

Viscosity of porous sintered glasses

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Following an analogy between flow properties and field or transport properties, an equation which describes the porosity, P , dependence of the viscosity in porous sintered glasses is presented. Not only the pore volume fraction but also pore structure parameters, such as pore shape and orientation, are considered in the calculation and the equation is valid for the whole porosity range. For low porosities ($P \leq 0.10$) the approach coincides with the prediction of Mackenzie for spherical pores with a precision of 1%. The calculated values are in good agreement with experimental data on porous glasses available from the literature, if appropriate pore geometry is assumed at the different porosity levels.

1. Introduction

Viscosity, relating shear stress and shear strain rate, is an important parameter when shear deformation, in addition to densification, occurs during sintering of glass. Shear stresses develop for example during sintering of glass–matrix composite materials since differential shrinkage rates result from the inclusion of rigid particles [1–3]. Therefore, evaluation of the effect of porosity and pore structure on the viscosity of the porous sintering glass compact is of great practical interest for the fabrication of glass–matrix composites.

Experimental data on the viscosity–porosity dependence of porous glasses obtained by means of sinter forging techniques [4, 5] have been fitted empirically to exponential functions of the form [4]

$$\eta_p = \eta_0 \exp[-\beta P] \quad (1)$$

and [5]

$$\eta_p = \eta_0 \exp\left[-\beta\left(\frac{P}{1-P}\right)\right] \quad (2)$$

where β is an adjustable variable, η_p the shear viscosity of the porous glass, η_0 the intrinsic shear viscosity of fully dense glass, and P is the porosity. No correlation of the value of β with the porosity structure was given. Theoretical models to describe the effect of porosity on viscosity have been developed by Mackenzie [6] and Scherer [7]. Mackenzie analysed the case of a dilute concentration ($P < 5$ –10%) of spherical pores. His result can be expressed by the equation

$$\eta_p = \eta_0(1 - \beta P) \quad (3)$$

Scherer's model [7] assumes a particular pore morphology, continuous pores between a cubic array of cylinders of the solid phase, and therefore it does not take into account different pore shapes and orientations which can develop during sintering. Comparison of the model with the experimental data of Rahaman *et al.* [5] was not successful and this was attributed to

the lenticular pore morphology observed, which deviated from the geometry assumed in the model. However, data on compacts made from spherical glass powders [8], having a less lenticular pore shape, showed good agreement with the theory. Pore geometry as a variable influencing viscosity was considered by Sura and Panda [9]. They applied a viscous analogy to the elastic analysis of porous materials and obtained, on the basis of the elastic approach of Nielsen [10], the following expression for the viscosity of a porous glass

$$\eta_p = \eta_0 \frac{3\Omega(1-P)^2}{3\Omega(1-P) + 2P} \quad (4)$$

where Ω represents a shape factor varying between 0 and 1. By comparison of the calculated values with experimental data they found, that Ω lies between 0.15 and 0.22 for $P \geq 0.15$ and approaches 1 for closed spherical pores ($P < 0.10$). For $P \approx 0.15$ –0.10 a transition in the pore structure occurs, with Ω varying continuously. However, the exact correlation between the shape factor, Ω , and the real features of the pore structure was not given.

The objective of this study is to present a simple expression for the porosity dependence of the viscosity in porous glasses by taking into account microstructural parameters which describe the porosity structure. The analysis is based upon the analogy between the fluidity of suspensions and the field properties of two-phase materials. In a companion paper the applicability of this approach to the calculation of the viscosity of melted glasses containing solid phase aggregates is discussed [11].

2. Discussion

The analogy between the equations governing transport or field properties and viscosity has been given in the past [12], and by means of this analogy the

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viscosity of suspensions has been modelled using general equations for the transport properties of two-phase materials [12,13]. In this context the following equation for viscosity, (η_c), of suspensions with rigid particles was derived [13]

$$\eta_c = \eta_0(1 - c)^{-m} \quad (5)$$

where c is the volume fraction and m is a function of the shape and orientation of the inclusions, which are modelled by mean spheroids of equal axial ratio. Equation 5 was successfully compared with experimental data for different suspension systems [13] and its application for calculating the creep behaviour of composite materials has also been shown [14].

The extension of this approach for the porous case follows readily, as shown already for field properties [15]. Thus, the porosity dependence of the viscosity of porous glasses may be written as

$$\eta_p = \eta_0(1 - P)^n$$

$$n = \frac{1 - \cos^2 \alpha}{1 - F} + \frac{\cos^2 \alpha}{2F} \quad (6)$$

where F is the shape factor of the mean spheroids substituting the real pores and $\cos^2 \alpha$ is the orientation factor, with α being the angle between the velocity of flow and the rotational axis of the spheroids. The shape factor, F , is identical to the well known delectrification factor, which is only dependent on the axial ratio of the substituting spheroid (z/x), as shown in Fig. 1. For statistical orientation of the pores, $\cos^2 \alpha = 0.33$; and for the special case of spherical porosity, $F = 0.33$. The important advantage of this equation is that the shape and orientation factors can be determined on plane sections of a real microstructure by measuring the area and perimeter of sectioned pores and from stereological equations [15]. Thus, the equation has predictive character since no fitting parameters are introduced in the calculations.

Since the microstructure of a porous compact changes continuously as sintering progresses, the viscosity-porosity relationship should take into account this continuous variation. However, some assumptions can be made in order to derive a unique equation for the whole porosity range. On the basis of previous experimental results [4, 5, 8, 9] the porosity range can be divided into the following stages: for $P < 0.10$ the pores can be considered spherical and thus without preferred orientation ($\cos^2 \alpha = 0.33$), so that for this porosity range the exponent in Equation 6 is fixed at $n = 3/2$. For $P > 0.15$, the pores have a pronounced lenticular shape and they can be described by a unique oblate spheroid ($z/x \ll 1$), and n in Equation 6 will be of the order of four to five, considering statistical pore orientation. In the transition zone between $P \approx 0.10$ and $P \approx 0.15$ the viscosity should experience a more or less abrupt variation.

These considerations can be expressed mathematically by means of the following equation

$$\eta_p = \eta_0[(1 - s)(1 - P)^{3/2} + s(1 - P)^n] \quad (7)$$

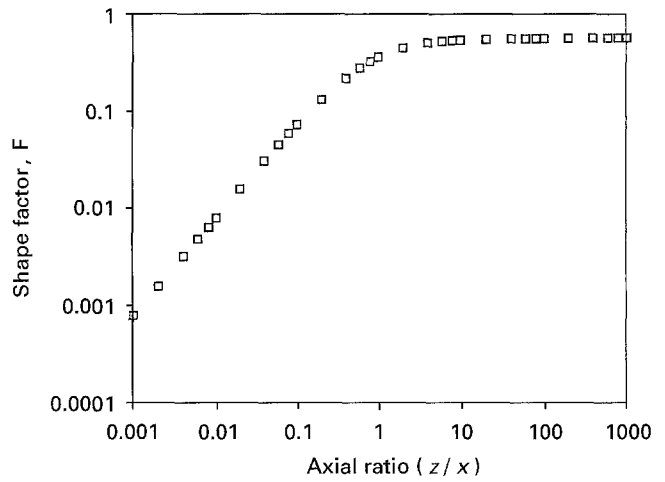


Figure 1 Shape factor, F , as a function of the axial ratio of spheroidal pores, after Ondracek [15].

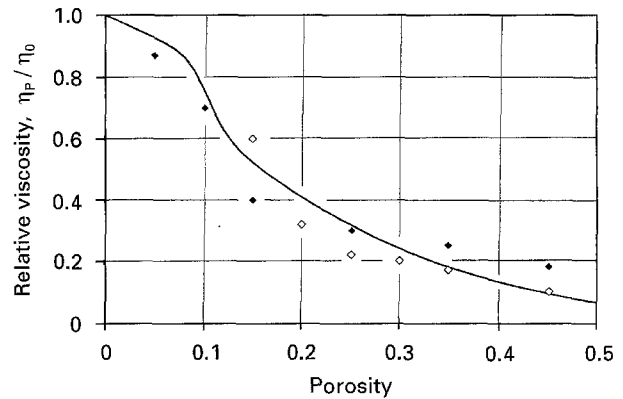


Figure 2 Normalized viscosity η_p/η_0 , as a function of porosity, P . Experimental values for (\diamond) cordierite type glass [9] and (\bullet) commercial aluminosilicate glass [4], (—) calculated values according to Equation 7 with $z/x = 0.07$ and $\cos^2 \alpha = 0.33$.

where the function

$$s = \frac{1}{1 - \exp[-100(P - 0.10)]} \quad (8)$$

has been used to “join” mathematically the respective equations for the low and the high porosity ranges.

A first testing of Equation 7 is to study its behaviour at very low concentrations of pores ($P \leq 0.05$), where the pores are thought to be spherical and the model of Mackenzie given by Equation 3 is valid. The deviation between the values given by both equations is less than 1% confirming the applicability of Equation 7 for low porosities. To illustrate the suitability of the approach for a wide porosity range experimental data available for the viscosity of porous glasses are considered below.

2.1. Comparison with experimental data

The viscosity of porous aluminosilicate glass of commercial composition [4] and of cordierite type glass [9] as determined by sinter forging experiments can be conveniently used for comparison with the theoretical values. In both cases the intrinsic viscosity of the fully dense glass at the working temperature was measured. Fig. 2 shows the experimental and calculated values

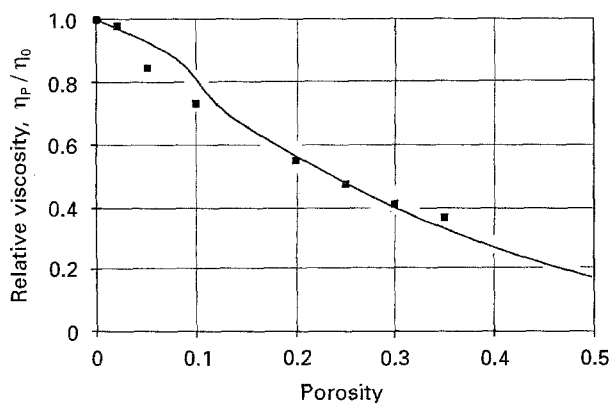


Figure 3 Normalized viscosity, η_p/η_0 , as a function of porosity, P . Experimental values for (■) spherical soda-lime glass [8], (—) calculated values according to Equation 7 with $z/x=0.15$ and $\cos^2\alpha=0.33$.

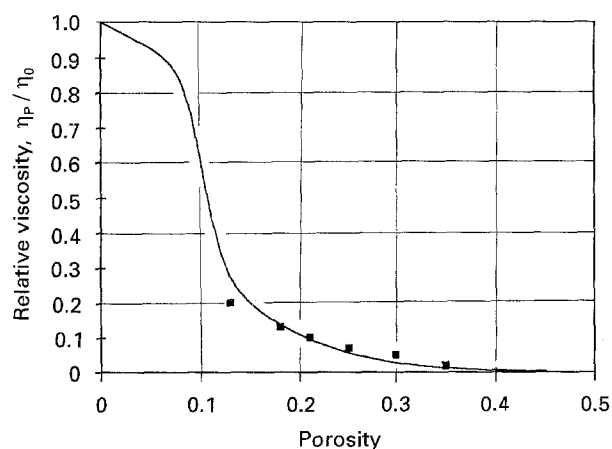


Figure 4 Normalized viscosity, η_p/η_0 , as a function of porosity, P . Experimental values for (■) crushed soda-lime glass [5], (—) calculated values according to Equation 7 with $z/x=0.07$ and $\cos^2\alpha=1$.

for the normalized viscosity, η_p/η_0 , as a function of pore volume fraction, P . The theoretical curve was calculated according to Equation 7 for randomly orientated pores ($\cos^2\alpha=0.33$) and $F=0.05$, which corresponds to lenticular pores of axial ratio $z/x=0.07$. Since no preferred orientation of the microstructure was reported in the experimental studies, the assumption of statistical pore orientation seems plausible. Moreover, the microphotographs of the microstructure shown in one of the studies [9] seem to confirm the pore geometry assumed here. The experimental data are in good agreement with the analysis.

A third experimental study can be considered for comparison with the model. In this case spherical soda-lime glass powder was sintered under uniaxial stress and the viscosity was measured for porosities up to $P\approx 0.4$ [8]. The experimental and calculated values are shown in Fig. 3. Values $z/x=0.15$ and $\cos^2\alpha=0.33$ (statistical pore orientation) were used in the calculations. The higher value for the axial ratio of the oblate pores used in this case was chosen since the glass powder investigated was spherical and the authors reported a less pronounced lenticular shape

than in a previous study [5]. Again there is good agreement between theory and experiment.

The last study to be considered is the earlier experimental work of Rahaman *et al.* on crushed soda-lime glass powder [5]. Here a strong anisotropic behaviour of the shrinkage during sintering under stress was found, which was attributed to pore orientation. Assuming a fully orientated pore structure ($\cos^2\alpha=1$) and lenticular pore shape as before ($z/x=0.07$) the theoretical viscosity-porosity relationship was calculated. The results are shown in Fig. 4 together with the experimental values. Again the applicability of Equation 7 is demonstrated.

3. Conclusions

It has been shown that Equation 7, derived on the basis of the analogy between flow properties and field properties of two-phase materials, can be conveniently applied to describe the viscosity-porosity dependence of porous glasses. Not only the pore volume fraction but also pore structure parameters, such as shape and orientation, are taken into account in the calculation. These parameters can be determined by means of quantitative microstructural analysis on plane sections of porous samples. For low porosity contents the approach coincides with the prediction of the model of Mackenzie, valid for spherical pores, with a precision of 1%. Although the experimental studies considered for comparison do not contain precise information on the porous structure at the different levels of porosity, the equation presented here describes the experimental data fairly well assuming reasonable pore shapes and orientations according to the experimental conditions. However, for a rigorous experimental verification of the equation, viscosity data on porous glasses accompanied with a sufficient and precise description of the porous structure are required.

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