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Modeling of the Matrix Porosity Influence on the Elastic Properties of Particulate Biocomposites

For a wide range of engineering structures such as ceramics, porous shape memory alloys, foam-like structures and thermal spray deposits, porous materials have been used. Recently, porous biocomposites for the applications to bone implants and hard tissue engineering have become increasingly important. The effect of matrix porosity on the elastic properties of particulate biocomposite was studied by two-and three-phase unit cell finite element models. A 3D FCC unit cell model of particulate composite with included matrix porosity is developed and compared with the simple theoretical models. It is found that the matrix porosity has noticeable influence on the composite elastic properties. The two-phase predictions overestimate the three-phase ones because of the physical threshold for three-phase model determined by the particle content.

Keywords: *Particulate reinforced composites, Biomaterials, Elastic constants, Finite element analysis, Porosity.*

1. INTRODUCTION

The development and application of porous materials is enforced by the continuous demand for lightweight constructions with enhanced mechanical properties. Porous materials have a wide range of applications in various engineering structures such as ceramics, porous shape memory alloys, foam-like structures and thermal spray deposits. As regards biomaterial implants, besides the desired porosity in porous metallic implants or temporary scaffolds for the regeneration of bone tissue [1], in major load-bearing biocomposite implants initial mechanical properties are degraded by the presence of matrix porosity [2].

Recently, the development of hydroxy-apatite related porous biocomposite structure for the applications to bone implants and tissue engineering has become increasingly important, because interconnected porosity with a diameter of at least 100 μm in the structure allows cell penetration and proper vascularization of the ingrown tissue [3]. The rate of integration and the volume of newly regenerated bone have been shown to be very dependent on porosity, pore size and shape. Previous analysis shown that porous HAP with sphere-like pores has better strenght properties compared to non-spherical pore shapes, wich was also confirmed by FEM the results [4].

In particulate composites, porosities can appear in a form of particle-matrix debonding, cluster induced and matrix pores. The effects of clustering and interfacial debonding of particles on the mechanical properties of composites were the topic of the majority of prior studies.

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Several predictive models have been developed to correlate porosity and the effective elastic constants by assuming the porous material as a special case of a two-phase composite in which the second phase consists of pores. A detailed summary of these methods can be found in Herrmann and Oshmyan [5] and Wang and Tseng [6]. The unit cell approach requires relatively little computational efforts in comparison to simulations of real structures and allows to study the effect of the mutual arrangement of phases in composite [7,8] or cellular materials [9].

In this work, the influence of the isolated porosities in the matrix phase on the elastic properties of particulate biocomposites is investigated. A face-centered-cubic (FCC) finite element (FE) unit cell model was designed to evaluate the compressive elastic constants of the composite for a range of porosity volume fractions in ceramic particle reinforced polymer composites. The matrix was chosen to be poly-L-lactide (PLLA) polymer and the reinforcement were taken to be hydroxyapatite (HAp) particles. Simple semi-emphirical models for predicting elastic constants of porous particulate composites are proposed for comparison purposes.

2. MODELING PROCEDURE

The present work aims at carrying out a comparative evaluation of two-versus three-phase unit cell descriptions of composite consisting of elastic reinforcing particles embedded in an elastic porous matrix. To fully simulate such a microstructure, a three-dimensional (3D) model of a random distribution of particles and pores is required. Although, attempts at FE analysis of 3D multiparticle periodic unit cells have been made (see, for example, [10]), a model of this size is still not computationally feasible for most demands. In this study, random distribution is idealized by periodicaly distributed particles and pores represented here by a periodic repeating cell. The irregular shape of porosity and particles appearing in real microstructure, [4], is idealized to be spherical, as shown in Fig. 1.

In the two-phase (composite-porosity) FCC porosity cell, there is one spherical porosity at each corner and one spherical porosity in each face of the cube cell. The three-phase (particle-matrix-porosity) model differs from previous by the fact that spherical particles are introduced at the corners of the reduced cell opposite from the porosity location. Due to the symmetry of the unit cell and the applied loads, as well as isotropic material properties, the models were reduced to one eighth of the unit cell, as shown in Figs. 2(a) and (b). The models are considered by introducing boundary conditions, which constrains the unit cell to remain in its original shape (cube). After loading, the sides remain parallel and orthogonal, but changes in length. The unit cell is loaded in compression along the y direction with adequate displacement steps. The local coordinate system aligns with the global one. Dimensions of these reduced unit cells are 0.5 × 0.5 × 0.5 µm.

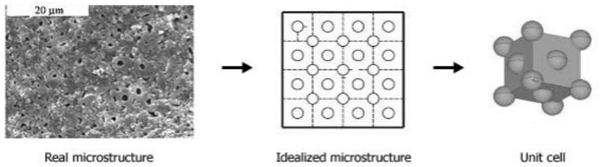

Figure 1. Idealization of the random pore distribution, shape and size by arranging the pores on a FCC paking array

The assumptions for both models are: (1) the elastic property of composite, particle and matrix is linear; (2) the particle and matrix phases as well as the whole composite are isotropic; (3) all spherical particles are of the same size; (4) all spherical porosities are of the same size; (5) the adhesion between the constituents is perfect and (6) the composite, particle and matrix phases will not fail at the prescribed loads.

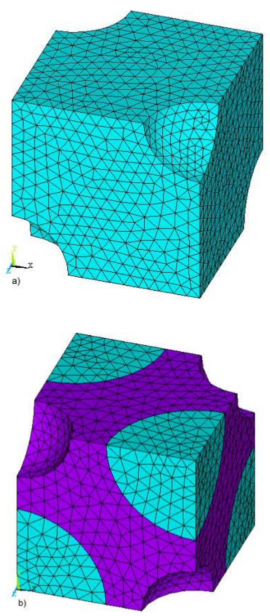

Figure 2. FE grid of unit cell model with 0.262 particle volume fraction (Vf) and 0.0565 porosity volume fraction (Vp): (a) two-phase model; (b) three-phase model.

All 3D FE models were produced using ANSYS 5.4, a general purpose finite element software package. The elements used are 10-node tetrahedral structural solid elements (an option of 20-node solid brick elements). A representative FE grid for evaluation of compressive modulus for a two-phase model, shown in Fig. 2a, consists of 22,582 elements and 32,916 nodes. A representative FE grid for evaluation of compressive modulus for a three-phase model, shown in Fig. 2b, consists of 21,423 elements and 30,773 nodes. Each node has three degrees of freedom corresponding to the three degrees of translation. The simulations were performed for the two values of HAp volume fractions, V_f, namely 0.262 and 0.4524, while the porosity volume fractions, V_p, were in the range of 0-0.262.

For the two-phase model the material properties were taken to be: E_{LC} = 10.63 GPa, ν_{LC} = 0.435, E_{HC} = 16.04 GPa and ν_{HC} = 0.421, where E is Young's modulus, and ν is a Poisson's ratio. The subscripts LC and HC represent the composite model with V_f equal to 0.262 and 0.4524, respectively. It should be mentioned that the input properties for the two-phase model were determined by setting values of V_p in three-phase model equal to zero. For the three-phase model the material properties were adopted on the basis of literature data [11,12]: E_1 = 117 GPa, ν_1 = 0.28, E_2 = 6.50 GPa, ν_2 = 0.45. The subscripts 1 and 2 represent HAp and PLLA, respectively.

Due to the assumption that the overall composite material is isotropic, values of shear modulus, G, can be calculated from the predicted values of Young's modulus and Poisson's ratio using the well-known relationship

$$G = \frac{E}{2(1+\nu)}. \tag{1}$$

The Halpin-Tsai model (HT) [13] is applied here to predict the compressive elasticity and shear moduli of the composite, which are dependent on the porosity content. These semi-empirical equations propose that compressive Young's modulus and shear modulus can be calculated from:

$$M = M_m \frac{1+\xi\eta V_f}{1-\eta V_f}, \tag{2}$$

where M is the corresponding composite constant (E or G), M_m is the corresponding matrix constant (E_m or G_m), ξ is a measure of particle filler that depends on particle geometry, packing geometry and loading conditions and η is an additional parameter defined as:

$$\eta = \left(\frac{M_f}{M_m} - 1\right) \Big/ \left(\frac{M_f}{M_m} + \xi\right), \tag{3}$$

where M_f is the corresponding particle constant (E_f or G_f). The values of ξ are obtained by comparing (2) and (3) with 3D FE solutions and assessing a value of ξ by curve fitting technique. When porosity is considered it is obvious that particle becomes pore ($V_f \rightarrow V_p$), $M_f = 0$ and M_m becomes M_c, which leads to

$$\eta = -\frac{1}{\xi}, \tag{4}$$

so (3) becomes

$$M = M_c \frac{(1 - V_p)\xi}{\xi + V_p}. \tag{5}$$

On the other hand, we propose that the corresponding composite constant M for porous material can be obtained by modifying Hashin-Shtrikman, HS [14] equation to

$$M = M_c - \frac{V_p M_c}{(1 + \gamma(V_p - 1))}, \tag{6}$$

where the values of γ are obtained in a similar manner as values of ξ. It could be instructive to compare the results of the numerical approach with the prediction of semi-empirical equations proposed to describe the variation of elastic constants with porosity.

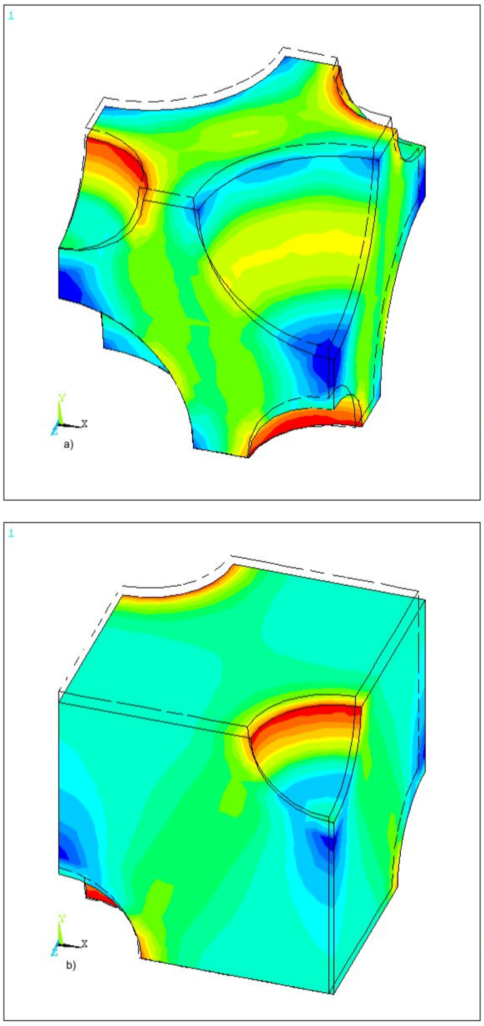

Figure 3. Von Mises stress distribution (stress values are in daN/mm^2 = 10^1 MPa): (a) in the porous composite, for the two-phase unit cell model with the composite that contains 0.262 V_f and 0.0565 V_p; (b) in the PLLA matrix, for the three-phase unit cell model with 0.262 V_f and 0.0565 V_p.

3. RESULTS AND DISCUSSION

The stress distributions of the deformed matrix, shown in Figs. 3(a) and (b), were achieved by loading the grid shown in Figs. 2(a) and (b) by a prescribed displacement in the y–direction of the nodes positioned at the upper surface of the cube (y = 0.5 μm). In order to extend the uniaxial stress information to the multiaxial stress state, the Von Mises equivalent stress was used. The nominal stress was determined by summing the reactions on the constrained surface opposite the loaded surface and dividing by the area. The side surfaces remain parallel to their original directions arising from the equal and opposite forces of the neighbouring material, while the resultant force acting on these surfaces is equal to zero. The stress values, shown in Figs. 3(a) and (b), are a result of loading which corresponds to applied compressive strain of 1% and nominal stresses of 94.7 MPa and 85.5 MPa, respectively. A common feature for both modeling cases is that the maximum Von Mises stress values are found in the equatorial region of the matrix in the vicinity of the pore. The particle/matrix interface is free from high stress spikes. In both model cases, the maximum value of stress concentration factors slightly increases with the higher pore content. The composite with lower particle content exhibits higher stresses in the matrix. The region of the matrix where the maximum stress occurs is usually the place of the initiation of the local plastic deformation. The stresses considered are those within the PLLA matrix, because failure of the HAp particles had not been reported in the experiments so far.

The compressive Young's modulus of elasticity was calculated from the applied strain and the average applied stress. The overall modulus results versus porosity content, obtained for two V_f and modeling procedures under uniaxial compressive loading, are shown in Fig. 4. The numerical solutions are additionally compared with the HT and modified HS predictions and the results provided by the two approaches to computing the elastic constants of a monolith material with spherical porosities, namely Ramakrishnan and Arunachalam (RA) and Hasselman and Fulrath (HF) [15,16]. The former one has been successfully used for the description of an oral implant coating consisting of a bioactive glass matrix containing spherical porosity [17]. The expressions for the elastic constants can be found in the cited references, and are not given here for sake of brevity.

As expected, compressive modulus of the composite increases with the higher particle content and decreases with the increase in porosity content. For instance, an increase in porosity of 13.4 % leads to a modulus decrease of approximately 25 and 30 %, as estimated by two- and three-phase model, respectively. It is interesting that modulus decrease is similar for both particle volume fractions. The FE simulations were restricted to an upper level of V_p of 0.262. Exceptionally, for the three-phase model with higher V_f, the calculations were terminated at the V_p of 0.134 because at higher particle and porosity content, matrix phase becomes geometrically disconnected, which certainly leads to unconvincing results. The two-phase FE predictions overestimate the three-phase ones, by as much as to 15 %, over the whole porosity range because of the physical threshold for three-phase model that is determined by the V_p, and the fact that the two-phase model neglects the interactions between matrix, particles and porosities. Maximum V_p for three-phase model is equal to $(1 - V_f)$, opposite to the two-phase that allows hypothetically the V_p to be equal to 1. This demonstrates that microstructure (the geometrical nature of the composite constituents) is an important factor besides the porosity content and the overall composite properties. Semi-empirical HT and modified HS results (dotted lines) approach more closely to the FE results than RA and HF models, but since the fitting of coefficients to FE curves is required, their usefulness as a quick tool for the estimation of elastic properties of porous particulate composites is limited. The good correlation between theoretical and two-phase simulations is a consequence of the similarity between the assumptions of the theory and the definition of the model.

As regards shear modulus (Fig. 5), the two-phase model results seem to overestimate the three-phase over the whole V_p range. Fig. 5 gives the apparent Poisson's ratio, ν, calculations by present numerical model.

In previous work we have compared our modeling results with several sets of previously published experimental data [12,18]. In cases where the microstructure of the composite roughly matched that of the models, as in the cold forge processed HAp/PLLA [11], the agreement was very good. High pressures and low temperatures during processing would not cause significant decrease of matrix molecular weight or pore formation. The residual porosity developed in the matrix during hot pressing procedure, and an insufficiently intimate bond between the phases, could cause a discrepancy between experimental and numerically predicted values [4,19]. For the composite system investigated in this study, the assumption of perfect bonding is reasonable because the surface microporosity of the HAp particle enabled a potentially existing liquid phase to penetrate into its structure, which is one of the phenomena on which the mechanical theory of phase adhesion is based [20]. In general, the PLLA polymer matrix has a net-like shape with spherical pores and during compacting by hot pressing, the system porosity could decrease, providing a more intimate contact of the two components. Conversely, thermal degradation could lead to the formation of new matrix porosities from solvents such as chloroform, methanol and water. Therefore, in order to utilize particulate biocomposites effectively, it is desired to know their mechanical behavior as a function of matrix porosity.

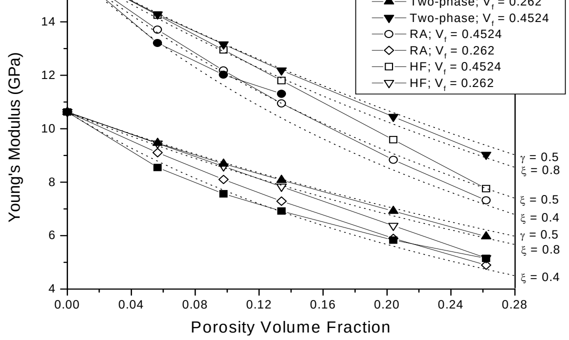

Figure 4. Young's modulus versus porosity for FE calculations and theoretical models. HT and modified HS predictions are represented by dotted lines .

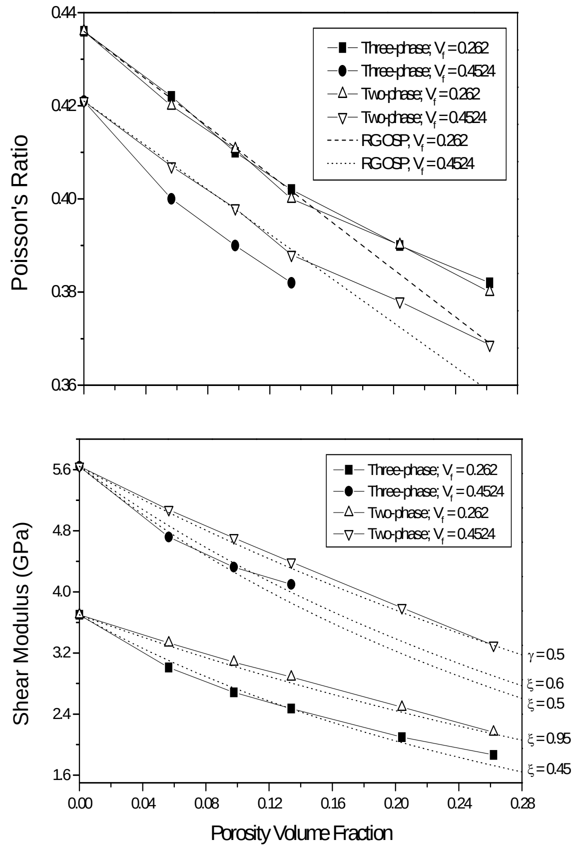

Figure 5. Poisson's ratio and shear modulus versus porosity for FE calculations and theoretical models. HT

4. CONCLUSIONS

A 3D FCC unit cell model of particulate composite with included matrix porosity is developed and compared with the simple theoretical models. The low-level matrix porosity has noticeable influence on the composite elastic properties. Two-phase FE modeling results as well as the calculations from theoretical equations overestimate the three-phase FE calculations as a result of neglecting the physical threshold and possible interactions between particle, matrix and porosities existing in real particulate composite microstructure. The two-phase modeling results match the theoretical ones, because of the similarity between the assumptions of the theory and the definition of the model.

In the future it would be useful to extend this work to describe particle/matrix debonding and by using information obtained from micrographs, to generate models that actually mimic physical microstructures. Besides predicting the properties of particulate composites with low-level porosity, proposed procedure could be effective for designing the challenging materials with desired controlled porosity (pore shape, size and volume fraction).

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МОДЕЛИРАЊЕ УТИЦАЈА МАТРИЧНЕ ПОРОЗНОСТИ НА ЕЛАСТИЧНЕ ОСОБИНЕ ПОРОЗНИХ БИОКОМПОЗИТА

Игор Балаћ, Катарина Чолић, Милорад Милованчевић, Петар Ускоковић, Милорад Зрилић

Порозни материјали се користе за широки спектар инжењерских структура направљених на бази керамике, порозних легура са меморијским ефектом, пенастих структура, термички заштитних филмова. У скорије време примена порозних биокомпозита у инжењерству тврдих ткива као и импланата код коштаних дефеката привлачи посебну пажњу. Утицај матричне порозности на карактеристике еластичности честичних биокомпозита анализиран је применом методе коначних елемената употребом двофазног и трофазног модела направљеног на бази репрезентативног запреминског елемента - РЗЕ. Развијен је трофазни модел РЗЕ са честичним

ојачањем распоређеним у површински центрирано кубном распореду са матричном порозношћу облика сфере, чији су резултати упоређени са једноставним аналитичком моделима. Примећено је да матрична порозност значајно утиче на карактеристике еластичности ових врста композита. Резултати добијени на основу двофазног модела имају више вредности од оних добијених на основу трофазног модела у скоро целом анализираном опсегу услед физичке границе за запремински удео порозитета код трофазног модела која је очигледно одређена вредношћу запреминског удела честице ојачања.