literature cited therein).

Many years ago (in 1902), W. Ostwald introduced the terms nucleation catalysis and nucleation catalysts ("Katalyse zweiter Art", see reference [9]) to indicate

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that in the cases of initiated nucleation known at his time as nucleation rate was increased (as in experiments of chemical catalysis) by a decrease of the thermodynamically determined rate barrier.

In the present contribution, however, we examine another possibility for nucleation catalysis, namely that the kinetic factor of crystallization rather than the thermodynamic barrier is reduced. There is abundant literature on the classical thermodynamic nucleation catalysis as a function of the influence of active substrates, external fields or electric charges that decrease the thermodynamic barrier to nucleation [8, 10–12]. However, there is not, to our knowledge, a single paper in which an analysis and a theoretical explanation of rheologically induced melt crystallization catalysis is attempted. The main aim of this paper is to provide such an analysis.

2. Basic rheological dependences

The Newtonian flow behaviour of liquids is defined by:

$$\dot{\gamma} = (1/\eta_0)F \qquad (1)$$

where $\dot{\gamma} = \mathrm{d}\gamma/\mathrm{d}t$ is the rate of shear flow caused by an applied shear stress, F and η_0 denotes a material constant of the liquid which is independent of both the shear stress and flow rate. It is called the Newtonian viscosity of the liquid.

Equation 1 is an idealization, which is only fully valid in the limiting case of $F \to 0$. Real liquids deviate from Equation 1 in two possible ways: the increase of γ is either steeper (pseudoplastic non-Newtonian behaviour) or slower (dilatant non-Newtonian liquids) than the linear dependence implied by Equation 1.

In order to retain the classical form of Equation 1, even in cases of non-Newtonian behaviour, an effective (or apparent) F-dependent value of the viscosity $\eta_{\mathrm{eff}} \equiv \eta(F)$ is usually introduced (see references [6, 7, 13] and the references cited there) so that:

$$\dot{\gamma} = (1/\eta_{\mathrm{eff}})F = [A^* f(F)/\eta_0]F \qquad (2)$$

$$(\eta_{\mathrm{eff}}/\eta_0) = 1/[A^* f(F)] = 1/\psi(F) \qquad (3)$$

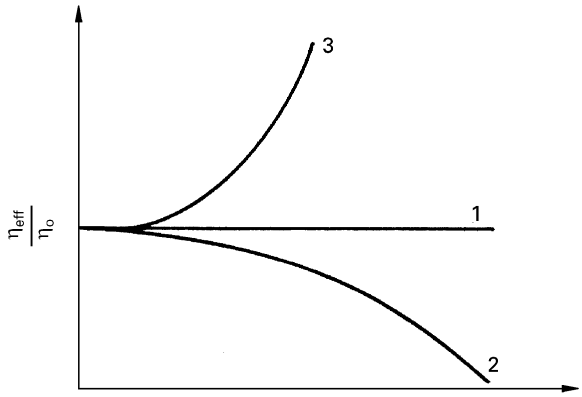

Figure 1 $\eta_{\mathrm{eff}}/\eta_0$ curves: illustration of the Newtonian law dependence (1) compared with pseudoplastic (2) and dilatant (3) rheological behaviour.

In above equations, A^*, is a constant, $f(F)$ is an empirically or theoretically derived function of F, and $\psi(F) = A^* f(F)$ is the corresponding dimensionless F-dependence. For pseudoplastic liquids η_{eff} is a decreasing function of F (with the $\psi(F)$ function increases with F), while for dilatant liquids η_{eff} increases with increasing shear stress (i.e., $\psi(F)$ is a decreasing function of F, see Fig. 1). The $\dot{\gamma}$ as a function of F dependence can be theoretically predicted [6–8, 13] using different molecular models: e.g., the Prandtl–Eyring energy barrier model or by flow models specific for polymer solutions. A detailed description of such models may be found in the classical rheological literature [14–17]. A reassessment of the basic merits and limitations of the Prandtl–Eyring model is given in references [6, 7] and [16]. According to this model, which strictly speaking is applicable only to pseudoplastic liquids:

$$\dot{\gamma} = (A^*/\eta_0)\sinh(a_0^{\#}F) \qquad (4)$$

where $a_0^{\#} = 1/A^*$ is determined by the so called rheological volume, V_{R}^0, of the building units of the melt. Thus for the Prandtl–Eyring model we obtain with Equations 2 and 3:

$$(\eta_{\mathrm{eff}}/\eta_0) = (a_0^{\#}F)/\sinh(a_0^{\#}F) \qquad (5)$$

A generalization of this model so as to also include systems with dilatant behaviour is discussed in reference [6].

For more recent theoretically founded, $\psi(F)$, functions for the non-Newtonian behaviour of liquids we have to mention the $\eta_{\mathrm{eff}}/\eta_0$ dependences for polymer solutions, e.g., the Bueche formula [13, 17] or the thermodynamically derived Botinga expression [18]:

$$\eta_{\mathrm{eff}}/\eta_0 = \exp[-b_0F^2] \qquad (6)$$

where $b_0 > 0$ is a constant.

Of considerable significance in the analysis to follow are simple empirical $\gamma(F)$ relations often employed in experimental and phenomenological rheology, e.g., the de Waele–Ostwald equation:

$$\dot{\gamma} = (A_1^*/\eta_0)F^n \qquad (7)$$

according to which:

$$(\eta_{\mathrm{eff}}/\eta_0) = (1/A_1^* F^{n-1}) \qquad (8)$$

With $n > 1$ (usually $n \cong 1.5$), it describes fairly well the pseudoplastic and with $n < 1$ the dilatant behaviour of liquids (with $n = 0.5$ follows Darcy's Law for dilatant liquids). Amongst the recently phenomenologically derived relations we have to also mention those proposed by Brückner and Yue [19] which are in some respects similar to the dependence given by Equation 6. It is also to be noted [6] that by simple Taylor expansion both theoretically derived $\eta_{\mathrm{eff}}/\eta_0$ functions (Equations 5 and 6) can be transformed (at least for small to medium F-values) to dependences similar to either Equation 8 or to functions of the type:

$$(\eta_{\mathrm{eff}}/\eta_0) \approx 1 - a^{\#}F^2 \qquad (9)$$

corresponding to the equations used in organic polymer rheology.

Both theoretical prediction and experimental finding show that the viscosity η and all other kinetic and rheological characteristics of melts are changed upon the application of a tangential stress. However, in existing nucleation theories it is tacitly assumed that the Newtonian viscosity η_0 rather that the real value η_{eff} of the viscosity has to be introduced in the derivations related to the kinetics of crystallization processes via the Stokes–Einstein equation:

$$D \cong kT/d_0\eta \tag{10}$$

In this equation D as usual denotes the coefficient of self diffusion of the building units of the liquid, d_0 the corresponding mean intermolecular distance in it, and k and T the Bolzmann constant and the absolute temperature, respectively.

For inorganic glass forming melts Newtonian-like behaviour is observed even at relatively high tangential stress values and this is why the intrinsic pseudoplastic behaviour of inorganic glasses was revealed only a few years ago (see experimental evidence summarized in references [6, 7] and the paper by Li and Uhlmann [20]). Thus in the rheology of inorganic melts $\eta \approx \eta_0$ can be accepted as an appropriate approximation even for melts flowing under medium tangential stresses. However, for organic polymer melts the preudoplastic behaviour is easily revealed even at low F-values and this is why the previously mentioned hydrodynamic effects in nucleation and crystallization kinetics have been experimentally verified, firstly by Pennings *et al.* [2] in these systems.

Let us now introduce into Equation 10, and thus into the whole kinetics of crystallization, not the imaginary Newtonian value, η_0 of the viscosity of crystallizing liquids, but its real value, η_{eff}. This procedure is in fact adopted (and was employed by us in Part I of the present investigation) when the real viscosity value, $\eta(P)$, of the melt subjected to hydrostatic pressure is employed in the Stokes–Einstein formula to determine $D(P)$. In this way the stress dependence of the viscosity (η) defined with Equations 1–8 should enter into Equation 10 and thus in the dependences describing crystal nucleation and growth rates in undercooled liquids.

A set of equations describing melt crystallization at normal and at increased hydrostatic pressure, P, is given in reference [1]. The influence of P is accounted for by introducing a number of dimensionless coefficients $f_i(P)$, defined in such a way that under normal pressure ($P = P_0$, i.e., for $(P - P_0) = 0$), we have to introduce the values of $f_i(P) \equiv 1$ in these equations.

For pseudoplastic liquids under tangential stress we should expect reduced η values, the $(\eta_{\text{eff}}/\eta_0)$ ratio depending (via the corresponding $f(F)$ function according to Equations 4–8), on the applied stress F. The decrease in η should induce corresponding changes in the three basic parameters of melt crystallization: the steady-state nucleation rate l_{SS} (which is proportional to $1/\eta$, the non-steady-state nucleation time lag, $\tau^{\#}$ (proportional to η), and the linear crystallization rate g (again proportional to $1/\eta$). At $F = 0$, the dimensionless η_{eff}/η_0 ratio becomes $(\eta_{\text{eff}}/\eta_0) = 1$ in the same way as the coefficients $f_i(P) = 1$ at normal pressure.

For pseudoplastic liquids the ratio η_{eff}/η_0 decreases with increasing F values: thus increased values of $I_{\text{SS}}(F)$, $g(F)$ and a reduced $\tau^{\#}(F)$ should result in an undercooled liquid under stress. For dilatant liquids, however, $f(F)$ increases with F and we should expect increased η_{eff} values and thus decreased I_{SS}, g and increased $\tau^{\#}$ values.

Denoting with a tilda sign the crystallization parameters in the process under tangential strain and with an (o)-sign those for the unstrained case we have to write:

$$\tilde{I}_{\text{SS}}(T, P_0) = I_{\text{SS}}(o)\psi(F) \tag{11}$$

$$\tilde{\tau}^{\#}(T, P_0) = \tau^{\#}(o)/\psi(F) \tag{12}$$

$$\tilde{g}(T, P_0) = g(o)\psi(F) \tag{13}$$

In doing so we have adopted the assumptions that the definition of $\psi(F)$ given with Equation (2) and the structure of the I_{SS}, $\tau^{\#}$ and g functions already discussed in detail in reference [1], i.e.,

$$I_{\text{SS}} = \text{const } (1/\eta) \exp(-\Delta W/kT) \tag{14}$$

$$\tau^{\#} = \text{const } \sigma\eta/\Delta\mu^2 \tag{15}$$

$$g = \text{const } (1/\eta)\Omega(T, \Delta\mu) \tag{16}$$

Here, as in reference [1], $\Delta W = A_0/\Delta\mu^2$ denotes the thermodynamic barrier of nucleation, $\Delta\mu$ is the thermodynamic driving force of the crystallization process, σ is the melt/crystal specific interface energy, and $\Omega(T, \Delta\mu)$ is a function of $\Delta\mu$ and T determined by the corresponding mechanism of crystal growth.

If a combined action of both hydrostatic pressure ($P \gg P_0$) and tangential stress F is to be expected, we can write (assuming the cumulative effect):

$$\tilde{I}_{\text{SS}}(T, P) = I_{\text{SS}}(T, P)\psi(F) \tag{17}$$

$$\tilde{\tau}^{\#}(T, P) = \tau^{\#}(T, P)/\psi(F) \tag{18}$$

$$\tilde{g}(T, P) = g(T, P)\psi(F) \tag{19}$$

Here again the tilda sign denotes the case under strain and $I_{\text{SS}}(T, P)$, $\tau(T, P)$ and $g(T, P)$ are derived from the respective $I_{\text{SS}}(o)$, $\tau^{\#}(o)$ and $g(o)$ values by introducing the $f_i(P)$ functions, as discussed in detail in reference [1].

3. Formulation via tangential flow rate

In many cases it is more convenient to define the ratio η_{eff}/η_0 not by the $f(F)$ or $\psi(F)$ function and the applied stress F, but directly by the rate of the tangential flow, $\dot{\gamma}$. This can be done if we determine F in Equation 2 as:

$$F \equiv \varphi[(\eta_0/A^*)\,\dot{\gamma}] \tag{20}$$

where

$$\varphi[(\eta_0/A^*)\,\dot{\gamma}] = \psi^{-1}(F) \tag{21}$$

is the inverse function of the F $\psi(F)$ (or F $f(F)$) dependence (i.e., $\varphi(Y) = f^{-1}(x)$).

Substituting Equation 20 into Equation 2 we obtain:

$$\eta_{\text{eff}}/\eta_0 = (1/\eta_0\gamma)\varphi[(\eta_0/A^*)\dot{\gamma}] \qquad (22)$$

The above procedure applied to the Prandtl–Eyring or the de Waele–Ostwald dependences (Equations 5 or 8) gives respectively:

$$\eta_{\text{eff}}/\eta_0 = \operatorname{arsinh}[(\eta_0/A^*)\dot{\gamma}]/\eta_0\dot{\gamma}, \quad A^* = 1/a_0^* \qquad (23)$$

and

$$\eta_{\text{eff}}/\eta_0 = [\eta_0\dot{\gamma}]^{-n}\,(1/[A_1^*]^n) \qquad (24)$$

Expanding the arsinh (x) functions in Equation 23 for $(\dot{\gamma}\eta_0)/A^* < 1$ as arsinh $(x) \approx x(1\text{–}1/6\,x^2)$ and introducing the physical meaning of a_0^* according to Eyring via the rheological volume V^* (see references [8, 15]) as:

$$a_0 = V^*/2\,RT \qquad (25)$$

we obtain

$$\eta_{\text{eff}}/\eta_0 \approx 1 - 1/24\,\{[V^*(T)/RT]\dot{\gamma}]^2\} \qquad (26)$$

which is a dependence identical with those following from polymer flow models.

The de Waele–Ostwald formula (Equation 8) gives with Equation 24 for $n = 1.5$ (i.e., for the semi-cubic parabola equation, see reference [6]):

$$\eta_{\text{eff}}/\eta_0 \approx \{[A_1^*]^2\eta_0\dot{\gamma}]\}^{-1/3} \qquad (27)$$

For $n = 2$ (corresponding to Adams–Williamson relaxation kinetics, see reference [7]) we have:

$$\eta_{\text{eff}}/\eta_0 \approx \{A_1^*\eta_0\dot{\gamma}\}^{-1/2} \qquad (28)$$

i.e., in both cases the η_{eff}/η_0 dependence decreases with increasing $\dot{\gamma}$ values.

For the dilatant case of Equation 8 ($n = 1/2$, corresponding to Darcy's Law) Equation 22 gives, however, the following dependence:

$$\eta_{\text{eff}}/\eta_0 \approx [(\eta_0\dot{\gamma})/A_1^*] \qquad (29)$$

i.e., a η_{eff}/η_0 ratio increasing linearly with $\dot{\gamma}$.

In many experimental situations measurements of tangential flow rates may be more easily performed than determinations of the stress F applied and in such cases the formalism developed in this section may be of use.

4. Comparison with experimental findings

In order to estimate the possibilities of a rheologically induced nucleation processes we have first to analyse the probable changes in η_{eff} under real tangential flow conditions. An appropriate model glassforming substance is $Li_2O \cdot 2SiO_2$ which has been frequently used as a crystallization model in nucleation and crystal growth experiments [21–24]. Detailed viscosity measurements have also been performed with $Li_2O \cdot 2SiO_2$ melts so that the $\eta(T, P_0)$ function of this substance is well known. The maximum nucleation rate of this melt is achieved at approximately 450 °C (see the $I_{\text{SS}}(T, P_0)$ curves for this substance obtained by various authors as summarized in reference [8]). The maximum of the linear crystal growth dependence $g(T, P_0)$ for $Li_2O \cdot 2SiO_2$ melts is observed at 930 °C [25].

Detailed measurements by Deubener and Brückner [23] and Deubener [24] have shown that under experimentally reproducible tangential flow conditions the viscosity of $Li_2O \cdot 2SiO_2$ melts is significantly reduced at temperatures and viscosities corresponding to the nucleation region (at 483 °C and $\eta_0 = 2.2 \times 10^{11}$ dPa s).

Thus, as seen from Fig. 2, at $\dot{\gamma} = 10^{-2}\ \text{s}^{-1}$, the viscosity of a $Li_2O \cdot 2SiO_2$ melt falls to only 30% of the initial η_0 value.

It is evident from Fig. 3 that the η_{eff}/η_0 versus $\dot{\gamma}$ data of Fig. 2 can be described in terms of Equation 23, i.e., in co-ordinates log $(\eta_{\text{eff}}/\eta_0)$ versus log arsinh $\{[(V_{\text{m}}f^*\eta_0)/2RT]\dot{\gamma}\}$, following from the energy barrier model with a fairly reasonable value of Eyrings' f^* factor (for $f^* = 5$). This experimentally adjustable factor gives the number of structural units in the melt involved in the collective molecular movement, thereby determining the viscous flow [8]. An accurate description of the $\varphi(\dot{\gamma})$ function for this substance can be achieved also with other empirical equations using more experimentally adjustable constants [19]. Here it is essential to mention that Fig. 2 also gives the limits (for $\dot{\gamma} \to \infty$) up to which η_0 can be reduced under tangential flow. These limits indicate the extent to which according to Equation 10 nucleation and crystal growth rates can be increased and the possible decrease in the non-steady-state time lags.

Such a reduction of viscosity under tangential stress may explain the increase of nucleation and crystal growth rates observed in the extrusion pressure experiments. Here we would like to mention again that in these experiments with melts having a composition nearly corresponding to $Li_2O \cdot 2SiO_2$ the hydrostatic pressure applied was so low that under these conditions,

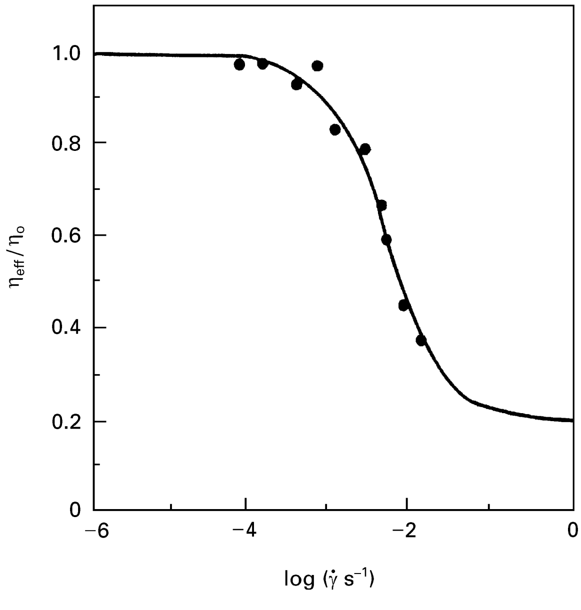

Figure 2 Changes of the effective viscosity η_{eff} of $Li_2O \cdot 2SiO_2$ melts as a function of the rate of shear flow at 483 °C and $\eta_0 = 2.24$ d.Pa.S (according to Deubener and Brückner [23, 24]).

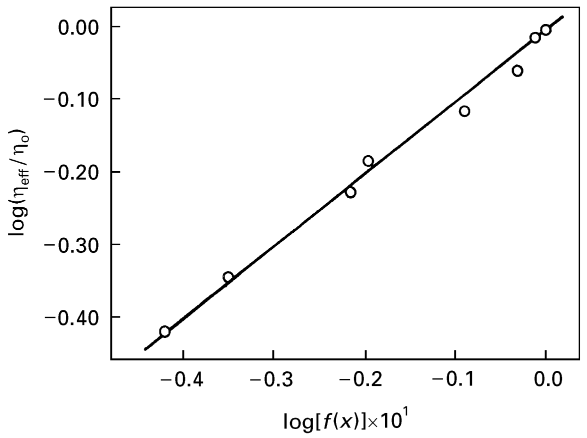

Figure 3 The $\eta_{\mathrm{eff}}/\eta_0$ data for $Li_2O \cdot 2SiO_2$ from Fig. 2 in co-ordinates corresponding to the Prandtl–Eyring barrier model. Here $f(x) = \operatorname{arsinh}[(a_0 f^*/2)\eta_0\dot{\gamma}]$ and $\log[\eta_{\mathrm{eff}}/\eta_0] = \log[a_0 f^* \dot{\gamma}] + \log f(x)$ with $a_0 = V_{\mathrm{m}}/2RT = 4.8 \times 10^{-9}$ m^3 J. Thus for the corresponding gram formula molar weight and the corresponding molar volume it follows that $f^* \cong 5$.

as shown by the analysis in Part I of the present study, no substantial change of either I_{SS}, $\tau^{\#}$ or g could be expected (e.g., $T_{\mathrm{m}}(P)$ for $Li_2O \cdot 2SiO_2$ increases at the mentioned P-values only by several degrees). Nevertheless, relatively high growth and nucleation rates in the extruded melts were observed at 540 °C i.e., at a temperature, where both I_{SS} and g are practically zero for the non-stressed samples. A sequence of further experiments showed that a hydrostatic pressure (0.05 GPa), applied to the melt in the apparatus could not infact initiate crystallization. In Equations 17–19 that summarize the combined effect of hydrostatic pressure and tangential stress, a notable influence on the crystallization of $Li_2O{\cdot}2SiO_2$ melts can only be expected from the flow reduced $\eta_{\mathrm{eff}}/\eta_0$ ratio.

The experiments performed by Burkhart and Russel [26], discussed in more detail in reference [1], also show that no shift in the nucleation maximum occurs in the crystallization curves at a hydrostatic pressure of 0.05 GPa, with which to explain the increased nucleation rate in the extrusion pressure results.

On the other hand, the nucleation experiments of Pennings *et al.* [2] at increased tangential stress were performed under conditions at which a considerable reduction of the $\eta_{\mathrm{eff}}/\eta_0$ ratio is to be expected for organic polymer melts.

5. Discussion

The principal assumption made in the present contribution is that the real (or effective) viscosity value rather than the Newtonian viscosity is responsible for the self diffusion processes in undercooled melts. Under hydrostatic pressure, the viscosity increases, whereas under tangential flow it is reduced. In both cases, according to Equation 10, we have to expect that D_0 would change as does, η.

As mentioned in the introduction, the classical meaning of the term nucleation catalysis is related to a decrease in the thermodynamic barrier to nucleation. Here we consider another possible cause for nucleation catalysis: the reduction of the effective viscosity, and thus an increase in the self diffusion coefficient of the system. Thus a new mechanism for increasing the rate of melt crystallization is introduced for discussion.

The possibility of decreasing the kinetic barrier to crystallization could open new horizons to induced or controlled nucleation, extrusion pressing in the synthesis of glass ceramics being only one of many possible examples. The possibility of inducing crystallization in glasses by lowering their viscosity was mentioned many years ago [12]. One practical realization of this idea was to dissolve glasses in appropriate solvents and thus to bring them to crystallization (see the crystallization experiments with phenolpataleine glass initiated by dissolving of the latter in water [27]).

In polymer science, the viscosity decrease in a non-Newtonian liquid under stress is associated with the very nature of glass forming liquids and with their behaviour as non-Newtonian pseudoplastic or dilatant liquids. The non-Newtonian behaviour of undercooled melts is a significant factor that determines the kinetics of crystallization, as has been discussed in a series of papers (see [28]) dealing with nucleation and crystallization in viscoelastic non-Newtonian systems. It is also of particular importance to mention that in dilatant liquids (such as water) the reverse effect of this, observed in pseudoplastic systems could be expected at flow under tangential stress, namely an increase in the $\eta_{\mathrm{eff}}/\eta_0$ ratio and hence inhibited crystallization.

Taking into account the low values of tangential stress at which considerable reduction of the $\eta_{\mathrm{eff}}/\eta_0$ ratio can be expected in polymer systems, it is evident that rheologically induced nucleation and crystal growth are to be achieved most readily in organic polymers. The experiments of Pennings *et al.* [2] provided evidence in this respect. However, the experimental results in Section 4 show that in silicate melts under conditions of extrusion pressure it is also possible to initiate crystallization in this way.

Considering other possible applications of the results given here and in reference [1], geology appears to be a very promising field, e.g., in magmic crystallization under hydrostatic pressure and for magma flowing under shear stress. It is evident that magma, being a silicate melt with a non-Newtonian rheology [29], would crystallize more readily in flow than under static pressure. This could be of considerable geological significance.

A very important question arising in connection with the present study is the way pressure applied in extrusion pressure apparatus or in geological flow processes is distributed into hydrostatic pressure and shear stress. A thorough study in this direction has been initiated, computer simulation experiments are currently in progress and the results will be published in due course.

Usually the pseudoplastic non-Newtonian behaviour of liquids is related to molecular units (e.g., of organic polymer chain molecules) ordering under the influence of flow itself and thus reducing viscosity. It has to be pointed out that structural changes have to take place in any liquid (even constituted of billiard ball-like molecules) under tangential stress and flow. The rheological changes are the consequence of structural alterations, which in pseudo plastic liquids result in a higher configurational energy and increased fluidity.

A remarkable example in this respect was presented by Heyes *et al.* [30] for non-linear shear stress effects in a simple Lenard–Jones liquid constructed from spherical molecules. The results of their molecular dynamics study [30] demonstrated that a peculiar ordering is taking place in the model "liquid" and because of this structural reorganization "paths are created along which particles can readily move". The self diffusion coefficient is greatly reduced in the shear plane and (which is particularly important) in all other directions.

The application of luminescence techniques has shown that in fact in pressure-extruded $Li_2O \cdot 2SiO_2$ glass rods a concentration of intermolecular distances takes place perpendicular to the flow direction; in the direction of flow an elongation of structural distances appears [31].

It should be pointed out that such structural ordering effects could give rise to additional enhanced possibilities of molecular incorporation into the growing crystalline cluster, e.g., reducing the structural factors of nucleation and growth, introduced and discussed in detail in references [8] and [32].

In many cases (especially in crystallization from melts with chain-like structural elements forming a crystal of fibrous structure) such ordering effects could explain, at least in a qualitative manner, the orientational effects in crystallization under extrusion pressure and the formation of elongated, ellipsoidal or even needle-like crystals.

A possible molecular picture explaining such effects is given in Fig. 4 (a and b). However, for the time being we cannot propose a quantitative model of such orientational effects.

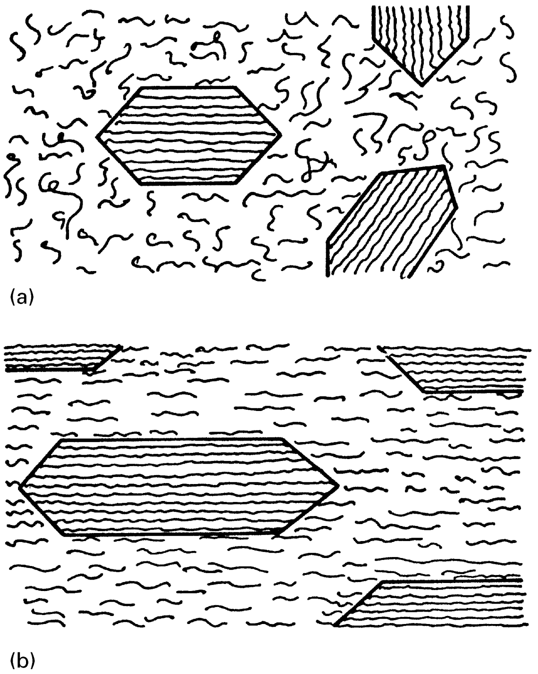

Figure 4 A qualitative illustration of ordering effects in pseudoplastic liquids under flow and crystallization orientational effects thus induced (a) liquid and crystal without flow; and (b) under tangential flow regime.

6. Conclusion

An analysis of the rheological behaviour of inorganic glass forming melts and of organic high polymer liquids has shown that under flow induced by tangential stress, their viscosity is reduced (pseudoplastic behaviour). In this way self-diffusion coefficients and thus crystallization rates of the melts increase and an interesting case of rheologically determined crystallization catalysis can be observed. Existing experimental evidence, both on viscosity changes with increasing rates of shear flow and on crystallization under tangential stress, are in good agreement with theoretical expectations.

Acknowledgements

These results of the present investigation have been obtained as part of an Innovation Programme sponsored by the Deutsche Forschungsgemeinschaft (DFG), Bonn. We would like to express our gratitude to the DFG for the financial support which made possible this research as an international cooperative project.

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Received 28 May 1996
and accepted 26 February 1997