A generalized model to predict the effect of voids on modulus in ceramics

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An equation recently developed by the present author to describe the modulus of particulate composites as a function of the volume fraction of particles was modified in this study to describe modulus as a function of porosity. This new equation was applied to available modulus literature for ceramics where voids were the particulate phase. By varying the porosity interaction coefficient, σ, this new generalized void/modulus equation was shown to be able to yield equations previously used to predict modulus as a function of voids for ceramics. Wang theoretically described the mode of porosity interaction during compaction with a constant, α, to calculate the void/modulus relationship for three different compaction conditions. The generalized void/modulus equation developed in this study fit Wang's theoretical data exceptionally well, even though the porosity interaction coefficients, σ, obtained did not agree closely with Wang's values of α. Wang also experimentally measured the porosity and Young's modulus of manufactured alumina rods prepared with spherical and "egg-shaped" powders. The optimum fit for spherical particles occurred at $\sigma = 0.9$ and an initial porosity of $P_i = 0.405$ and for "egg-shaped" particles at $\sigma = 1.05$ and $P_i = 0.475$. The generalized void/modulus the equation for $\sigma = -1$ yields an equation that has the same form as Wang's proposed empirical equation that utilized two empirical constants, b and c. Wang's experimental data fitted with his proposed empirical equation gave a positive value for the constant c of 0.982 which corresponded to a negative value of P_i of -0.0743 which was not defined in the theoretical considerations developed in this study. While this value of the initial porosity, P_i, does give a better fit of the data for the interaction constant $\sigma = -1$, it still did not fit all the data as well as the results calculated for interaction coefficients nearer 1.0. The results of this study have shown that an excellent fit of most void/modulus data can be obtained using the generalized void/modulus equation developed in this study without making assumptions inconsistent with the theory presented.

1. Introduction

The void content of ceramic and metallic parts prepared by powder consolidation is typically minimized using processing techniques such as sintering, hot pressing, and hot isostatic pressing (HIPing) [1–5]. The large void concentration occurring in the starting powder is continually reduced with processing until a final part is prepared with very low void content. Mechanical properties, i.e. modulus and strength, are directly related to the residual volume fraction of voids in these parts [1–5]. Different processing techniques apparently reduce the void content in different ways which can result in different relationships between mechanical properties and void content [3,5]. For this reason, mathematical formulations that effectively describe the relationships between mechanical properties and void content can be useful when trying to understand better these different processing techniques.

A number of expressions for the effect of porosity on the elastic constants of solids have been proposed by various investigators [1, 5–14]. Several significant expressions relating the effects of voids on the modulus

of brittle solids have recently been reviewed by Phani and Niyogi [14].

One example of such an expression is Spriggs equation which can be written as

$$E = E_0 e^{-bP} \tag{1}$$

where E is the Young's modulus of a porous polycrystalline solid, E_0 the Young's modulus of a non-porous polycrystalline solid, b a constant, and P the porosity or fractional pore volume of the solid.

Some authors [13,14] have expressed a concern that Spriggs equation does not satisfy the boundary condition that $E = 0$ for $P = 1$. Phani and Niyogi [14] have further indicated that the boundary condition of $E = 0$ should occur at some critical porosity, P_{crit}, such that $P_{crit} \leq 1$ where the elastic modulus, E, becomes zero. Similarly, other modulus/porosity equations in the literature do not identify a P_{crit} in their formulations.

Because a powder by definition is a group of particles that do not stick together in tension, then the elastic modulus of the starting powder must also be

zero. The void content of this starting powder, P_i, would be expected to be the maximum expected during ceramic processing. Therefore, it is possible to state that the modulus of a porous solid should approach zero at some critical value of porosity, P_{crit}, which is, in fact, the initial porosity, P_i.

Available empirical equations in the literature generally describe the modulus at low void concentrations adequately; however, they have had limited success in describing the effect of voids at high concentrations [5, 14]. In addition, little consideration has been given to the theoretical significance of the constants generated from these empirical equations.

Several attempts have been made in the literature to describe the theoretical effect of void size reduction on the mechanical properties as a result of ceramic and/or metallic powder compaction processing [3, 4, 15]. Further discussion of the evaluation of these theoretical concepts will be explored in the later section of this paper.

A new generalized equation that addresses the modulus of particulate composites has recently been derived in a series of articles [16–20]. This new generalized equation for the first time addresses the detailed effects of particle size, particle-size distribution and packing fraction. The initial slope of this equation, $[G]$, at particle concentrations near zero has been defined as the "intrinsic modulus" [20]. The sign of this initial slope or intrinsic modulus was found to be determined by the ratio, G_f/G_0, of the modulus of the filler particle, G_f to the modulus of the matrix, G_0. When $G_f/G_0 > 1$ then the intrinsic modulus, $[G]$, is positive and when $G_f/G_0 < 1$ then the intrinsic modulus, $[G]$, is negative. In a previous paper [20] this new equation was successfully applied to available literature data where the modulus of the particle was greater than the modulus of the matrix. This new equation was found to predict successfully literature data for modulus as a function of the volume concentration of particles over the full range of particulate concentration.

In this paper this new equation will be applied to literature data where the modulus of the particle, in this case a void, is significantly less than the modulus of the matrix. In addition, it will be shown that equations previously used to predict modulus as a function of voids can also be obtained from this new equation by varying the porosity interaction coefficient, σ.

2. Description of a new generalized shear modulus equation

The processing of a ceramic from a starting powder will consist of consolidating hard particles and compacting voids such that at any time

$$\varphi_n + P = 1 \tag{2}$$

where φ_n is the hard particle and/or grain volume fraction, and P is the porosity or void volume fraction. This last relationship is probably most easily defined for the starting powder which consists of hard particles and the initial maximum porosity, P_i, that the ceramic component will see during its processing life. At this point it is useful to address the evaluation of

the starting powder as a particulate composite where the void phase would initially be considered to be the matrix and the hard particles the particulate phase.

In an earlier paper [20] this author showed that the following generalized equation can be used to describe the modulus–particulate concentration relationship of particulate composites.

$$\ln(G_c/G_0) = \left(\frac{[G]\varphi_n}{\sigma - 1}\right)\left[\left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{1-\sigma} - 1\right] \text{ for } \sigma \neq 1 \tag{3}$$

$$[G] = \left(\frac{G_f}{G_0} - 1\right)15(1 - v_0)\Big/\left[(8 - 10v_0)\frac{G_f}{G_0} + (7 - 5v_0)\right] \tag{4}$$

For the case where $\sigma = 1$, the resulting equation can be written as

$$\ln(G_c/G_0) = -[G]\varphi_n \ln\left(\frac{\varphi_n - \varphi}{\varphi_n}\right) \tag{5}$$

or

$$G_c = G_0\left(\frac{\varphi_n - \varphi}{\varphi_n}\right)^{-[G]\varphi_n} \tag{6}$$

where G_c is the composite shear modulus, G_f the shear modulus of the filler, G_0 the shear modulus of the matrix, $[G]$ the intrinsic modulus, v_0 Poisson's ratio, σ particle interaction coefficient, φ particle volume concentration in the matrix, and φ_n the particle packing fraction.

It has previously been shown [17] that the maximum volume fraction occupied by a given group of particles within a confined volume defined as the particle packing fraction, φ_n, can be evaluated from the particle-size distribution as described by the following equations

$$\varphi_n = \varphi_{nult} - (\varphi_{nult} - \varphi_m)e^{\alpha[1 - (D_5/D_1)]} \tag{7}$$

$$\varphi_{nult} = 1 - (1 - \varphi_m)^n \tag{8}$$

$$D_5 = \frac{\sum_{i=1}^{n} N_i D_i^5}{\sum_{i=1}^{n} N_i D_i^4} \tag{9}$$

$$D_1 = \frac{\sum_{i=1}^{n} N_i D_i}{\sum_{i=1}^{n} N_i} \tag{10}$$

where D_x is the xth average particle diameter, n number of different particle diameters in a batch combination, N_i the number of particles of the ith particle diameter, D_i the diameter of the ith particle size, α (a constant) $= 0.268$, φ_n the packing fraction, φ_{nult} the ultimate packing fraction for a specific number of particle sizes, and φ_m the monodisperse packing fraction. If an adequate description of the particle-size distribution is available, the D_5 and D_1 particle size averages described by Equations 9 and 10 can be replaced with more convenient equations for the evaluation of particle blends that have been developed in previous papers [17, 18].

It has also been previously shown [19] that the optimum particle-size distribution to give the maximum value for the D_5/D_1 ratio for a blend of n different monodisperse particles can be calculated. The volume fraction of monodisperse particle of size i, f_i, in a blend of n different exactly monodisperse particles to obtain a maximum value of the ratio D_5/D_1 can be calculated as [19]

$$f_i = \frac{V_i}{V_T} = \frac{D_i^{1/2}}{\sum_{i=1}^{n} D_i^{1/2}} \qquad (11)$$

where V_i is the volume of particles of the ith particle size in the blend, and V_T the total volume of all particles in the particle blend.

Based on the equations presented in this section it is possible to optimize the particle-size distribution and to minimize the void content of the starting powder used in processing a ceramic component. Such a smaller void volume fraction in the starting powder should result in a ceramic with acceptable strength and modulus with less high-pressure processing. To appreciate this concept better, it is useful to show how the equations presented in this section have been used to predict successfully the optimum compositions and the optimum packing fraction for the data generated by McGeary [21].

3. Comparison of theoretical volume fraction, f_i, and packing fraction φ_n

3.1 Predictions with McGeary's experimental results

McGeary [21] developed the experimental optimum composition for several binary, tertiary and quaternary mixtures of spherical particles. Several optimum compositions generated by McGeary [21] are summarized in Table I together with the diameters making up the particles in each of these mixtures. The predicted optimum compositions calculated using Equation 11 for these diameter combinations are also included in Table I. The maximum packing fraction,

φ_n, measured by McGeary [21] for several particle blends have been included in Table I together with the maximum packing fractions predicted using Equation 7. For values of D_5/D_1 greater than 40 it is easy to show that the maximum packing fraction calculated using Equation 7 will essentially equal the ultimate packing fraction. For reference, the value of R_{max} is simply the ratio of the largest particle diameter to the smallest particle diameter in each blend. It has been shown [17] that the maximum possible value of D_5/D_1 is equal to R_{max}.

The ultimate packing fractions, φ_{nult}, in Table I were calculated from Equation 8 using the monodisperse packing fraction ($\varphi_m = 0.589$) as determined by Lee [22]. This monodisperse packing fraction was obtained for loose random packing from literature results obtained from five different sets of authors [22]. Further details of the simplified calculation procedures used to generate the results in Table I will not be presented here, but are available elsewhere [19] to the interested reader. Some observations indicated from a comparison of the theoretical and experimental results in Table I include:

(i) the volume fractions calculated using Equation 11 agree very well with the optimum volume fractions determined experimentally by McGeary [21] for binary, tertiary and quaternary blends;

(ii) the packing fractions, φ_n, calculated using Equation 7 agreed very well with the packing fractions determined experimentally by McGeary [21].

Values of the ultimate packing fraction, φ_{nult}, calculated for particle blends with up to six ($n = 6$) monodisperse particles are compared with McGeary's measured maximum packing fractions, φ_n, for blends with up to four monodisperse particles ($n = 4$) in Fig. 1. Note that in general, it does not appear necessary to use more than six particles to obtain the initial packing of particles down to less than 2% voids. This would suggest that the void content of the starting powder blend for ceramic or metallic parts could be significantly reduced by simply using a blend of up to six monodisperse particles.

TABLE I Comparison of theoretical predictions with McGeary's particle composition measurements

| i	D_i (in.)	f_i Theory	Measured	Δf_i (% Diff.)	D_5/D_1	R_{max}	Q_m	Q_{nult}	Q_n Theory	Measured	ΔQ_n (% diff.)
1	0.5050	0.645	0.607	3.76							
2	0.0610	0.244	0.230	− 0.60							
3	0.0110	0.095	0.102	− 0.69							
4	0.0016	0.036	0.061	− 2.47	288.7	315.6	0.589	0.971	0.971	0.951	2.05
1	0.5050	0.669	0.647	2.18							
2	0.0610	0.232	0.244	− 1.15							
3	0.0110	0.099	0.109	− 1.03	41.5	45.9	0.589	0.931	0.931	0.898	3.26
1	0.1240	0.708	0.670	3.85							
2	0.0110	0.211	0.230	− 1.90							
3	0.0016	0.080	0.100	− 1.95	72.1	77.5	0.589	0.931	0.931	0.9	3.06
1	0.5050	0.742	0.726	1.61							
2	0.0610	0.258	0.274	− 1.61	7.7	8.28	0.589	0.831	0.791	0.8	− 0.91
1	0.5050	1.000	1.000	0.00	1	1	0.589	0.589	0.589	0.58	0.9
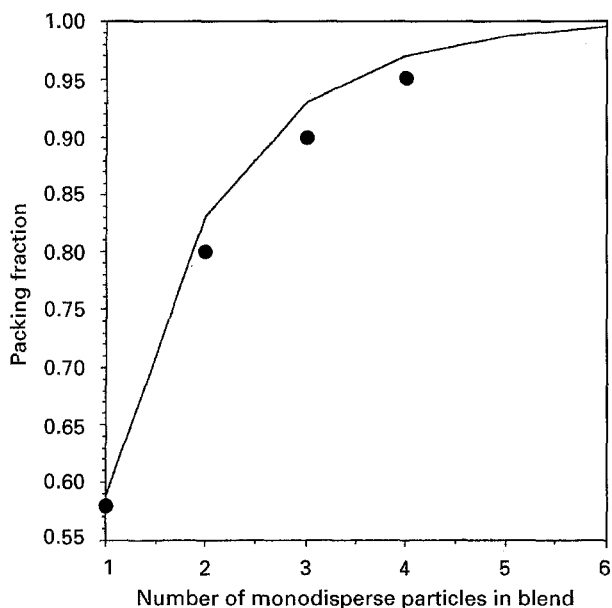
Figure 1 (—) Theoretical ultimate packing fraction, $\emptyset_{\text{nult}}$ and (●) McGeary's maximum measured packing fractions for blends of monodisperse particles.

3.2. Elucidation of the limits of the intrinsic modulus

When the modulus of the filler material, G_f, is significantly greater than the modulus of the matrix, G_0, such that $G_f \gg G_0$, then the intrinsic modulus defined by Equation 4 reduces to

$$[G] = \frac{15(1 - v_0)}{(8 - 10v_0)} \tag{12}$$

In general, it can be shown [23] that the volume change of a homogeneous material is related to Poisson's ratio as

$$\frac{\Delta V}{V} = \frac{(1 - 2v_0)}{E} 3\sigma_m \tag{13}$$

where ΔV is the change in volume, V the original volume, E is Young's modulus, σ_m the uniform three-dimensional stress, and v_0 is Poisson's ratio. It is apparent from Equation 13 that a material will have a negligible volume change and be incompressible if the Poisson's ratio is approximately 0.5. If the assumption is made that a particulate composite is incompressible such that Poisson's ratio is $v_0 = 0.5$, then the intrinsic modulus defined by Equation 12 reduces to

$$[G] = 2.5 \tag{14}$$

This is also the familiar result obtained by Einstein [24,25] as the intrinsic viscosity, $[\eta]$, of a liquid suspension. The assumptions required to reduce the intrinsic modulus to $[G] = 2.5$ were also the same ones specified by Einstein. The upper limit of the intrinsic modulus, $[G]$, as described by Equation 12 is shown in Fig. 2 for other values of Poisson's ratio, v_0, ranging from 0–0.7. As indicated in this figure, the upper limit of the intrinsic modulus ranges only from 1.88–3 when Poisson's ratio ranges from 0–0.6. Above a Poisson's ratio of 0.6 the intrinsic modulus increases more rapidly.
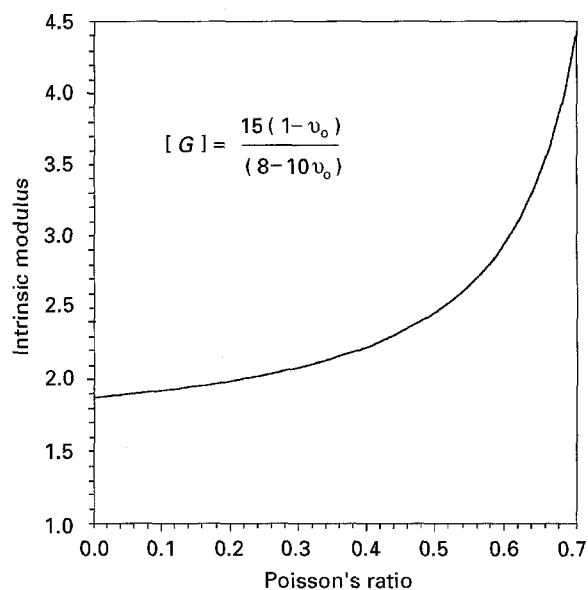

Figure 2 Calculated intrinsic modulus versus Poisson's ratio for modulus ratios $\gg 1$.
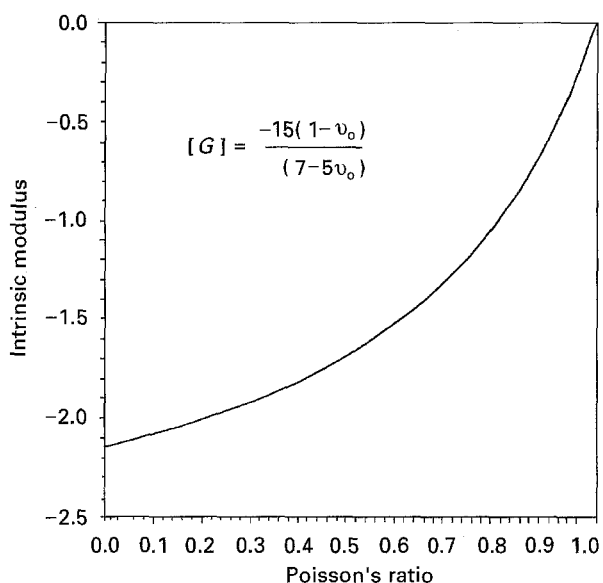

Figure 3 Calculated intrinsic modulus versus Poisson's ratio for modulus ratios $\ll 1$.

The second limit of generalized intrinsic modulus occurs when the modulus of the filler, G_f is essentially zero such that $G_f \ll G_0$. This condition would apply, for example, if the particles were voids with essentially no mass or strength. For this case the intrinsic modulus reduces to

$$[G] = \frac{-15(1 - v_0)}{(7 - 5v_0)} \tag{15}$$

The lower limit of the intrinsic modulus, $[G]$, as described by Equation 15 is shown in Fig. 3 for values of Poisson's ratio, v_0, ranging from 0–0.7. It is interesting that the lower limit of the intrinsic modulus is negative when Poisson's ratio ranges from $0 \le v_0 < 1$.

The limits defined by Equations 12 and 15 represent the extremes of the intrinsic modulus. Between these extremes there is one range of values where the intrinsic modulus is positive and a second range where
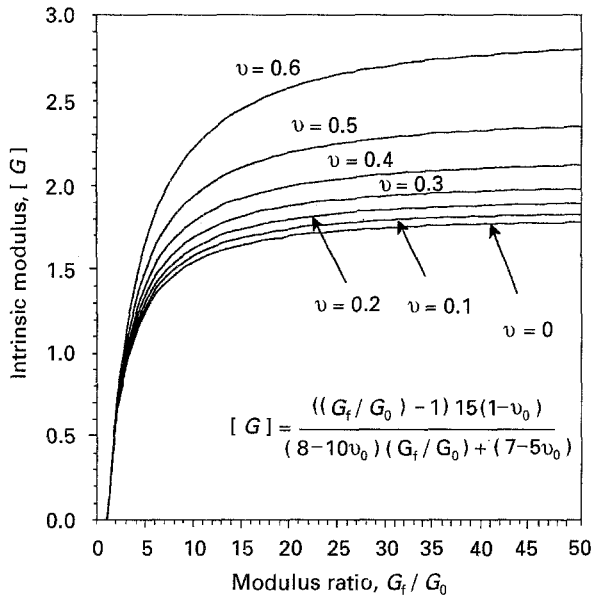
Figure 4 Calculated intrinsic modulus versus modulus ratio and Poisson's ratio.
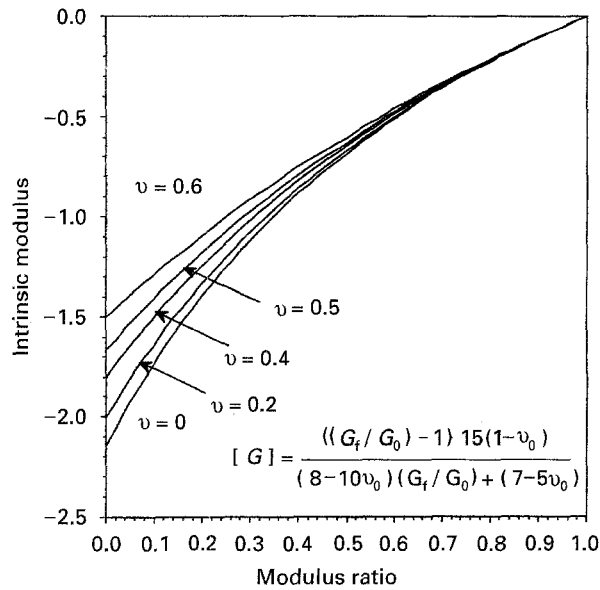

Figure 5 Calculated intrinsic modulus versus modulus ratio and Poisson's ratio.

the intrisic modulus is negative. In general, these ranges for the intrinsic modulus are

$$[G] \geq 0 \quad \text{when } 1 \leq \frac{G_f}{G_0} \leq \infty \qquad (16)$$

and

$$[G] \leq 0 \quad \text{when } 0 \leq \frac{G_f}{G_0} \leq 1 \qquad (17)$$

The effect of Poisson's ratio, v_0, on the intrinsic modulus, $[G]$, when the modulus ratio ranges from $1 \leq G_f/G_0 \leq 50$ is shown in Fig. 4. This figure indicates that the upper limit of the intrinsic modulus is nearly reached for most values of the Poisson's ratio at relatively low values of the filler to the matrix modulus ratio G_f/G_0.

Fig. 5 shows the effect of Poisson's ratio, v_0, on the intrinsic modulus, $[G]$, when the modulus ratio ranges from $0 \leq G_f/G_0 \leq 1$. For modulus ratios ranging from

0.5–1.0 the lower limit of the intrinsic modulus is nearly independent of Poisson's ratio.

Based on the results presented in this section it is possible to consider a ceramic to be a two-phase composite with the void phase being either the matrix or the particulate phase. The simplified intrinsic modulus equations resulting for these cases would be Equations 12 or 15, respectively. However, because the Poisson's ratio of a void is undefined, the only case that can be considered is one in which the matrix phase is the ceramic itself and the voids are the particulate phase.

4. Revision of the generalized modulus equation to apply to the relationship between voids and modulus

Because Poisson's ratio must be defined, the relationship between voids and modulus can only be considered to be valid when the void phase is considered to be the particulate phase. For this configuration of Equation 3, a maximum void volume fraction must be defined to replace the maximum packing fraction limit in this equation. The maximum void volume fraction or critical pore volume, P_{crit}, occurs in the starting powder and can be measured relatively easily as the initial porosity, P_i, at the beginning of the ceramic powder processing. This initial pore volume, P_i, can also be minimized by carefully blending several monodisperse particles when making up the starting powder, as discussed earlier.

Because modulus/void literature data for ceramics often involves Young's modulus, the relationship between Young's modulus and the shear modulus needs to be addressed. Young's modulus, E, the shear modulus, G, and Poisson's ratio, v_0, are related through the following formulation [26]

$$G = \frac{E}{2(1 + v_0)} \qquad (18)$$

As the shear modulus and Young's modulus are directly related, ratios of shear modulus are essentially equivalent to ratios of Young's modulus.

Based on these considerations, then, the generalized modulus Equation 3 can be rewritten to describe the void/modulus relationships for ceramics as

$$\ln(E/E_0) = \left(\frac{[E]P_i}{\sigma - 1}\right)\left\{\left(\frac{P_i - P}{P_i}\right)^{1-\sigma} - 1\right\} \quad \text{for } \sigma \neq 1 \qquad (19)$$

$$[E] = \frac{-15(1 - v_0)}{(7 - 5v_0)} \qquad (20)$$

For the case where $\sigma = 1$, the resulting equation can be written as

$$\ln(E/E_0) = -[E]P_i \ln\left(\frac{P_i - P}{P_i}\right) \qquad (21)$$

or

$$E = E_0\left(\frac{P_i - P}{P_i}\right)^{-[E]P_i} \qquad (22)$$

Porosity interaction coefficient, σ	Simplified form of generalized equation	Original reference for equation
−1	$\ln(E/E_0) = [E]\left[P - \left(\frac{P^2}{2P_i}\right)\right]$	Wang [4]
0	$\ln(E/E_0) = [E]P$	Spriggs [8]
0.5	$\ln(E/E_0) = 2[E]P_i\left[1 - \left(\frac{P_i - P}{P_i}\right)^{0.5}\right]$	
1	$\ln(E/E_0) = -[E]P_i\ln\left(\frac{P_i - P}{P_i}\right)$	Phani–Niyogi [14]
2	$\ln(E/E_0) = [E]P_i\left(\frac{P}{P_i - P}\right)$	
3	$\ln(E/E_0) = \left(\frac{[E]P_i}{2}\right)\left[\frac{2PP_i - P^2}{(P_i - P)^2}\right]$	
4	$\ln(E/E_0) = \left(\frac{[E]P_i}{3}\right)\left[\frac{3PP_i^2 - 3P^2P_i - P^3}{(P_i - P)^3}\right]$	

where E is Young's modulus of a porous polycrystalline solid, E_0 Young's modulus of a non-porous polycrystalline solid, $[E]$ is the intrinsic modulus, ν_0 Poisson's ratio of the matrix, σ the porosity interaction coefficient, P the porosity or fractional pore volume of solid, and P_i the initial porosity or volume fraction voids in solid.

It is interesting to note that several of the modulus/void equations that have previously appeared in the literature can be obtained from Equation 19 by modifying the porosity interaction coefficient, σ. For example, Wang's [5] equation results when $\sigma = -1$, Spriggs [8] equation results when $\sigma = 0$, and the equation of Phani–Niyogi [14] results when $\sigma = 1.0$. Some of these options are indicated in Table II together with the author that first noted the form of these equations. However, the interaction coefficient should be considered to be an adjustable constant that can be modified as required to fit the data. Fractional values of the interaction coefficient are perfectly acceptable and have been found to be very useful in several instances [16, 18] to fit data adequately.

To appreciate better the interaction coefficient, consider a MacLaurin series expansion of Equation 19 which gives

$$E = E_0\left(1 + [E]P + \left(\frac{[E]}{2}\right)\left\{[E] + \left(\frac{\sigma}{P_i}\right)\right\}P^2\right.$$

$$+ \left(\frac{E}{6}\right)\left\{[E]^2 + 3\left(\frac{\sigma}{P_i}\right)[E]\right.$$

$$\left.\left. + \left(\frac{\sigma}{P_i}\right)\left(\frac{\sigma + 1}{P_i}\right)\right\}P^3 + \cdots\right) \qquad (23)$$

The first two terms are similar to the Einstein [24, 25] limiting terms for the viscosity of suspended particles. These first two terms are also the same ones for all possible values for the interaction of coefficient, σ, and the initial porosity, P_i. It has also been found that σ and P_i always occur as a paired ratio for second-order and higher expansion terms. Because these two parameters are paired in second order and higher

terms, if $\sigma = 0.0$, then the initial porosity, P_i, does not enter into the modulus calculation and it does not become a part of Spriggs [8] equation, consistent with Hasselman's [13] observation. In general, the particle interaction coefficient should be considered to be a measure of the interaction of the pore voids with each other during powder compaction. This interaction process can better be understood from a review of the theoretical considerations of Wang [4].

5. Application of the generalized modulus equation to Wang's theoretical modulus versus pore volume fraction data

Two of the more significant analytical approaches attempting to understand the interactions of voids during a powder compaction process have been generated by Knudsen [3] and Wang [4]. Knudsen addressed the effect of voids on strength and Wang addressed the effect of voids on modulus. Both of these authors developed models to predict the effect of shrinking voids during the coalescing of spherical particles.

Knudsen [3] developed his theoretical model to address the coalescing of monodisperse spherical particles over the full range of porosity for three possible packing arrangements; simple cubic, orthorhombic and rhombohedral. The primary assumptions used by Knudsen in making his theoretical calculations included:

(1) the spherical particles draw together on their centres without changing their relative angular orientation with respect to one another;

(2) each sphere flattens at the areas of contact with its neighbours;

(3) each deforming sphere maintains its original volume, the displaced material redistributing itself evenly over the residual curved surfaces;

(4) as the porosity of the specimen decreases, the size of the flattened areas of contact increases until the original spheres eventually become polyhedrons at zero specimen porosity;
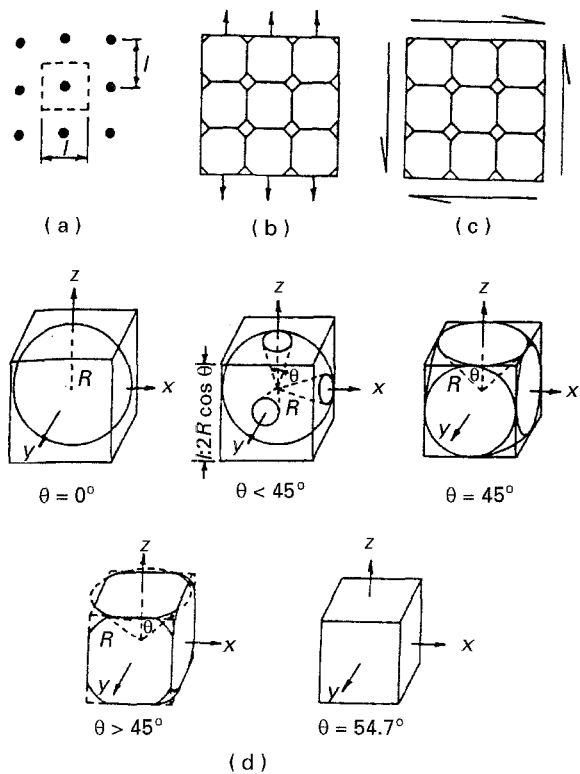
Figure 6 Wang's schematic illustration of the sequence of events upon densification for a simple cubic array (reproduced by permission of author). (a) Cubic array, (b) in tension, (c) in shear, (d) sequence of events upon densification.
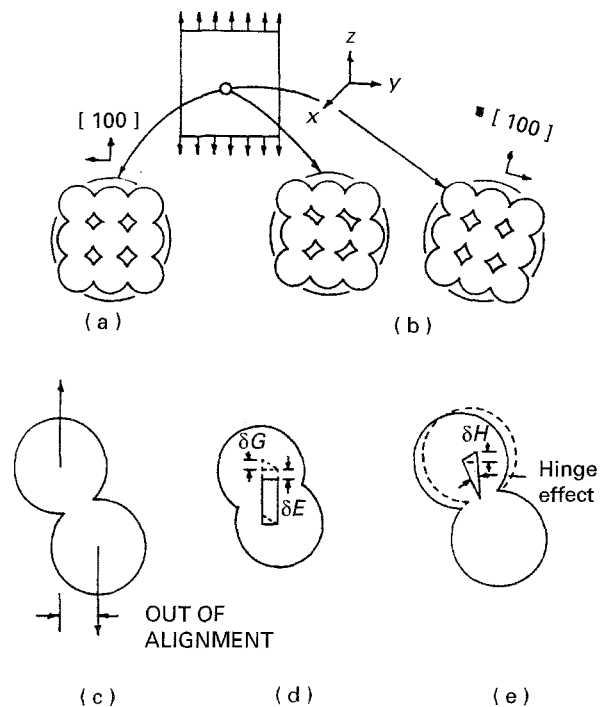

Figure 7 Wang's proposed effects of non-ideal alignment on the elongation in the z-direction (reproduced by permission of author). (a) The ideal case, (b) non-ideal cases, (c) misalignment, (d) shearing, (e) bending.

(5) the strength of an individual sphere is stronger than the cohesion of the intergranular contact area, the latter being the weakest link of the material;

(6) the strength of a porous material is proportional to the load-bearing contact area.

Wang [4] addressed the theoretical evaluation of coalescing monodisperse spherical particles starting with the assumption of simple cubic packing and essentially the same assumptions used by Knudsen. However, Wang developed his theoretical model with modulus in place of strength in Knudsen's assumptions (5) and (6). The initial density for simple cubic packing was defined as the density at which the spheres just touch giving an initial porosity of $P_i = 0.4764$. To describe the compaction process analytically, Wang [4] defined an angle, θ, that described the limit of the flattened areas as described in Fig. 6. Wang then derived the relationship between Young's modulus and a detailed function of the compaction angle, θ, that can be described in simplified form as

$$\frac{E^{\text{eff}}}{E_0} = \left(\frac{P_i - P}{P_i} + \frac{G_0}{E_0}\frac{P}{P_i}\right)^\alpha \left[\frac{E(\theta)}{E_0}\right] \qquad (24)$$

(where E^{eff} is the effective Young's modulus of a porous polycrystalline solid, E_0 the Young's modulus of a non-porous polycrystalline solid, $E(\theta)$ the differential Young's modulus function of θ, G_0 the shear modulus of a non-porous polycrystalline solid, α a constant, θ the angle describing the limit of the flattened areas, P the porosity or fractional pore volume of solid, and P_i the initial porosity or volume fraction of voids in a solid.

Because the detailed relationship defining the function $E(\theta)$ has been described by Wang [4] elsewhere, further details of this function can be obtained from that reference.

Three different compaction conditions were evaluated by Wang [4] using finite difference computer calculations by adjusting the constant α in Equation 24. These three compaction modes, shown in pictorial form in Fig. 7, can be summarized in terms on the constant, α, as in Table III.

TABLE III

Case	Compaction mode	Value of α
I	Undistorted void compaction	0
II	Misalignment with a shearing component	1
III	Misalignment with a shearing component and a hinged bending component	2

According to Wang, undistorted void compaction ($\alpha = 0$) occurs when particles are uniformly compacted without distortion and the maximum modulus can be achieved as a result of the compaction process. If misalignment of particles occurs during compaction, then Wang [4] claims that particle distortion causes distortion of the load-carrying capability and modulus reduction results. Wang [4] accounts for misalignment during compaction by multiplying the undistorted case by a correction factor that indicates particle distortion from an evaluation of void distortion. Misalignment during compaction involving primarily a shearing component was found by Wang

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[4] to be accounted for by a correction factor of the form

$$\left(\frac{P_i - P}{P_i} + \frac{G_0}{E_0}\frac{P}{P_i}\right)$$

resulting in $\alpha = 1$. Wang found that the correction factor for a hinged bending component should be the same as that for the shearing component during compaction, and when these two components are acting simultaneously, these correction factors must be multiplied together giving $\alpha = 2$. Based on these considerations, then, Wang's constant α is indicative of the interaction of the voids making up the porosity that is in some way a measure of the mode of particle deformation, which in turn can effect modulus modification.

At this point it is useful to compare the first derivative of Equation 19 with Wang's detailed modulus calculation described by Equation 24. The first derivative of the generalized modulus Equation 19 gives.

$$\frac{dE}{dP} = E\left[[E]\bigg/\left(\frac{P_i - P}{P_i}\right)^\sigma\right] \tag{25}$$

Before discussing the relationship between the constant α and the porosity interaction coefficient, σ, in Equation 25, consider the understanding that has been developed previously from experience with the particle interaction coefficient, σ, as utilized in the generalized modulus equation described by Equation 3.

In previous papers dealing with particles in viscous suspensions [16–18] and composites [20], the particle interaction coefficient, σ, was found to be a direct measure of the interaction of particles with each other and their interaction influence on the viscosity or modulus. For these cases it was found that the term $(\varphi_n - \varphi)/\varphi_n$ expressed to a power described by the particle interaction coefficient, σ, was more than adequate to describe the interaction of particles and their interaction effect on the shear modulus or viscosity. The initial derivation of this interaction process for particles leading to the derivative of Equation 3 has been discussed in some detail elsewhere [16] and will not be repeated here.

However, Wang felt that the $(P_i - P)/P_i$ term applied only to Young's modulus component of the porosity interaction and that the term P/P_i was required for the interaction with the shear modulus component. If the $(P_i - P)/P_i$ term is applicable to both the shear modulus and Young's modulus components, then the differential described by Equation 25 would be an improved description of Equation 24. For this case, the integral of Equation 25 would be described by Equation 19.

One measure of this evaluation process is to see how well Equation 19 fits the theoretical computer data generated by Wang. Wang's [4] theoretically calculated modulus as a function of void content for each of his three different modes of compaction is shown in Fig. 8. The generalized void/modulus equation described by Equation 19 has also been optimized for each of Wang's three cases and is also included in Fig. 8. Because each of the three cases described in
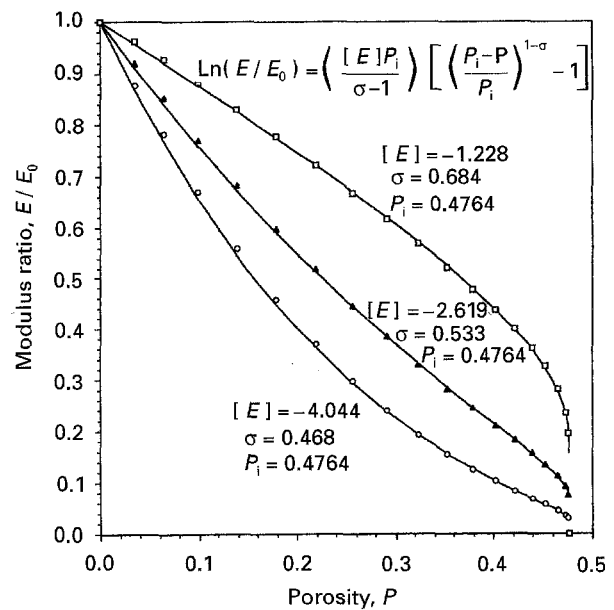

Figure 8 Wang's theoretical modulus values for three compaction modes and void/modulus equation results for three porosity interaction coefficients. (□) case I, (▲) case II, (○) case III.

Fig. 8 used the same initial porosity, P_i, and the same Young's modulus at zero porosity, E_0, then the calculation of modulus over the full range of porosity for these three cases was modified by adjusting only two constants; the intrinsic modulus, $[E]$, and the porosity interaction coefficient, σ. It is also interesting that Wang's theory does not include a constant equivalent to the intrinsic modulus, $[E]$, even though it did include the other three constants. More importantly, it is remarkable that the full range of data in Fig. 8 was so easily fit with only two adjustable constants.

Several surprises were identified when evaluating the constants obtained in fitting the data in Fig. 8. First, in going from case I to case III it was found that the porosity interaction coefficients decreased instead of increased as expected by the Wang theory. However, the ratio of the differences between the first and third and the first and second interaction coefficients were shown to give

$$\frac{\sigma_I - \sigma_{III}}{\sigma_I - \sigma_{II}} = \frac{0.216}{0.151} = 1.43 \tag{26}$$

According to Wang's theory, this ratio should have been 2.0, which is very close to the actual ratio obtained, even though the interaction coefficients decreased instead of increased. This ratio does suggest though that the correction factor for a combined interaction resulting from a shear component and a hinged bending component is nearly double the shear component consistent with Wang's model. But it was not necessary for the interaction constants to yield results expected from Wang's models. The primary value of Wang's theory is that it has shown that the porosity interaction coefficient, σ, can be a valuable indicator of the process of void compaction to obtain some measure of the mode of particle deformation which influences modulus modification.

For the three cases evaluated by Wang in Fig. 8, the intrinsic modulus, $[E]$, played a major role in the superior fit of the data and in many ways countered the effect of interaction constant, σ. Both of these constants worked together to compensate for the effect of Wang's interaction constant, α. However, utilization of two constants with Equation 19 is still a significant improvement over using the computer iteration evaluation process required for Wang's detailed model. In addition, because the generalized void/modulus equation fits the data so easily, a significant amount of additional information is available to characterize solid-state processing that is not available in Wang's model.

The surprise in the case of the intrinsic modulus was that the Poisson's ratios calculated from the intrinsic moduli data appear to be unrealistic. When calculated from Equation 20 the Poisson's ratio calculated for these different cases were as given in Table IV.

TABLE IV

Case	Intrinsic modulus	Poisson's ratio
I	− 1.23	0.72
II	− 2.62	− 1.75
III	− 4.04	2.55

While intrinsic moduli showed a consistent trend in going from case I to case III the calculated values of Poisson's ratio did not. Theoretical values of Poisson's ratio for porous solids have been calculated by Agarwal et al. [15] as a function of porosity. The Poisson's ratio for these materials ranged from 0.163 to 0.255 when the volume fraction of pores ranged from 0.438 to 0.0303. It is apparent that the Poisson's ratios calculated from the intrinsic modulus values are significantly different from the values predicted by Agarwal et al. and an explanation is needed to account for this difference. One explanation involves the formulation of the intrinsic modulus developed from Budiansky's modulus derivation for a particulate composite.

5.1. Development of the intrinsic modulus from Budiansky's modulus equation for a particulate composite

The evaluation of the intrinsic modulus, $[E]$, of a general function, $E(P)$, describing the modulus is, in general, evaluated from the second term of a MacLaurin series expansion that can be put in the following form

$$\frac{E(P)}{E(0)} = 1 + \left[\frac{E'(0)}{E(0)}\right]P + \left[\frac{E''(0)}{E(0)2!}\right]P^2$$

$$+ \left[\frac{E'''(0)}{E(0)3!}\right]P^3 + \left[\frac{E''''(0)}{E(0)4!}\right]P^4 + \cdots \quad (27)$$

where the intrinsic modulus, $[E]$, is defined as

$$[E] = \left[\frac{E'(0)}{E(0)}\right] \quad (28)$$

Budiansky [27] derived an equation that predicts the modulus of a particulate composite as a function of particulate concentration that Smith [28] showed could be written in the form

$$\frac{G_c - G_0}{G_f - G_0} = \left[\frac{(8 - 10v_c)G_c + (7 - 5v_c)G_c}{(8 - 10v_c)G_f + (7 - 5v_c)G_c}\right]\varphi \quad (29)$$

where G_c is the composite shear modulus, G_f the shear modulus of the filler, G_0 the shear modulus of the matrix, v_c the Poisson's ratio of the composite, and φ the particle volume concentration in the matrix. This equation results in a quadratic equation for the shear modulus of the particulate composite, G_c. It can be shown that the first derivative of this equation can be described as

$$\frac{dG_c}{d\varphi} = \left[\frac{(G_f - G_0)15(1 - v_c)}{(7 - 5v_c) + (8 - 10v_c)(G_f G_0/G_c^2)}\right] +$$

$$\frac{\partial v_c}{\partial \varphi}\left[\frac{5(G_c - G_0) + 10G_f[1 - (G_0/G_c)] - 15(G_f - G_0)\varphi}{(7 - 5v_c) + (8 - 10v_c)(G_f G_0/G_c^2)}\right]$$

$$(30)$$

The evaluation of this derivative will result in an intrinsic modulus as described by a MacLaurin series expansion when $\varphi = 0$. For this reason this derivative will be developed into a limit in two simplifying steps. First, if the filler is assumed to be a void, then $G_f = 0$. If $G_f = 0$ and $\varphi = 0$, Equation 30 reduces to

$$\frac{dG_c}{d\varphi} = \left[\frac{- G_0 15(1 - v_c)}{(7 - 5v_c)}\right] + \frac{\partial v_c}{\partial \varphi}\left[\frac{5(G_c - G_0)}{(7 - 5v_c)}\right]$$

$$(31)$$

Now, if the ratio of shear moduli is equivalent to the ratio of Young's moduli then

$$\frac{G_c}{G_0} = \frac{E}{E_0} \quad (32)$$

If the volume fraction of particles is, in fact, the same as the volume fraction of voids, then

$$\varphi = P \quad (33)$$

Substituting Equations 32 and 33 into Equation 31 gives

$$\frac{dE/E_0}{dP} = \left[\frac{- 15(1 - v_c)}{(7 - 5v_c)}\right] + \frac{\partial v_c}{\partial P}\left[\frac{5(E/E_0 - 1)}{(7 - 5v_c)}\right]$$

$$(34)$$

At this point if it is assumed that $E = E_0$ and $v_c = v_0$ at $P = 0$, then Equation 33 reduces to the intrinsic modulus found earlier of

$$[E] = \frac{- 15(1 - v_0)}{(7 - 5v_0)} \quad (20)$$

This same result for the intrinsic modulus, $[E]$, can be obtained in a much more straightforward manner using the three other primary derivations [28–31] relating modulus and the particulate concentration.

However, it is not clear that Budiansky's form of the intrinsic modulus described by Equation 34 can be evaluated from the simple assumption that $E = E_0$

and $v_c = v_0$ as the Porosity, P, approaches zero. Based on the peculiarity of the Poisson's ratios determined from the calculated intrinsic moduli in Fig. 8 it is expected that under certain circumstances that the intrinsic modulus will need to be determined from Budiansky's equation described by Equation 34. For these cases the intrinsic modulus may not be able to be estimated from the pure matrix properties. However, it is not yet clear how to estimate the influence of composite properties on the intrinsic modulus for these materials. At this time, the influence of composite properties on the intrinsic modulus can best be estimated from experimental evaluations of the intrinsic modulus.

5.2. Evaluation of Wang's experimental results

Wang [5] evaluated the Young's modulus of two sets of manufactured alumina rods with different levels of compaction and void content. The difference between these two series was the powder shape: the first series was comprised of spherical powder while the second series was comprised of "egg-shaped" powder. The modulus for both of these series was measured using either a sonic velocity technique or the static Young's modulus determined by a three-point bending test. For the purpose of this analysis, no distinction was made between the two measurement techniques used to measure Young's modulus. However, Wang's data for the modulus/void curves for these two types of powders were distinctly different, as indicated in Figs. 9 and 10. For comparative purposes, the optimum fit of the data of spherical powder in Fig. 9 was evaluated using the generalized modulus Equations 19 and 20 at three different values of the particle interaction constant, σ, at $\sigma = -1, 0$ and 1. As indicated in Table II these values of the particle interaction
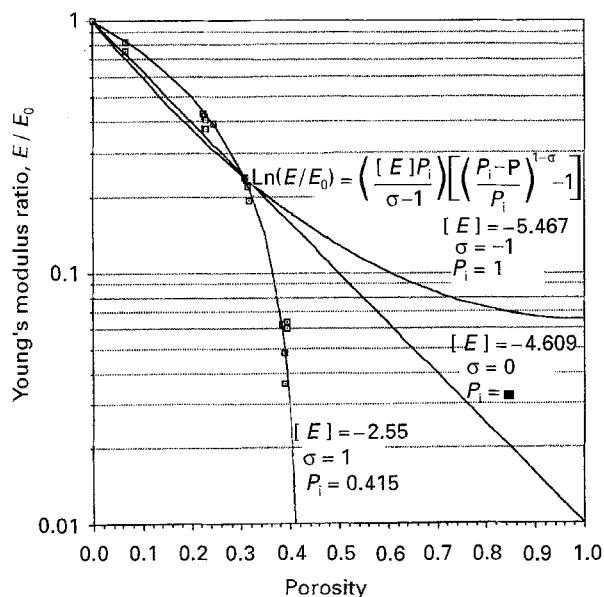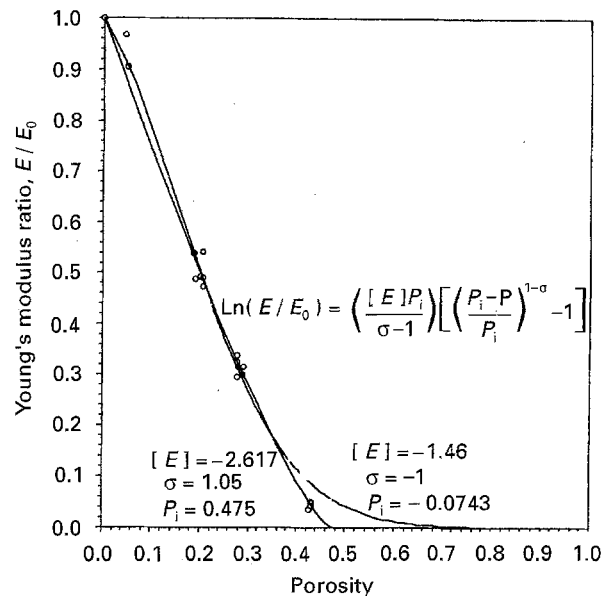

Figure 10 ($\square$) Wang's data for alumina rods prepared with "egg-shaped" particles and void/modulus equation results for two porosity interaction coefficients.
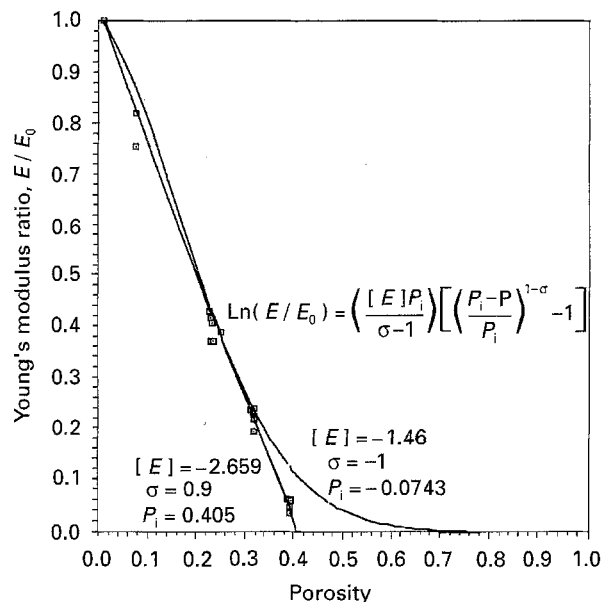

Figure 11 ($\blacksquare$) Wang's data for alumina rods prepared with spherical particles and void/modulus equation results for two porosity interaction coefficients.

coefficient correspond, respectively, to the empirical equations proposed by Wang, Spriggs and Phani–Niyogi. From these three results it is apparent that a particle interaction coefficient of $\sigma = 1$ gave the best fit of the data. However, the optimum fit of the spherical particle data occurred for a value of a particle interaction coefficient of $\sigma = 0.9$ as shown in Fig. 11. For analysis purposes it is useful to compare the optimum constants obtained for the spherical particle data interaction coefficients of $\sigma = 1$ and 0.9. For these cases the results were: $\sigma = 0.9$, $[E] = -2.659$, $P_i = 0.405$, $E_0 = 58.1 \times 10^6$ p.s.i. (4.01×10^5 MPa), av. % error $= 9.85\%$; $\sigma = 1.0$, $[E] = -2.552$, $P_i = 0.415$, $E_0 = 58.1 \times 10^6$ p.s.i. (4.01×10^5 MPa), av. % error $= 10.00\%$. It should be noted that the value of E_0 found by Wang [5] was used for all data sets to

Figure 9 ($\square$) Wang's data for alumina rods prepared with spherical particles with void/modulus equation results for three porosity interaction coefficients.

simplify the analysis. Only the values of σ, $[E]$ and P_i were adjusted to optimize the fit of the data. It is interesting to note that the average literature value of the monodisperse packing fraction for loose random packing was found by Lee [22] to be ($\varphi_m = 0.589$). This packing fraction would give an initial void content of $P_i = 1 - 0.589 = 0.411$. This value is remarkably close to the value of the void content obtained for the packed spherical particles indicated above from the fit of the data in Figs. 9 and 11.

By comparison the constants for the best fit of the "egg-shaped" particle data in Fig. 10 were: $\sigma = 1.05$, $[E] = -2.617$, $P_i = 0.475$, $E_0 = 58.1 \times 10^6$ p.s.i. (4.01×10^5 MPa), and av. % error $= 6.14\%$.

The fit of these "egg-shaped" particle data appears to have been slightly better than the fit of the data for the spherical particles as indicated by the average per cent error. A comparison of the constants for these two different types of particles indicates that the intrinsic modulus, $[E]$, and the particle interaction coefficient, σ, appear to be nearly the same values for these two types of particles. However, the initial volume fraction of porosity increased to $P_i = 0.475$ for "egg-shaped" particles. While this value is close to the porosity of 0.476 found for cubic packing of spherical particles, it is not expected that egg-shaped particles pack the same as spherical particles. The increased value of porosity does appear to indicate that "egg-shaped" particles are a little more difficult to pack in a loose random arrangement than spherical particles.

The empirical equation proposed by Wang can be described as

$$\ln(E/E_0) = -(bP + cP^2) \tag{35}$$

where b and c are constants. The results calculated using this equation with the constants $b = 1.46$ and $c = 0.982$ and plotted in Figs. 10 and 11. Wang indicated that his recommended equation with the above constants should only be used below a void fraction of 0.32 because it did not fit the data above this void fraction. Wang's equation, described by Equation 35, can also be obtained from the generalized modulus Equations 19 and 20 for an interaction coefficient of $\sigma = -1$ giving

$$\ln(E/E_0) = [E]\left[P - \left(\frac{P^2}{2P_i}\right)\right] \tag{36}$$

While the value of $[E]$ can be either negative or positive in this equation, the value of P_i cannot be negative according to the derivation in this paper. Using Wang's constant $c = 0.982$, a value of -0.0743 is obtained for the value of P_i using Equation 36. While this value of P_i does give a better fit of the data than the optimum value for the constant developed for the interaction constant $\sigma = -1$ shown in Fig. 9, it still did not fit all the data as well as the results calculated for interaction coefficients of nearly 1. The results of this study have shown that an excellent fit of the data can be obtained without making assumptions inconsistent with the theory presented.

6. Conclusion

An equation recently developed by this author to describe the modulus of particulate composites as a function of the volume fraction of particles was modified in this study to describe modulus as a function of porosity. For this analysis a ceramic was considered to be a two-phase composite with the void phase being the particulate phase. By varying the porosity interaction coefficient, σ, this new generalized void/modulus equation was shown to be able to yield equations previously used to predict modulus as a function of voids for ceramics. For example, Wang's [5] equation results when $\sigma = -1$, Spriggs [8] equation results when $\sigma = 0$, and the equation of Phani–Niyogi [14] results when $\sigma = 1.0$.

The maximum void volume fraction was found to occur as the initial porosity, P_i, at the beginning of their ceramic powder processing. One modification of the particulate composite equation to make it apply as a void/modulus equation was to replace the maximum packing fraction, φ_n, with initial porosity, P_i. This initial pore volume, P_i, was also found to have the potential to be minimized by carefully blending several monodisperse particles when making up the starting powder. Based on an evaluation of McGeary's packing fraction data, it was found that a mixture of six different particle sizes should be able to produce an initial packing of particles down to less than 2% voids.

Wang theoretically described the mode of porosity interaction during compaction with a constant α to calculate the void/modulus relationship for three different compaction conditions. While Wang's constant α was a measure of the mode of porosity deformation, it was also important in measuring the influence of the effect of modulus modification. The generalized void/modulus equation developed in this study was found to fit each of Wang's three void/modulus interaction cases over the full range of porosity, by adjusting only the intrinsic modulus, $[E]$, and the porosity interaction coefficient, σ. The values of initial porosity, P_i, and Young's modulus at zero porosity, E_0, were the same as used by Wang. While the porosity interaction coefficients, σ, obtained using the generalized void/modulus equation to fit Wang's data did not agree closely with Wang's values of α, the fit of the Wang's data was exceptionally good. However, Wang's models were able to show that the porosity interaction coefficient, σ, can be a valuable indicator of the process of void compaction to obtain some measure of the mode of porosity deformation which influences modulus modification.

The surprise in the evaluation of Wang's three cases was that some of the Poisson's ratios calculated from the intrinsic moduli data appeared to be unrealistic. Based on the peculiarity of the calculated Poisson's ratios, the intrinsic modulus determined from Budiansky's equation will probably need to be evaluated in some circumstances. For these cases the intrinsic modulus may not be able to be estimated from the pure matrix properties. It is not yet clear how to estimate the influence of composite properties on the intrinsic modulus for these materials. At this time, the influence of composite properties on the intrinsic

modulus can best be estimated from experimental evaluations of the intrinsic modulus.

Wang also experimentally measured the porosity and Young's modulus of manufactured alumina rods prepared with two differently shaped powders. One series was comprised of spherical powder while the second series was comprised of "egg-shaped" powder. Only the values of σ, $[E]$ and P_i were adjusted to optimize the fit of the data while the value of E_0 found by Wang was used for all data sets to simplify the analysis. The optimum fit of the spherical particle data occurred for a value of a particle interaction coefficient of $\sigma = 0.9$ and $P_i = 0.405$. It is interesting that this void fraction is very close to the average literature value of the void fraction of 0.411 found by Lee for loose random packing of spherical particles.

The fit of the "egg-shaped" particle data appears to have been slightly better than the fit of the data for the spherical particles, as indicated by the average per cent error. Nearly the same intrinsic moduli, $[E]$, and porosity interaction coefficients, σ, were obtained for spherical and "egg-shaped" particles. However, the initial volume fraction of porosity increased to $P_i = 0.475$ for "egg-shaped" particles. While this value is close to the porosity of 0.476 found for cubic packing of spherical particles, it is not expected that egg-shaped particles pack the same as spherical particles. The increased value of porosity does appear to indicate that "egg-shaped" particles are a little more difficult to pack in a loose random arrangement than spherical particles.

The generalized void/modulus the equation for $\sigma = -1$ yields an equation that has the same form as Wang's proposed empirical equation that utilized two empirical constants, b and c. Wang's experimental data fitted with his equation gave a positive value for the constant c of 0.982 which corresponded to a negative value of P_i of -0.0743. Unfortunately, a negative value of the initial porosity P_i was not defined in the theoretical considerations developed in this study. While this value of P_i does give a better fit of the data for the interaction constant $\sigma = -1$, it still did not fit all the data as well as the results calculated for interaction coefficients nearer 1.0.

The results presented here have shown that an excellent fit of most void/modulus data can be obtained using the generalized void/modulus equation developed in this study without making assumptions inconsistent with the theory presented.

References

1. R. L. COBLE and W. D. KINGERY, *J. Am. Ceram. Soc.* **39** (1956) 377.
2. EUGENE RYSHKEWITCH, *ibid.* **36** (1953) 65.
3. F.P. KNUDSEN, *ibid.* **42** (1959) 376.
4. J. C. WANG, *J. Mater. Sci.* **19** (1984) 801.
5. *Idem, ibid.* **19** (1984) 809.
6. J.K. MACKENZIE, *Proc. Phys. Soc. (Lond.)* **63B** (1) (1950) 2.
7. F. GATTO, *Allumino* **19** (1) (1950) 19.
8. R. M. SPRIGGS, *J. Am. Ceram. Soc.* **44** (1961) 628.
9. F. P. KNUDSEN, *ibid.* **45** (2) (1962) 94.
10. I. SOROAKA and P. J. SEREDA, *ibid.* **51** (1968) 337.
11. R. D. CARNAHAN, *ibid.* **51** (1968) 223.
12. D. F. PORTER, J. S. REED and DAVID LEWIS III, *ibid.* **60** (1977) 345.
13. D. P. H. HASSELMAN, *ibid.* **45** (1962) 452.
14. K. K. PHANI, and S.K. NIYOGI, *J. Mater. Sci.* **22** (1987) 257.
15. B. D. AGARWAL, G. A. PANIZZA and L. J. BROUTMAN, *J. Am. Ceram. Soc.* **54** (1971) 620.
16. RICHARD D. SUDDUTH, *J. App. Polym. Sci.* **48** (1993) 25.
17. *Idem, ibid.* **48** (1993) 37.
18. *Idem, ibid.* **50** (1993) 5.
19. *Idem, ibid.* **52** (1994) 985.
20. *Idem, ibid.* **54** (1994) 1243.
21. R. K. MCGEARY *J. Am. Ceram. Soc.* **44** (1961) 513.
22. DO IK LEE, *J. Paint Technol.* **42** (1970) 579.
23. GEORGE E. DIETER, "Mechanical Metallurgy" 2nd Edn (McGraw Hill, New York, (1976) p. 51.
24. A. EINSTEIN, *Ann. Phys.* **19** (1906) 289.
25. *Idem, ibid.* (1911) 591.
26. D. C. DRUCKER, "Introduction to Mechanics of Deformable Solids" (McGraw Hill, New York, (1967) pp. 64-5.
27. B. J. BUDIANSKY, *J. Mech. Phys. Solids.* **13** (1965) 223.
28. JACK C. SMITH, *J. Res. Nat. Bur. Stand.* **78A** (1974) 355.
29. C. VAN DER POEL, *Rheol. Acta* **1** (1958) 198.
30. E. H. KERNER, *Proc. Phys. Soc.* **B69** (1956) 808.
31. Z. HASHIN and S. J. SHTRIKMAN, *J. Mech. Phys. Solids* **11** (1963) 127.