SIMULATION AND DESIGN OF NANOCOMPOSITE FOR APPLICATION IN BALLISTIC PROTECTION

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ABSTRACT

The objective of this research is to develop a modeling, simulation, and design tool for nano-composites in order to predict, with accepted fidelity, nano-composite behaviors; and to design optimum nano-composites for specific Army applications such as ballistic protection. Based on a unit cell model created for nanoclay-epoxy composites, the effect of nanoparticle distribution on the maximum stress developed in epoxy resin was investigated using the Meshfree Particle Method based simulation tool developed at MKP. The ensemble average of mechanical property for nanoclay-epoxy composite was also studied. The increase in the mechanical properties for nanoclay-reinforced epoxy was evidenced from the simulations. It is found that statistical analysis is crucial to predict the performance of nanoparticle reinforced composite. Several armor samples reinforced with nanoclay-epoxy composites were fabricated and ballistic tests were conducted on the nanoclay-reinforced composite armor. It was found that higher mechanical properties, such as modulus and strength, will help to improve the performances of composite armor system. A numerical simulation was initiated to investigate the protection difference between armor with nanoclay-reinforced epoxy and armor with pure epoxy resin. Efforts have been made to reproduce similar ballistic protection behavior using the simulation tool in comparing with the actual test results.

1. INTRODUCTION

Inspired by the excellent results obtained by a group of researchers in Japan by the embedment of nanoclay into nylon [1], extensive work has been carried out over the past decades on the incorporation of nanoclay into polymers for the purpose of enhancing the polymer properties. Normally the properties under investigation include tensile modulus, tensile strength, glass transition temperature, resistance against the absorption of moisture, resistance against flammability, and fracture toughness. Ahmadi et al. [2] used X-ray diffraction and transmission electron microscopy to investigate the morphology of clayed-reinforced ethylene propylene diene terpolymer (EPDM) nanocomposites with organo-montmorillonite (OMMT). It was found that the tensile modulus can be increased by 60% and tensile strength can be increased by 175%. Avila et al. [3] investigated the penetration mechanism on polymer-nanoclay-fiber glass nanocomposite using low-velocity impact tests (ASTM D5628-01). The sample was made of S2-glass plain-weave woven fabric and nanoclay-epoxy. It was shown that the front side delamination area was reduced 22% with 1 weight % nanoclay addition. The back area delamination reduction ranged from 10-21% with respect to different impact energy. It was also found that slow cure in epoxy-nanoclay mixture leads to much better nanocomposites without bubble formation. Wetzel et al. [4] used a Charpy impact strength test to investigate the fracture toughness of nanocomposites. The test sample is composed of epoxy resin, titanium dioxide (TiO₂) nano-particles and calcium silicate (CaSiO₃) micro-particles. The improvement in stiffness, impact strength and wear resistance were witnessed at low nano-particle filler contents. Optimal TiO₂ nano-particle content is found at 4 volume %. Additional 3 volume % CaSiO₃ micro-particles into epoxy/TiO₂ (4 volume %) can further improve the impact toughness of the nanocomposite. Yao et al. [5] carried out dynamic tests on a nanoclay-epoxy beam with a manufactured initial crack. The beam is made of 3 weight % Montmorillonite (MMT) silicate clay particles and epoxy resin. It was found that fracture toughness improved with the addition
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of clay particles. The toughness improvement can be attributed to the increasing interfaces from particle reinforcement at the nanoscale. Zheng et al. [6] carried out impact tests (ASTM-D256) and tensile tests (ASTM-D638) for nanoclay (SiO2) – epoxy composites. For a glass fiber nanocomposite, additional three-point bending tests (ASTM-D790), compression tests (ASTM-D6641) and shear tests (ASTM-D2344) were also carried out. Two kinds of nanocomposite samples were made for the mechanical tests: nano-particle (SiO2)- epoxy composite and glass-fiber-epoxy nanocomposite. For nano-epoxy polymer, it was found the tensile strength increased 115%, tensile modulus increased 13% and impact strength increased 60% at the optimal 3 weight % of nano-particle addition. From the impact test, it was seen that small curvatures occurred at the surface of the nanocomposite, indicating that massive new surfaces were created under impact loading. As a result, much more impact energy could be dissipated through these new surfaces in the SiO2-epoxy nanocomposite. For the nano-glass fiber composite, the mechanical property improvements were found as: bending strength 69.4%, tension modulus 21%, tensile strength 23% at 5 weight % nano-particle addition. However, shear and compression strength enhancement were limited. Lan et al. [7] described various different nano-polymer applications, especially for nylon 6 nanocomposite with 2 weight % nanomer and for Polyolefin nanocomposites (HPP). For nylon 6 nanocomposite, the property enhancement reached its optimal value at 2 weight % nano-particle addition and the improvement was reported as: flexural modulus 35%, tensile modulus 28%. For HPP with 6 weight % nano-particle, the property enhancement was even greater: 98% in tensile modulus and 78% in flexural modulus.

The addition of nano-particle is also beneficial to composite chemical and electrical properties. Bharadwaj [8] investigated the relative permeability of layered nanoclay samples based on a modified tortuosity model. The effects of sheet length, concentration, orientation, and degree of delamination on the relative permeability were explored. The layered silicate clay was 1 nm in thickness. The length of the sheet ranged from 30 – 2000 nm. It was found that the gas barrier property was enhanced with less than 5 weight % nanoclay addition. Pan et al. [9] investigated electricity conductivity for one kind of nanocomposite (nylon 6 with 0.5-2.5 weight % nano graphite flake). The nano graphite was shown to be a good conducting filler for polymers. Singh and Balazs [10] discovered that grafting short-chain surfactants to the clay sheets could increase the gallery spacing and promote polymer permeation. Self consistent field (SCF) theory was used to investigate the effect of varying the properties of both the surfactants and polymers on the miscibility of the polymer/clay mixture. It was found that the blending of polymers and clay under optimal conditions could yield nanocomposites with a great tensile strength, heat resistance and gas permeability compared to the pure polymer matrix. Furthermore, only 1-10 weight % nano additives were needed for performance enhancement. For detailed discussion of chemical and electrical properties of nanocomposites, the review paper by Hussain et al. [11] is suggested.

Numerical simulation for nanocomposites has also been a research focus in recent years. Hackett et al. [12] used Monte Carlo and molecular dynamics (MD) computer simulations to explore the atomic scale structure and dynamics of intercalated PEO-layered silicate nanocomposites. Srivastava et al. [13] also studied the computational nanotechnology with molecular dynamics for fullerene and carbon nanotube (CNT) based molecular materials. It has been emphasized that quantum MD is needed for the simulation in picosecond (10^-12 second) scale, while classic MD is commonly used to the situation where the motion of atoms and molecules is treated using finite difference equations of Newtonian mechanics. Tight-binding molecular dynamics (TBMD) was proposed as a bridge between quantum MD and classic MD [13].

Instead of molecular-dynamics-based simulation method, Li and Chou [14] modeled the deformation of CNT using a structural mechanics approach. Potential energy was used to model the bonding between molecules. The tensile modulus and shear modulus of single-walled carbon nanotube were examined. Zhao and Hoa [15] also examined tensile modulus, tensile strength and fracture toughness of a nanoclay reinforced epoxy cell using FEM simulation. The amount of nanoclay addition modeled was 5 volume %. It was shown that nano-particle volume percentage is the main factor for increased elastic modulus. Stress concentration in nanocomposite depends highly on the nano-particle dispersion. The more dispersive the nanoparticle distribution, the less stress concentration exists in the composite.

The simulation techniques can be summarized as follows. In principle, any problem associated with molecular/atomic motions can be simulated by molecular dynamics, tight-binding molecular dynamics and density function theory (DFT). However, due to their huge computational tasks, practical applications of these atomistic modeling techniques are limited to systems containing a small number of molecules or atoms and are usually confined to studies of relatively short-lived phenomena, from picoseconds to nanoseconds.

The continuum mechanics modeling approach can be used to analyze the static or dynamic mechanical properties of composites with nanoparticles. However, these models neglect the detailed characteristics of nanoparticle, and are unable to account for forces acting on the individual atoms. Therefore, there is a need for
developing a modeling technique that analyzes the mechanical response of nanocomposites at small scale but is not overburdened by the time scales. Such a modeling approach would benefit novel nanodevice design and multi-scale simulations of nanosystems. We will extend the theory of classic structural mechanics into the modeling of nano-particle incorporated polymer. The bonding between nano-particles will be approximated as potential functions of molecular mechanics. The nanocomposite property will be simulated in a micro-scale unit cell. The obtained mechanical property can then be used in macro-scale for design optimization.

2. DEVELOPMENT OF SIMULATION MODEL

2.1 Nanoclay Simulation Model

A multiscale decomposition [16] was utilized to couple simulations at different scales. The fundamental idea is to decompose the total displacement field \( u(x) \) into coarse and fine scales \([17]\)

\[
u(x) = \bar{u}(x) + u'(x), \tag{1}\]

where the coarse scale \( \bar{u} \) is that part of the solution which can be represented by a set of basis functions, i.e. finite element shape functions. The fine scale \( u' \) is defined as the part of the solution whose projection onto the coarse scale is zero. An example of this decomposition is to model the epoxy region using a coarse scale and model the nanoclay region using a fine scale:

\[
u = N d + Q q. \tag{2}\]

Here, \( N \) is the shape function set for the coarse scale domain and \( d \) is the FEM nodal displacement vector. In the fine scale region, \( q \) is the “exact” solution obtained from any atomic or molecular-level simulation tool, i.e. molecular dynamics. \( Q \) is the complimentary projection operator defined in reference \([17]\).

With the definition in Eq. (2), a Lagrangian \( L \) can be defined to be the difference between the kinetic energy and the potential energy,

\[
L(u, \dot{u}) = \frac{1}{2} \dot{u}^T M_d \dot{u} - U(u), \tag{3}
\]

where \( M_d \) is the mass matrix obtained from FEM and MD, \( U \) is the interatomic potential energy, and velocity

\[
\dot{u} = N d + Q \dot{q}. \tag{4}
\]

Substituting Eqs. (2) and (4) into the Lagrangian (3), results in

\[
L(d, \dot{d}, q, \dot{q}) = \frac{1}{2} \dot{d}^T M_d \dot{d} + \frac{1}{2} \dot{q}^T M_q \dot{q} - U(d, q), \tag{5}
\]

where the coarse scale mass matrix \( M \) is given by \( M = N^T M_d N \), and the fine scale mass matrix \( M_q \) is \( M_q = Q^T M_q Q \).

The multiscale equations of motion are obtained from the Lagrangian \([17]\) and have the following form:

\[
M \ddot{d} = N^T f, \tag{6}
\]

\[
M_q \ddot{q} = Q^T f, \tag{7}
\]

in which the interatomic force \( f \) can be expressed as

\[
f = -\frac{\partial U(u)}{\partial u}. \tag{8}\]

A Lennard-Jones (LJ) potential can be used to define the interatomic potential for nano materials:

\[
U(x, x_j) = U(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right],
\]

\[
r = |x_i - x_j|. \tag{9}\]

where \( r \) is the interatomic distance, \( \sigma \) is the collision diameter, and \( \varepsilon \) is the bonding energy.

2.2 Meshfree Particle Method

A Meshfree Particle Method \([17, 18]\) is applied to the simulation of nanocomposites. The nanocomposite field is discretized into particles with desired volume/mass. Compared to conventional grid-based methods, e.g. the finite element approach (FEM), the meshfree method is a more powerful way to simulate dynamic problems such as high-velocity impact. These problems often involve numerical difficulties such as large deformation, material inhomogeneity, moving material interface and deformable boundary, which make grid-based methods challenging in numerical simulations. Furthermore, the nanocomposite domain is considered as a set of discrete physical particles rather than a continuum. Consequently, the meshfree method is a natural choice in simulations.

The interatomic force on particle \( i \) is denoted as \( f_i \), which is the summation of interactions from neighboring particles,

\[
f_i = \sum_{j=1}^{N_i} f_{ij}, \tag{10}\]

where \( f_{ij} \) is the internal force from particle \( j \) to \( i \), \( N_i \) is the total number of particles in the support domain of particle \( i \).

The definition of support domain \([18]\) of particle \( i \) is illustrated in Fig. 1. The dimension of the support domain for particle \( i \) is denoted as \( h_i \). A particle \( j \) is considered within the support domain if the distance between particle \( j \) and \( i \), \( D_{ij} \), is less than the dimension of the domain, \( h_i \).
The interaction force between particle $i$ and $j$, $f_{ij}$, depends on the interatomic potential defined in Eq. (8). For the L-J potential defined in Eq. (9), the magnitude of force $f_{ij} = |f_{ij}|$ has the following form:

$$f_{ij} = 24 \frac{\varepsilon}{\sigma} \left[ 2 \left( \frac{\sigma}{D_{ij}} \right)^{12} - \left( \frac{\sigma}{D_{ij}} \right)^{6} \right] .$$

(11)

Figure 1. Support domain of particle $i$

3. A TWO-DIMENSIONAL CASE STUDY

A two-dimensional case is considered for unit cell nanocomposite property study. The case is similar to the case in reference [15]. We considered that the epoxy resin is dispersed well by 5% volume of nano silicate particles. The particle is assumed to have circular shape to simulate the configuration of the nanoclay flake. The material properties of silicate are given as below [15]: density 2.2 g/cm$^3$, modulus of elasticity 73 GPa, Poisson’s ratio 0.17, tensile strength 104 MPa. The epoxy properties are listed as below [15]: density 1.2 g/cm$^3$, modulus of elasticity 2.3 GPa, Poisson’s ratio 0.4, tensile strength 90 MPa. In the epoxy mixture plate, a square plate of dimensions 40 x 40 x 0.05 μm$^3$ is selected as a typical cell model. The cell model is fixed at the lower edge and subjected to tensile loading of 60 MPa at the top edge. With this cell model, the effects of nanoparticle size on the mechanical behavior of the material were studied.

The evenly distributed nanoparticle case was studied first with the regular FEM approach. Five cell models are considered and shown in Fig. 2. Figure 2a is the cell model with one nanoparticle of 10 μm in diameter. The particle size is obtained by calculating the requirement of 5% volume fraction of silicate particles. In Figs. 2b-2e, the particle is partitioned to 4(2x2), 9(3x3), 36(6x6), and 144(12x12) smaller particles, respectively, with the same particle volume fraction. The corresponding particle diameters are 5, 3.4, 1.7, and 0.84 μm. Figure 2 also shows von Mises stress distribution results of various cell models obtained by FEM simulations.

![Figure 2. Cell models of different sizes of particles (FEM approach)](image)

The evenly distributed nanoparticle case was then studied with the meshfree particle method. The result is compared to the one obtained from the FEM method. In the meshfree particle method, the epoxy region and nanoparticle domain are discretized into small particles. The neighboring particles interact with each other in a way determined by the potential energy between particles. By this means, no particular meshing technique is needed for particle partitioning.

Figure 3 shows the comparison of nanocomposite strength and stiffness based on two different simulation methods. The variation of the material tensile strength is plotted in Fig. 3a as a function of particle dispersion. As can be seen, the nanoclay-epoxy composite strength increases as the nano reinforcement is dispersed using increasingly fine particles. In this particular example,
the diameter of the nanoclay reaches 840 nm for the partition case 144(12x12). The tensile strength of the nanocomposite reaches its peak value at this partition case. The determination of material strength follows the rule suggested by Zhao and Hoa [15] in the study of nanoclay-epoxy composite strength for a similar load case. Compared to the FEM-based result (see Fig. 3a), the change of material strength is more apparent in meshfree particle method. The tensile strength obtained by meshfree particle method converges to similar value as the one obtained from FEM approach. Consequently, the precision of the meshfree particle method is acceptable in the nanocomposite simulation.

A similar tendency can also be seen in material tensile modulus (see Fig. 3b), although the change of modulus is much smaller compared to the change in strength. Furthermore, the tensile modulus does not vary significantly as the function of particle size, which matches the reported results in reference [15].

In Figs. 2 and 3, the nanoparticle is assumed to have same size and to be distributed evenly in the epoxy resin. In practice, it is natural to have a random distribution of particle size and position in the dispersion process. The effect of particle randomization is studied for 5% volume fraction of nanoparticle reinforcement using FEM approach. Figure 4 shows four cell models and stress plots with random particle distribution obtained from FEM simulations. The corresponding tensile modulus and strength are plotted in Fig. 5 and are compared to the results for evenly distributed cases. As can be seen, the tensile modulus is almost identical for the randomized cases compared to the evenly distributed ones, while the tensile strength will depart from the evenly distributed counterpart. The difference is so large that the one particle partition case will have the best tensile strength after randomization, which is contradictory to the evenly distributed case in that the same partition has the worst strength performance.

Figure 4. Cell models for nanoparticle randomization study (FEM approach)
This study of randomized particle distribution shows the importance of the statistical evaluation for nanocomposite properties in the particle dispersion process. It is necessary to create numerous random samples for particle partitions under given particle size. The mechanical properties of the nanoclay-epoxy mixture will be the ensemble averages of the results for all samples. The statistical tensile strength and modulus have been studied for nanoclay-epoxy composite with 5 volume % nanoparticle concentration. For each group of particle partition, 13 samples were created to approximate the randomization of particle size and location. Meshfree particle method was used to simulate the material property for each sample.

Figure 5. Comparison of tensile modulus and strength for randomized and even nanoparticle distributions

Figure 6. Statistical nanocomposite property for 5 volume % nanoparticle concentration

Figure 6 shows the ensemble averaged value, maximum value, and minimum value of the tensile modulus and tensile strength with respect to various partition groups. As can be seen, the change of tensile modulus is relatively small compared to the variation of tensile strength. For partition group 144 (the diameter of nanoparticle is about 840 nm), the minimum tensile strength is approximately two-thirds of the maximum strength. The averaged strength is closer to the minimum value than to the maximum one. Consequently, statistical analysis is crucial to understand the mechanical properties of nanocomposites.

In the final numerical example, nanocomposite with defects was considered for evaluating tensile strength. FEM approach is used to simulate the nanocomposite property. Figure 7 shows the stress distribution for pure epoxy and nanoclay embedded epoxy. The defect in the composite is assumed to have circular shape and a diameter close to 1.0 micrometer. The circular shaped
defect is used to mimic the bubble created during the epoxy manufacturing process. The nanocomposite has the same material property and geometrical configuration as the composite shown in Fig. 2d. The epoxy region is evenly distributed with 36 nanoparticles, while the 9 bubble defects are also evenly distributed in the epoxy. As can be seen in Fig. 7, the maximum stress is located near the edge of the circular shaped defect. The tensile strength for nanoclay-epoxy and pure epoxy are compared in Fig. 7c. The tensile strength of nanocomposite is 10 percent higher than the strength of pure epoxy. As a result, the nanoclay embedded epoxy is much stronger than pure epoxy. Furthermore, the strength of nanocomposite is relatively insensitive to the existence of defect compared to the property of pure epoxy.

![Bubble defect and Nanoparticle](image)

Figure 7. von Mises stress in nanocomposite and epoxy with defects (FEM approach)

4. NANOCLAY-REINFORCED ARMOR FOR BALLISTIC PROTECTION

![Penetration process for composite armor](image)

Developed at MKP Inc., nanoclay-epoxy resin is used as the gluing polymer in the ceramic pellet faceplate of a composite armor. It has been found that the armor with nanoclay insertion maintained the faceplate integrity after two rounds of shooting, while the faceplate with pure epoxy resin damaged after the same shooting condition. As part of our virtual prototyping process, a numerical simulation was utilized to investigate the difference in protection provided by
armor with nanoclay reinforced epoxy and armor with pure epoxy resin. Efforts have been made to reproduce similar ballistic protection by comparison of simulation to actual test results. In this part of research, the improvement of mechanical properties for epoxy with nanoclay was represented by increases of modulus and strength.

The simulation was based on LS-DYNA3D and the results are shown in Fig. 8. It can be seen that projectile (shown in red) was stopped earlier with nanoclay-reinforced matrix material (see Fig. 8a). For armor with pure epoxy as the bonding media, the projectile will penetrate deeper into the backplate (see Fig. 8b). The improvement of armor protection can be explained by the fact that higher strength matrix material can survive longer and contribute more to the defeat of projectiles.

5. CONCLUSIONS

The development of simulation models and design methods for nanocomposite will enable the prediction, design, and prototyping of ballistic-protective composite structures in a broad range of military and civilian applications where enhanced structural and mechanical performance is required. Those that potentially benefit from the SBIR program include DOD organizations: the Army, Air Force, and Navy. Commercial applications include a large number of automotive applications to improve the strength, stiffness, weight, surface finish, flame retardancy, resistance to high temperature and corrosion, among many desirable characteristics.

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