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Modelling the nanomechanical response of micro particle-matrix system for nanoindentation tests

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Abstract :

A lot of experimental, numerical simulation and analytical modelling work have been done on how the substrate affects the measured hardness and elastic modulus of the coating/substrate system for nanoindentation tests. Little work has been done for the elastic-plastic behaviour of micro particle-matrix systems. Clifford et al. have proposed an empirical model to describe the spatial dependent composite modulus during nanoindentation tests for linear elastic particle embedded in linear elastic matrix. However, no such models have been developed for elastic-plastic composites. In this study, finite element (FE) simulations were used to determine elastic modulus and hardness of hard particles embedded in soft matrix and vice versa. An extended Clifford model has been developed to determine elastic modulus and hardness for elastic-plastic composites with various particle shapes and volume fractions.

Key words: Hydroxyapatite (HA), Biopolymers, Nanoindentation, Finite element analysis Modelling

1. Introduction

Nanoindentation has been used to determine the mechanical properties of thin coatings [1-4], synthetic [5-7] and biological composite materials [8-14]. In such case, it is important to understand how the underlying substrate or surrounding matrix will affect the measured mechanical properties. In coating/substrate systems, for a typical indenter with a semi-included angle between 60-70°, when the maximum indentation depth exceeds 10-30% (depending on coating/substrate combinations) of the coating thickness, the significant effect on the indentation hardness caused by substrate deformation is evident [15]. For the substrate effect on the indentation modulus, such critical indentation depth can be much smaller [15, 16], but it would strongly depend on the material combinations.

For the indentation tests of particle-polymer matrix systems, the spatial dependent mechanical properties have been mainly investigated by numerical simulations [17, 18]. The empirical model to describe the spatial dependent elastic modulus for such particle-polymer matrix system has only been established for linear elastic materials [17]. Actually, many particle-matrix systems exhibit the elastic-plastic behaviour, which has not been well studied. Such particle-matrix systems have wide industrial applications. Recently, these particle-matrix systems have been used for biomedical applications [19-26]. For example, hydroxyapatite (HA) particles embedded in biodegradable polymers have been used as scaffold materials for bone tissue engineering [22-24]. Such composites have better bioactivity and improved toughness compared to HA particles only. Therefore, it is essential to study the spatial dependent elastic and plastic properties of HA particles embedded in various biopolymers such as polylactic acid (PLA) and polyglycolic acid (PGA).

2. Analytical method

The commonly used approach to extract the Young's modulus and hardness for an indentation test is the Oliver and Pharr method [27], which is based on the analysis of the load-displacement curve (see figure 1). It was found that the unloading curve can be described by a power law equation [27] ,

$$P = B(\delta - \delta_{res})^m \quad (1)$$

Where B and m are fitting constants. Thus, the unloading stiffness S is given by,

$$S = \left. \frac{dP}{d\delta} \right|_{\delta=\delta_c} = mB(\delta_{\max} - \delta_{res})^{m-1} \quad (2)$$

Figure 1. Schematic of a typical load-displacement curve for an elastic-plastic material indented by a conical tip.

Based on the analysis for the elastic unloading of a flat punch, the reduced modulus E_r is given by [28],

$$E_r = \frac{S}{2} \sqrt{\frac{\pi}{A_C}} \quad (3)$$

The reduced modulus E_r is also related to the Young's modulus of the specimen (E_s),

$$\frac{1}{E_r} = \frac{(1-\nu_s^2)}{E_s} + \frac{(1-\nu_i^2)}{E_i} \quad (4)$$

The subscripts i and s refer to the indenter and specimen, respectively. For a diamond tip, $E_i = 1140 \text{ GPa}$ and the Poisson's ratio, ν_i is 0.070. For many ceramics, a value of $\nu = 0.25$ can be used without introducing significant errors into the moduli values calculated.

In equation (3) mentioned above, A_C is contact area which is given by [27],

$$A_C = C_0 \delta_C^2 + C_1 \delta_C^1 + C_2 \delta_C^{1/2} + C_3 \delta_C^{1/4} + \dots + C_8 \delta_C^{1/128} \quad (5)$$

Where, $C_0 = 24.5$ for Berkovich and its equivalent conical tip (with semi-included angle of 70.3°). The constants C_1 to C_8 are fitting parameters which are obtained by calibration tests on fused quartz. Particularly, the contact depth is also given by [27],

$$\delta_c = \delta_{\max} - \varepsilon \frac{P_{\max}}{S} \quad (6)$$

Where ε is a geometric constant that can be experimentally determined or calculated from finite element analysis (FEA). For a conical tip equivalent to a Berkovich tip, $\varepsilon = 0.72$. On the other hand, the nanoindentation hardness (H) is given by [27],

$$H = \frac{P_{\max}}{A_c} \quad (7)$$

Where $P_{\max}$ is the maximum indentation force.

Various methods have been proposed to study how the elastic deformation of thin coatings will be affected by the substrates [29-35]. There are also different empirical models to study how the plastic deformation of the coatings will be affected by the underlying substrates [32-36]. However, it was found that these models were not applicable to the particle-matrix systems [17]. Therefore, Clifford et al [17] have proposed the following empirical model to describe the spatial dependent composite modulus (E_c) for a spherical tip indenting linear elastic particles embedded in the linear elastic matrix. In their study, the soft particle has the same thickness to the matrix.

$$\frac{E_P^* - E_C^*}{E_P^* - E_M^*} = \frac{lz^n}{1 + lz^n + uz} \quad (8a)$$

$$z = \frac{a}{t} \left(\frac{E_P^*}{E_M^*} \right)^b \quad (8b)$$

Where l , u , n , b are fitting parameters, the subscripts P , M and C refer to the particle, matrix and composite, respectively. The parameters a and t are contact radius during indentation and thickness of particles, respectively. As suggested in [15], the plastic deformation zone may be proportional to the effective elastic influence zone. Therefore, in this study, we assume that similar principles apply to hardness and we propose the following equations for the spatial dependent composite hardness (H_c):

$$\frac{H_P^* - H_C^*}{H_P^* - H_M^*} = \frac{lz^n}{1 + lz^n + uz} \quad (9a)$$

$$z = \frac{a}{t} \left(\frac{H_P^*}{H_M^*} \right)^b \quad (9b)$$

Where, the parameters in this equation are similar to what have been defined above.

3. Methodology

3.1. Finite element modelling

When the nano-HA particles were dispersed in the biopolymers, they tend to form a microscale or submicroscale agglomeration which are almost spherical shape [37]. For simplification, a semi-spherical hydroxyapatite (HA) particle (with a radius of $0.5\mu\text{m}$) embedded in a biopolymer was chosen for the modelling in this work. To evaluate shape and volume effects, two different cylindrical particles with radius of $0.437\mu\text{m}$ and $0.5\mu\text{m}$ were also considered. The vertical dimension of these cylindrical particles equal to their radii, which results in the volumes of $0.131\mu\text{m}^3$ and $0.196\mu\text{m}^3$, respectively. It was also assumed that particles were far away from each other so that the indentation stress field will not be affected by the neighbouring particles. As the volume fraction of the particles is low and thus we could assume the isotropic behaviour for the matrix for the nanoindentation tests. Detailed geometries and dimensions for these different particles were summarized in table1. A typical conical tip with semi-included angle of 70.3° (equivalent to a Berkovich indenter) and tip radius of 40nm was used. Such a tip radius represents a real test. Due to the symmetric nature of the indenter and the composite specimen, a 2D axisymmetric finite element model (FEM) was developed using ABAQUS 6.10 for computation efficiency.

Table 1. Summary of geometries and dimensions of the particles.

Particles	radius (r)	thickness (t)	volume
Semi-spherical particles	$0.5\mu\text{m}$	$0.5\mu\text{m}$	$0.131\mu\text{m}^3$
Cylindrical particles	$0.437\mu\text{m}$	$0.437\mu\text{m}$	$0.131\mu\text{m}^3$
Cylindrical particles	$0.5\mu\text{m}$	$0.5\mu\text{m}$	$0.196\mu\text{m}^3$

Figure 2 shows the finite element (FE) mesh of indentation of particle/matrix system. A total number of 10260 elements were used to model the particle and the matrix. The density of the FE mesh was designed to increase with proximity to the particle/indenter contact region. Roller boundary conditions were applied to the bottom of the specimen. Previous work has demonstrated that the influence of friction on the indentation responses was relatively small [38], thus the contact at tip/particle and particle platen interfaces was assumed to be frictionless in this case. The maximum applied displacement varied from 0.03 to $0.1\mu\text{m}$.

In addition, both the particle and matrix were modelled as elastic-plastic materials. The Young's modulus and hardness of HA was taken from [39]. For typical ceramic materials, the $H/Y=2.2-2.5$ [40]. Based on this, it is assumed that the yield strength of HA is 2.3GPa . The elastic moduli of PLA and PGA are $0.35-3.5\text{GPa}$ and $6-7\text{GPa}$ [41]. Also, it is assumed that the yield strength of the PLA and PGA are 0.03 and 0.12GPa , respectively, which are similar to what has been reported [41]. For comparison, an additional biomaterial with Young's modulus of 35GPa and yield strength of 0.6GPa is also considered. In these cases, the E/Y ratios for these biopolymers are the same. Table 2 summarizes the materials properties used in the FE model. We consider HA particles embedded into three different

biopolymer matrices (i.e. polymer1, polymer2, polymer3 in table 2). For comparison, the material properties of particle/matrix were switched, which represents biopolymer particles embedded in HA matrix. In this case, the elastic modulus ratio between the particle and matrix (E_p/E_M) varies from 0.012 to 83. The yield strength ratio between the particle and matrix (Y_p/Y_M) varies from 0.013 to 77. Such combinations would cover a wide range of composite materials.

Figure 2. Details of finite element mesh of indentation of nanoparticles embedded in the matrix, (a) semi-spherical particles, (b) cylindrical particles.

Table 2. The input parameters for materials properties in the FE model.

	E (GPa)	Y(GPa)	ν
HA	145	2.3	0.25
Polymer 1	1.75	0.03	0.3
Polymer 2	7	0.12	0.3

Polymer 3	35	0.6	0.3
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3.2 Calibration

In this study, the tip radius is 40nm, which is comparable to the indentation penetration. Similar to the experimental tip area function calibration, this study uses numerical simulation as calibration procedure. The substrate was assigned the same mechanical properties to the nanoparticles. In this case, the elastic modulus and hardness determined by Oliver and Pharr method were calibrated against the intrinsic elastic modulus and hardness. This will generate new area function for data calibration and also eliminate any numerical instability induced errors.

4. Results and discussion

4.1. Typical load-displacement curves

Figure 3 shows the typical load-displacement curves of semi-spherical HA particles embedded in different biopolymers. For very soft matrix (i.e. 1.75GPa and 7GPa), the clear transition from particle-dominated behaviour to matrix-dominated behaviour was observed.

(c)

Figure 3. The load-displacement curves for the indentation test upon a semi-spherical HA particle (145 GPa) within a polymer matrix with elastic modulus of (a) 1.75GPa, (b) 7GPa and (c) 35GPa.

For simplification, the apparent moduli (E_c) and hardness (H_c) of the composite were plotted against the relative indentation depth (RID, i.e. contact depth divided by the particle radius). The representative example (i.e. HA particles with varied geometries embedded in polymer 1) was shown in figure 4. Only for the soft particles in hard matrix, one may propose 5% thumb rule for estimating the particle modulus [18]. Otherwise, the critical depth to determine the elastic modulus of the particle is strongly dependent on the modulus ratio of particle over the matrix [18]. It was also reported elsewhere that hardness of a particle can be measured reliably when the indentation depth is below 13.5% of the particle's radius for the composites with Y_p/Y_M varying from 0.1 to 10 [38]. But such a thumb rule does not apply to the composites with large mismatch in mechanical properties in this study. For example, even at RID as small as 0.05, significant drops of the modulus (drop by 26%) and hardness (drop by 33%) were observed for the semi-spherical particle composite. This indicated that the matrix effect is still significant even when the indentation penetration is below 5% of the particle radius.

For the particle with the same volume but different geometries (semi-sphere and cylinder), the way how the composite elastic moduli change with RID is almost indistinguishable. This is because the ratio of radius and vertical dimension equals one for all particles. The volume effect is evident to play an important role in composite elastic moduli. While, for the given volumes specified in this study, the volume effect of the particle is less significant for the hardness. This is mainly due to the complicated elastic-plastic deformation mechanisms of the composite materials during indentation as suggested in [16]. This also suggests that it is more reliable to extrapolate the measured composite hardness to the zero penetration to extract the intrinsic hardness of the particle rather than relying on any thumb rules.

Figure 4. A typical example of modulus (E_c) and hardness (H_c) against RID for three different HA particles in polymer 1.

4.2. Model elastic-plastic responses of the composites during nanoindentation

When applying Clifford model (i.e. equation (8)) to the composite modulus in this study (see appendix A), it gives good estimations similar to what has been reported for viscoelastic composites [42]. When adopting equation (9), we have found that Clifford model can be extended to determine composite hardness for indentation tests. However, the fitting parameters in the Clifford model (see table A1-A3 in the appendix A) are very sensitive to the particle shape and volume fraction, which implies that this may not be a generic model. For example, for the soft particle/hard matrix, the power exponent b in equation (8) (i.e. elastic modulus) changes from 0.55–0.7. The parameter μ in equation (8) (i.e. elastic modulus) varies from -3.32 to 8.18. Similar observations ($\mu = -3.92 \sim 2.08$) were found for equation (9) (i.e. hardness). Both parameters (b and μ) will determine how the mismatch of particle and matrix elastic modulus (and yield strength) contributes to the composite modulus (and hardness). Such significant variations in these two parameters are due to the fact that the mismatch between the particle and matrix elastic modulus (and yield strength) is up to a factor of 80 in this study.

In order to compare the contributions on the composite modulus and hardness caused by the particle and matrix during an indentation test, we propose the following equations,

$$\frac{E_P^* - E_C^*}{E_C^* - E_M^*} = \frac{Lz^n}{1 + Lz^n + uz} \quad (10a)$$

$$z = \frac{a}{t} \left(\frac{E_P^*}{E_M^*} \right)^b \quad (10b)$$

Where, the fitting parameters in this equation are similar to what have been defined in equation (8). By replacing E_C^* with H_C^* , E_P^* with H_P^* , E_M^* with H_M^* in equation (10), the following equations for composite hardness can be obtained:

$$\frac{H_P^* - H_C^*}{H_C^* - H_M^*} = \frac{Lz^n}{1 + Lz^n + uz} \quad (11a)$$

$$z = \frac{a}{t} \left(\frac{H_P^*}{H_M^*} \right)^b \quad (11b)$$

When plotting γE (e.g. $\frac{E_P^* - E_C^*}{E_C^* - E_M^*}$) against z , all the data converge on a single curve (see figure 5). A similar observation was also found for the plot of γH (e.g. $\frac{H_P^* - H_C^*}{H_C^* - H_M^*}$) against z (see figure 6). A Matlab code was written to determine the key parameters in equations (10)-(11), which have been summarized in table 3, 4 and 5.

Figure 5. Plots of γE (e.g. $\frac{E_P^* - E_C^*}{E_C^* - E_M^*}$) against z using equation (10) for: (a) semi-spherical HA particles (0.5 μ m) in polymers; (b) semi-spherical polymers (0.5 μ m) in HA matrix; (c) cylindrical HA particles (0.437 μ m) in polymers; (d) cylindrical polymers (0.437 μ m) in HA matrix; (e) cylindrical HA particles (0.5 μ m) in polymers; (f) cylindrical polymers (0.5 μ m) in HA matrix.

Figure 6. Plots of γH (e.g. $\frac{H_P^* - H_C^*}{H_C^* - H_M^*}$) against z using equation (11) for: (a) semi-spherical HA particles (0.5 μm) in polymers; (b) semi-spherical polymers (0.5 μm) in HA matrix; (c) cylindrical HA particles (0.437 μm) in polymers; (d) cylindrical polymers (0.437 μm) in HA matrix; (e) cylindrical HA particles (0.5 μm) in polymers; (f) cylindrical polymers (0.5 μm) in HA matrix.

When the modified model is used, the value of b (i.e. $b=0.7$) for elastic modulus (i.e. equation (10)) is independent of the material combinations, particle shape and volume in this study. For the hardness, the value of b is independent of the particle shape and volume but depends on the constraints applied to the particles by the stiff matrix. For hard particle in soft matrix, the pair of b values for elastic modulus and hardness are 0.7 and 0.5 regardless of the particle shape and volume. While for soft particle in hard matrix, the pair of b values are 0.7 and 0.34. Such consistence in the b values cannot be achieved by Clifford model. The values of μ in the modified model are between -4.5 and -1.1 for the elastic modulus. These values are between -0.45 and -1.07 for hardness. The magnitudes of these μ values for hardness are consistently smaller than their counterparts for elastic modulus. This is due to the fact that the plastic deformation zone is much confined compared to the elastic deformation. However, the values of μ in the Clifford model seem random and do not reflect such physical insights.

Table 3. Best fitting parameters of modified Clifford model (equations (10)-(11)) for semi-spherical particles ($r=0.5\mu\text{m}$ with volume of $0.131\mu\text{m}^3$) in this study.

Composite (semi-spherical particle, $r=0.5\mu\text{m}$)		b	l	μ	n
Hard particle in soft matrix	Elastic modulus	0.7	3.169	-3.303	1.010
	Hardness	0.5	0.567	-1.046	1.284
Soft particle in hard matrix	Elastic modulus	0.7	1.045	-4.500	1.031
	Hardness	0.34	1.330	-1.065	2.597

Table 4. Best fitting parameters of modified Clifford model (equations (10)-(11)) for cylindrical particles ($r=t=0.437\mu\text{m}$ with volume of $0.131\mu\text{m}^3$) in this study.

Composite (cylindrical particle, $r=t=0.437\mu\text{m}$)		b	l	μ	n
Hard particle in soft matrix	Elastic modulus	0.7	2.440	-2.573	1.014
	Hardness	0.5	0.529	-0.949	1.246
Soft particle in hard matrix	Elastic modulus	0.7	1.393	-4.019	1.066
	Hardness	0.34	1.462	-0.509	2.731

Table 5. Best fitting parameters of modified Clifford model (equations (10)-(11)) for cylindrical particles ($r=t=0.5\mu\text{m}$ with volume of $0.196\mu\text{m}^3$) in this study.

Composite (cylindrical particle, $r=t=0.5\mu\text{m}$)		b	l	μ	n
Hard particle in soft matrix	Elastic modulus	0.7	1.305	-1.489	1.042
	Hardness	0.5	0.391	-0.848	1.360
Soft particle in hard matrix	Elastic modulus	0.7	1.620	-1.130	1.313
	Hardness	0.34	1.4	-0.45	2.77

5. Conclusion

Finite element (FE) modelling was done to study the spatial dependent composite modulus and hardness during nanoindentation tests. The reported thumb rules to determine the modulus and hardness of particles at the penetration below 5% and 13.5% are reasonable approximations for composites with relatively small mismatch in elastic modulus and hardness between particle and matrix. But they do not apply to the composites with large mismatch in elastic modulus and hardness between particle and matrix. Therefore, new models have been developed based on the original Clifford model, which enables us to determine elastic modulus and hardness for such composite materials. These models have been successfully applied to various composites regardless of particle geometries, volume and materials combinations. In principle, such models can also be extended to biological composites such as biofilms which can be treated as hard particles (bacteria) embedded in soft matrix (extracellular polymeric substance).

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Appendix A

Table A1. Best fitting parameters of Clifford model (equations (8)-(9)) for semi-spherical particles ($r=0.5\mu\text{m}$ with volume of $0.131\mu\text{m}^3$) in this study.

Composite (semi-spherical particle, $r=0.5\mu\text{m}$)		b	l	μ	n
Hard particle in soft matrix	Elastic modulus	0.75	2.6781	0.0031	1.3003
	Hardness	0.56	0.7360	0.4128	2.9204
Soft particle in hard matrix	Elastic modulus	0.7	1.2114	-3.3213	1.0764
	Hardness	0.34	1.4000	-0.5713	2.5597

Table A2. Best fitting parameters of Clifford model (equations (8)-(9)) for cylindrical particles ($r=t=0.437\mu\text{m}$ with volume of $0.131\mu\text{m}^3$) in this study.

Composite (cylindrical particle, $r=t=0.437\mu\text{m}$)		b	l	μ	n
Hard particle in soft matrix	Elastic modulus	0.73	2.052	0.0386	1.4815
	Hardness	0.53	0.6638	0.3721	2.9413
Soft particle in hard matrix	Elastic modulus	0.55	4.8779	-0.4358	1.6607
	Hardness	0.35	4.8964	-3.9193	2.1569

Table A3. Best fitting parameters of Clifford model (equations (8)-(9)) for cylindrical particles ($r=t=0.5\mu\text{m}$ with volume of $0.196\mu\text{m}^3$) in this study.

Composite (cylindrical particle, $r=t=0.5\mu\text{m}$)		b	l	μ	n
Hard particle in soft matrix	Elastic modulus	0.75	1.2532	-0.0119	1.2468
	Hardness	0.5	0.8464	0.6909	3.3698
Soft particle in hard matrix	Elastic modulus	0.57	5.57	8.1787	1.8
	Hardness	0.34	3.8765	2.0837	3.1373

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