JOURNAL OF MATERIALS SCIENCE 39 (2004) 3213–3215

Mooney-type relation for the porosity dependence of the effective tensile modulus of ceramics

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A widely used equation for fitting the porosity dependence of experimentally measured tensile modulus data is the exponential relation proposed by Spriggs in 1961 [1]:

$$E_r(\phi) = \exp(-b\phi), \tag{1}$$

where

$$E_r \equiv \frac{E}{E_0} \tag{2}$$

is the relative or reduced tensile modulus, with E being the effective tensile modulus of the porous ceramics and E_0 the tensile modulus of the matrix phase (dense, e.g., pore-free ceramic material), b is a fit parameter and ϕ the volume fraction of voids (porosity). Recently it has been shown [2] that the Spriggs relation, Equation 1, although usually considered to be purely empirical, can be derived from a simple functional equation of the form [3]

$$E_r(\phi) \equiv E_r(\phi_1 + \phi_2) = E_r(\phi_1) \cdot E_r(\phi_2). \tag{3}$$

This functional equation is set up on the basis of a virtual experiment dividing the total porosity present, ϕ, into two fractions, ϕ_1 and ϕ_2, not necessarily small [2].

Defining an intrinsic tensile modulus $[E]$

$$[E] \equiv \lim_{\phi \to 0} \frac{E_r - 1}{\phi} \tag{4}$$

Equation 1 can be rewritten in the form

$$E_r(\phi) = \exp([E]\phi), \tag{5}$$

which can easily be seen to reduce to the linear relation

$$E_r = 1 + [E] \cdot \phi \tag{6}$$

for small porosity values ϕ (micromechanical dilute approximation). For ceramics with isolated spherical pores in a matrix with a Poisson ratio of $\nu_0 = 0.2$, the intrinsic tensile modulus is $[E] = -2$, cf. [2] and [4]. With this value Equation 6 becomes

$$E_r = 1 - 2\phi, \tag{7}$$

which is identical to the result of the self-consistent scheme approximation [5]. Analogously, in the context of suspension viscosity, an intrinsic viscosity $[\eta]$ can be defined as

$$[\eta] \equiv \lim_{\phi \to 0} \frac{\eta_r - 1}{\phi_S} \tag{8}$$

(with the relative or reduced shear viscosity η_r, and the solids volume fraction ϕ_S) and an exponential relation of the Arrhenius type [6, 7] can be derived via a functional equation approach [2]:

$$\eta_r(\phi_S) = \exp([\eta]\phi_S) \tag{9}$$

(with positive $[\eta]$). In a similar way as Equation 5, also this relation reduces to the linear relation

$$\frac{\eta}{\eta_0} = 1 + [\eta] \cdot \phi_S, \tag{10}$$

in the case of small solids volume fractions ϕ_S. This is the Jeffery-Einstein equation [8, 9] for the effective viscosity of dilute suspensions with rigid particles of spherical or spheroidal shape. In particular, for rigid sphere suspensions the intrinsic viscosity adopts Einstein's value of 2.5, which can be considered as a benchmark value.

Now both Equations 5 and 9 suffer from the serious drawback, recognized as early as 1962 by Hasselman [10], that for large ϕ or ϕ_S (i.e., $\phi \to 1$ or $\phi_S \to 1$, i.e., 100% porosity or 100% solids volume fraction), respectively, they do not attain the respective values of zero or infintity as required. In order to circumvent this drawback, Hasselman, based on a previous work of Hashin [11] proposed a relation of the form

$$E_r = \frac{1 - \phi}{1 - B\phi}, \tag{11}$$

with B being a constant, which can in principle be calculated from theory [10, 11]. However, when B is treated as a fit parameter, another complication arises, which will be discussed below. Note also that the drawback mentioned above does not exist for power-law relations of the type

$$E_r(\phi) = (1 - \phi)^{-[\mathrm{E}]} \tag{12}$$

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and

$$\eta_{\mathrm{r}}(\phi_{\mathrm{S}}) = (1-\phi_{\mathrm{S}})^{-[\eta]}, \qquad (13)$$

respectively [2, 12], which contain the (correct version of the) Coble-Kingery relation for the relative tensile modulus of ceramics with isolated sphercial pores in a $\nu_0 = 0.2$ matrix material [4, 13],

$$E_{\mathrm{r}} = (1-\phi)^2, \qquad (14)$$

and the Roscoe-Brinkman relation for the relative viscosity of suspensions [14–16]

$$\eta_{\mathrm{r}} = (1-\phi_{\mathrm{S}})^{-2.5}, \qquad (15)$$

respectively, as special cases. Both Equations 14 and 15 follow from the differential scheme approximation [4, 5, 14–16], but can alternatively be derived via a functional equation approach [2]. Another alternative way to avoid the above mentioned drawback is implicitly included in Mooney's paper on suspension viscosity [17]. The widely used Mooney relation for suspension viscosity, also derived by via a functional equation, is

$$\eta_{\mathrm{r}}(\phi_{\mathrm{S}}) = \exp\left([\eta]\frac{\phi_{\mathrm{S}}}{1-\frac{\phi_{\mathrm{S}}}{\phi_{\mathrm{SC}}}}\right). \qquad (16)$$

It can be easily be verified that the Mooney relation satisfies both requirements for the limit behavior at small and large solids volume fractions. In viscosity context the critical solids volume fraction ϕ_{SC} can be interpreted as the maximum packing fraction, at which the suspension looses flowability (locking phenomenon). In the case of randomly close packed (rcp) monosized spheres ϕ_{SC} should be around 0.64, i.e., 64 vol% (the classical value [18] is 63.7%, while newer research [19] favors 64.4 vol% for the maximum packing fraction of monosized spheres in rcp arrangement).

Now we apply Mooney's argumentation to the elasticity context in order to derive a Mooney-type relation for the relative tensile modulus of porous ceramics. For this purpose we modify the simple functional equation given above (Equation 3) as follows: While in the virtual experiment mentioned above the total porosity ϕ is decomposed into the partial volume fractions ϕ_1 and ϕ_2,

$$\phi = \frac{V_1+V_2}{V_0+V_1+V_2} = \frac{V_1}{V_0+V_1+V_2} + \frac{V_2}{V_0+V_1+V_2} = \phi_1+\phi_2, \qquad (17)$$

note that this decomposition into partial volume fractions is only a virtual one. However, when the fractions are added in a real experiment, account must be taken of the fact that the first fraction of pores is added to a dense material, where the second fraction of pores is not yet present,

$$\phi_{12} = \frac{V_1}{V_0+V_1} = \frac{\phi_1}{1-\phi_2}, \qquad (18)$$

i.e., in order to obtain a partial volume fraction of ϕ_1 after mixing, the fraction to be added to the dense material (i.e., before the second fraction is present) must be larger than ϕ_1, by a factor of $(1-\phi_2)^{-1}$. In principle, the same reasoning applies to the second fraction with

$$\phi_{21} = \frac{V_2}{V_0+V_2} = \frac{\phi_2}{1-\phi_1}. \qquad (19)$$

Following Mooney's approach, what holds for the first fraction must hold also for the second fraction, and thus the corresponding functional equation is

$$E_{\mathrm{r}}(\phi) \equiv E_{\mathrm{r}}(\phi_1+\phi_2) = E_{\mathrm{r}}(\phi_{12})\cdot E_{\mathrm{r}}(\phi_{21}). \qquad (20)$$

It can easily be verified that this functional equation has the solution

$$E_{\mathrm{r}}(\phi) = \exp\left([E]\,\frac{\phi}{1-\phi}\right). \qquad (21)$$

Additionally, following Mooney, we adopt the analogue of Mooney's assumption that the space available for the addition of the second fraction is effectively reduced by the presence of the first fraction, i.e., in order to obtain a partial volume fraction of ϕ_1 after mixing, the fraction to be added to the dense material (i.e., before the second fraction is present) must be larger than ϕ_1, by a factor $(1-C\phi_1)^{-1}$ with $C > 1$, i.e. by more than only $(1-\phi_1)^{-1}$ above. In physical terms, the inverse of C can be interpreted as a critical porosity, i.e., $\phi_{\mathrm{C}} \equiv C^{-1}$ has the properties of a percolation threshold. With this additional assumption the volume fractions to be added are

$$\phi'_{12} = \frac{\phi_1}{\left(1-\frac{\phi_2}{\phi_{\mathrm{C}}}\right)}. \qquad (22)$$

and

$$\phi'_{21} = \frac{\phi_2}{\left(1-\frac{\phi_1}{\phi_{\mathrm{C}}}\right)}. \qquad (23)$$

The corresponding functional equation is

$$E_{\mathrm{r}}(\phi) \equiv E_{\mathrm{r}}(\phi_1+\phi_2) = E_{\mathrm{r}}(\phi'_{12})\cdot E_{\mathrm{r}}(\phi'_{21}), \qquad (24)$$

and its solution is

$$E_{\mathrm{r}}(\phi) = \exp\left([E]\frac{\phi}{\left(1-\frac{\phi}{\phi_{\mathrm{C}}}\right)}\right). \qquad (25)$$

This is the relation for the relative tensile modulus, derived in analogy to the Mooney relation for suspension viscosity. In contrast to the Spriggs relation, Equation 1 or 5, and the Hasselman relation, Equation 11 (with $\phi_{\mathrm{C}} \equiv B^{-1}$), this relation predicts a tensile modulus approaching zero when $\phi \to \phi_{\mathrm{C}}$, corresponding to physical experience. Similar to the Spriggs relation and in contrast to the Hasselman relation, the limit behavior for $\phi \to 0$ is predicted correctly by Equation 25. Similar to the Hasselman relation and in contrast to the

Spriggs relation, Equation 25 allows for the possible occurrence of a percolation threshold. For ceramics with spherical pores the intrinsic tensile modulus should be $[E] = -2$. When used as a two-parameter fit equation, a deviation from this value may be interpreted as being due to deviations of the pore shape from sphericity.

Acknowledgment

This work was part of the project "Mechanics and Thermomechanics of Disperse Systems, Porous Materials and Composites" supported by the Grant Agency of the Czech Republic (Grant No. 106/00/D086). The support granted to one of the authors (W. P.) is gratefully acknowledged.

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Received 26 June
and accepted 24 November 2003