JOURNAL OF MATERIALS SCIENCE **39** (2004) 3501 – 3503

New relation for the porosity dependence of the effective tensile modulus of brittle materials

W. PABST, E. GREGOROVÁ
*Department of Glass and Ceramics, Institute of Chemical Technology Prague, Technická 5,
166 28 Prague 6, Czech Republic*
E-mail: pabstw@vscht.cz

In a series of recent publications it has been shown that there is an almost complete formal analogy in the relations describing the effective shear viscosity of suspensions and the effective tensile modulus of porous media [1–5]. Note that this analogy originates from the possibly analogous microstructures or microstructural models of suspensions and porous media, i.e., it concerns micromechanical relations and is therefore of a different character than the well-known continuum mechanical analogy between linear elasticity and linear viscosity [6].

Inter alia, it has been shown [4, 5] that the frequently used Phani–Niyogi relation [7],

$$E_r = \left(1 - \frac{\phi}{\phi_C}\right)^N, \tag{1}$$

is the porous media analog of the Krieger relation of suspension rheology [8], when the "critical" (in the sense of percolation theory [9]) exponent N is interpreted as $N = -[E]\,\phi_C$, i.e., as the negative product of the critical volume fraction of voids ϕ_C (the critical porosity at which the material looses integrity) and the "intrinsic tensile modulus" defined (in analogy to the intrinsic viscosity of suspension rheology) as

$$[E] \equiv \lim_{\phi \to 0} \frac{E_r - 1}{\phi}. \tag{2}$$

In these relations

$$E_r \equiv \frac{E}{E_0} \tag{3}$$

is the relative tensile modulus, with E being the effective tensile modulus of the porous material, E_0 the tensile modulus of the matrix phase (dense, e.g., pore-free material) and ϕ the volume fraction of voids (porosity). Thus, an alternative formulation of the Phani–Niyogi relation, Equation 1, is

$$E_r = \left(1 - \frac{\phi}{\phi_C}\right)^{-[E]\phi_C}. \tag{4}$$

In the sense of percolation theory, the critical porosity may be interpreted as a percolation threshold [10], although the prediction of this percolation threshold is dependent on the pore shape and is highly non-trivial because of the possibility for the pores to overlap. Nevertheless, results of successful model calculations for materials with isotropic, uniform, and random microstructure have been reported in the literature [11], and the critical porosities predicted appear rather realistic.

The Phani–Niyogi relation, Equation 4, seems to be the most universal and flexible relation for the fitting of experimentally measured porosity dependence of effective tensile moduli. For spherical pores the intrinsic tensile modulus $[E]$ should be -2, since in the limit of very small porosities ("dilute" approximation in the sense of micromechanics [6, 12]) the Phani–Niyogi relation should reduce to the Dewey–Mackenzie relation [13–15] for the effective tensile modulus of materials with a small amount of (non-overlapping, i.e., isolated) spherical pores,

$$E_r = 1 - 2\phi. \tag{5}$$

Note that the latter relation is identical to the result of the self-consistent scheme approximation [12]. On the other hand, in the absence of a critical porosity, i.e., $\phi_C = 1$, the Phani–Niyogi relation reduces to the (corrected version of the) Coble–Kingery relation [1–5],

$$E_r = (1 - \phi)^2, \tag{6}$$

when $[E] = -2$, i.e., when the pores are spherical. Note that although porosities close to 100% are attainable in foams and network structures [16], for isolated spherical pores the case $\phi_C = 1$ would correspond to a highly idealized case, with a microstructure corresponding to a very special type of foam (fractal foam). Such a microstructure would be realizable, of course only approximately, by a strongly polydisperse size distribution arranged in a fractal microstructure with smaller pores in the interstices between larger ones.

The Phani–Niyogi relation, Equation 4, can be used as a three-parameter fit model (with E_0, ϕ_C and $[E]$ as adjustable parameters), as a two-parameter fit model (when the value of E_0 is reliably known), or for comparison purposes (when E_0 is known and ϕ_C and $[E]$ have been predicted for model microstructures via numerical simulations, cf. [11]). When used as a three-parameter fit model, depending on the non-linear regression software used, parameter guesses may be

0022–2461

required and/or covergence problems may arise, which may lead to failure of the fitting procedure.

In this brief note we present a new relation for the description of the porosity dependence of effective tensile modulus of brittle materials. It is simpler than the Phani–Niyogi relation, Equation 4, but retains the most important feature of the latter, viz. it allows for a critical porosity (percolation threshold) ϕ_C. In fact, our relation seems to be the simplest one allowing for a percolation threshold, which at the same time exhibits correct behavior in the dilute limit, cf. Equation 5, and reduces to the Coble–Kingery relation, Equation 6, in the absence of ϕ_C. A further requirement that must be met by such a relation is that for $\phi = \phi_C$ the relative tensile modulus must be zero. It can easily be verified that, for arbitrary intrinsic tensile moduli $[E]$, the following relation satisfies all these requirements:

$$E_r = (1 + [E]\phi - ([E] + 1)\phi^2) \cdot \left(\frac{1 - \phi/\phi_C}{1 - \phi}\right). \quad (7)$$

In the case of spherical pores the intrinsic tensile modulus $[E]$ is -2, and in this case Equation 7 adopts the extremely simple form

$$E_r = (1 - \phi) \cdot \left(1 - \frac{\phi}{\phi_C}\right). \quad (8)$$

As far as we know, this relation has never been used before in the elasticity context. We have tested Equation 8 with a large number of different data sets as a two-parameter fit model (or as a one-parameter fit model with E_0 assumed to be known). It turned out to be remarkably successful for this purpose, even in cases where fitting with the Phani–Niyogi relation failed because of "bad" (ill-behaved) data.

The idea for the construction of this new relation, Equation 7, and its special case, Equation 8, is very simple and has a certain analogy to a relation in suspension rheology, which has been derived by Robinson [17], cf. also Mooney [18]. Robinson's relation is

$$\eta_r = 1 + [\eta] \cdot \left(\frac{\phi}{1 - \phi/\phi_C}\right), \quad (9)$$

where η_r is the relative shear viscosity, defined in analogy to Equation 3, $[\eta]$ is the intrinsic viscosity (which adopts Einstein's [19] value of 2.5 in the case of rigid spheres), ϕ denotes the volume fraction of solids, and ϕ_C is its critical value. Evidently, the Robinson relation, Equation 9, which is the simplest relation for the relative shear viscosity allowing for a percolation threshold (critical solids volume fraction), reduces to the Jeffery–Einstein relation [19, 20],

$$\eta_r = 1 + [\eta] \cdot \phi, \quad (10)$$

in the dilute limit and yields an infinite value ($\eta_r \to \infty$) for $\phi \to \phi_C$, as required.

Finally, it might be of interest that the so-called Hasselman relation [21],

$$E_r = 1 + \frac{A\phi}{1 - (A + 1)\phi}, \quad (11a)$$

where A is a parameter (to be determined by fitting) can formally be rewritten as

$$E_r = \frac{1 - \phi}{1 - \phi/\phi_C}, \quad (11b)$$

with $\phi_C = 1/A$. This relation should be compared with our Equation 8. Evidently, the Hasselman relation violates both requirements mentioned above: it neither reduces to the Jeffery–Einstein relation, Equation 10, in the dilute limit, nor does it exhibit correct limit behavior ($E_r \to 0$) for $\phi \to \phi_C$. Thus, it is clear that the Hasselman relation has to be discarded for principal reasons.

Although the Phani–Niyogi relation, Equation 4, is and remains clearly the most universal and flexible fit model for the purpose in question, our new relations (7) and (8) are simpler than the latter, while at the same time retaining its most important feature, viz. the possible occurrence of a critical volume fraction (percolation threshold). In particular, Equation 8 is easier to handle (i.e., often more successful in fitting) than the Phani–Niyogi relation due to its extreme simplicity, i.e., the reduced number of parameters. In contrast to the Hasselman relation, Equation 11b, our new relation (8) exhibits correct limit behavior and has therefore to be preferred for principal reasons.

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.

References

1. W. PABST and E. GREGOROVÁ, *J. Mater. Sci. Lett.* **22** (2003) 959.
2. *Idem.*, *ibid.* (in press).
3. *Idem.*, *ibid.* (submitted).
4. *Idem.*, Effective Properties of Suspensions and Porous Materials from the Viewpoint of Micromechanics, in "Proceedings of the 5th Conference on Preparation of Ceramic Materials," edited by B. PLEŠINGEROVÁ and T. KUFFA (Technical University in Košice, Košice/Slovakia, 2003) p. 55.
5. *Idem.*, Effective Properties of Viscous Suspensions and Elastic Porous Media—Analogies and Differences, in "Proceedings of the 10th Annual Conference on Composite/Nano Engineering," edited by D. HUI (University of New Orleans, New Orleans/USA, 2003) p. 541.
6. S. TORQUATO, "Random Heterogeneous Materials—Microstructure and Macroscopic Properties" (Springer, New York, 2002).
7. K. K. PHANI and S. K. NIYOGI, *J. Mater. Sci.* **22** (1987) 257.
8. I. M. KRIEGER, *Adv. Coll. Interf. Sci.* **3** (1972) 111.
9. M. SAHIMI, "Applications of Percolation Theory" (Taylor & Francis, London, 1994) p. 183.

10. J. KOVAČIK, *J. Mater. Sci. Lett.* **18** (1999) 1007.
11. A. P. ROBERTS and E. J. GARBOZCI, *J. Amer. Ceram. Soc.* **83** (2000) 3041.
12. K. Z. MARKOV, in "Heterogeneous Media," edited by K. Z. MARKOV AND L. PREZIOSI (Birkhäuser, Basel, 2000) p. 1.
13. J. M. DEWEY, *J. Appl. Phys.* **18** (1947) 578.
14. J. K. MACKENZIE, *Proc. Phys. Soc. London* B **63** (1950) 2.
15. R. M. CHRISTENSEN, *Int. J. Solids Struct.* **83** (2000) 93.
16. L. J. GIBSON and M. F. ASHBY, in "Cellular Solids—Structure and Properties," 2nd ed. (Cambridge University Press, Cambridge, 1997).
17. J. V. ROBINSON, *J. Phys. Coll. Chem.* **53** (1949) 1042.
18. M. MOONEY, *J. Coll. Sci.* **6** (1951) 162.
19. A. EINSTEIN, *Ann. Physik* **19** (1906) 289.
20. G. B. JEFFERY, *Proc. Roy. Soc. Lond.* A **102** (1922) 161.
21. D. P. H. HASSELMAN, *J. Amer. Ceram. Soc.* **45** (1962) 452.

Received 4 December 2003
and accepted 21 January 2004