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Size-dependency of nano-scale inclusions

TEIK-CHENG LIM
Nanoscience and Nanotechnology Initiative, Faculty of Engineering, National University of Singapore,
9 Engineering Drive 1, S 117576, Republic of Singapore

Advances in nanotechnology in recent decades leads to progress in the research and developments of nanocomposites [1–3]. Nanocomposites are herein defined as either bulk materials that consist of inclusions with at least one dimension within 1 to 100 nm, or a nano-scale structure with inclusions. The latter, of course, involves nano-scale inclusions since these inclusions should be about one order smaller than the structure itself. Nanocomposites are of interest because characterization results reveal unconventional physical properties as compared to composites of similar constituents, volume proportion and shape/orientation of reinforcements. For example, nanocomposites of SiC-reinforced Al_2O_3 matrices were reported to display no size-dependency of the nano-inclusion [4], decreased fracture toughness with reduction of inclusion size [5], or even increased mechanical properties with reduction of inclusion size [6, 7] for fixed inclusion volume ratio. These contradictory size-dependencies (or size non-dependencies) on nano-scale particulates could possibly point to the quality of the interfacial bonding between nano-inclusions and the matrix material—whether superior, inferior, or similar—as a result of processing techniques. Another type of nanocomposite is the polymer-clay hybrids [8] such as Nylon6-montmorillonite (MMT) [9], PVC-MMT [10], PVB/Na^+-MMT [11], PAn-$BaTiO_3$ [12], EVA-MMT [13] and PU-Attapulgite [14], whereby clay platelets, or stack of platelets, are the reinforcing inclusion of the polymer matrix. Results reveal improved material properties using nano-scale (fully exfoliated) clay platelets than those using larger-sized clay reinforcements (stacked platelets) at equal inclusion volume fraction and orientation [15, 16]. Occurrence of size-dependency in the area of nanotechnology is well-known, having been investigated in terms of surface stresses in nano-scale thin films [17], cavities [18] and simple structures [19]. In conventional composite materials the elastic stiffness of the matrix and inclusion materials are considered, thereby taking into account the interatomic forces within each phase. For simplified modeling, it is assumed that the interface between the matrix and inclusion materials is perfect. When the inclusion is "broken" into smaller pieces while maintaining the volume fraction, the interface area increases. The interfacial area increases rapidly as the spherical inclusion size enters the region <100 nm radius (i.e. <0.1 micron), as indicated in Fig. 1. Hence in the case of nanocomposites the elastic properties of the interface should be given due consideration. To do so, it is essential to introduce the concept of "interface–interphase". While "interface" refers to the surface area between two phases, "interphase" corresponds to the volume defined by the narrow region sandwiched between the two phases. The influence of interphase on mechanical properties has been experimentally examined via different treatment to the nano-inclusion surface [20]. However, recent modeling approaches neglected the influence of interphase properties (e.g. [15, 16, 21]). Fig. 2a shows a simplified representative volume element with A and B as the matrix and inclusion materials respectively. The boundary between A and B appears as an interface surface area, as shown in Fig. 2b. The magnified version, in Fig. 2c, depicts the interface as an interphase volume, consisting of a gap (defined by the interatomic distance between atoms of regions A and B) and a particular stiffness between them (as defined from the interatomic potential energy). In view of the extremely small nature of interphase thickness, the use of molecular mechanics is of importance. In molecular mechanics, the equilibrium interatomic distance is the interatomic distance that gives the minimum interatomic potential energy. Suppose we assume the interphase to be a mechanical spring that connects the two phases A and B, then the spring constant is (e.g. [22, 23])

$$k = \left. \frac{\partial^2 U}{\partial r^2} \right|_{r=R} \tag{1}$$

where U is the interatomic potential energy, r the interatomic distance, and R the interatomic equilibrium distance. Alternatively, one may obtain the elastic coefficients (e.g. [24–26]) as

$$C_{ij} = \frac{1}{V_0} \frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j} \tag{2}$$

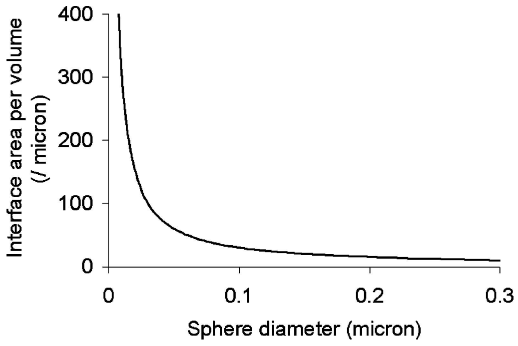

Figure 1 Sharp increase in interface area as spherical inclusion shrinks into the nano range.

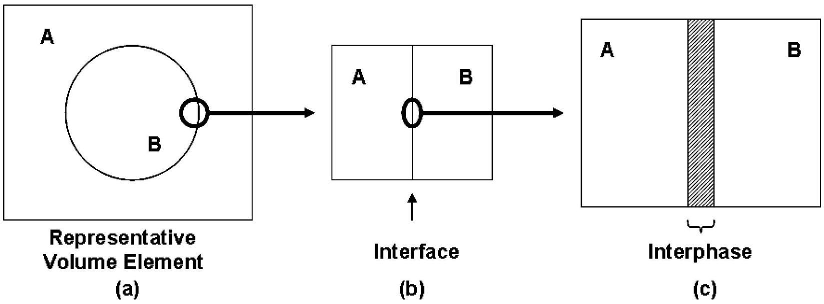

Figure 2 Concept of interface–interphase for nanocomposites.

whereby C_{ij} are elements of the stiffness matrix, ε_i and ε_j being the prescribed strain, and V_0 is the initial systems volume. As such, the elastic coefficients of the resultant interphase can be obtained when that region is taken as a system under consideration. Functional forms for the interatomic potential energy can exist as van der Waals forces, covalent bonds, ionic bonds or hydrogen bonds. Results of C_{ij} from double differential with respect to the interatomic potential function gives rise to Lame constants [25]

$$\lambda = \frac{1}{3}\sum_{i=1}^{3} C_{ii} - \frac{2}{3}\sum_{i=4}^{6} C_{ii} \tag{3}$$

$$\mu = \frac{1}{3}\sum_{i=4}^{6} C_{ii} \tag{4}$$

leading to the following elastic constants

$$E = \mu\left(\frac{3\lambda + 2\mu}{\lambda + \mu}\right) \tag{5}$$

$$G = \mu \tag{6}$$

$$K = \lambda + \frac{2}{3}\mu \tag{7}$$

$$v = \frac{1}{2}\left(\frac{\lambda}{\lambda + \mu}\right). \tag{8}$$

Obtained moduli may then be incorporated, for example, in a recently developed model for composites with coated inclusions (interphase material) [27]. An advantage of this model is that it was developed from earlier models that consider inclusion shape [28–31], thereby enabling both the nano-inclusion shape and the nano-interphase shape to be simultaneously accounted for in computing the overall composite stiffness. The nano-inclusion shape is of importance when dealing with nano-platelet [8–14] and nanotube [32–34] reinforcements. As such, size dependency of nano-scale inclusion on the mechanical properties of nanocomposites can be taken into consideration by means of the interatomic energy at the matrix-inclusion interphase, coupled with composite mechanics approach.

References

1. X. LI, Y. YANG and X. CHENG, *J. Mater. Sci.* **39** (2004) 3211.
2. Y. J. XUE, D. ZHU and F. ZHAO, *ibid.* **39** (2004) 4063.
3. L. WANG, W. JIANG and L. CHEN, *ibid.* **39** (2004) 4515.
4. L. CARROLL, M. STERNITZKE and B. DERBY, *Acta. Mater.* **44** (1996) 4543.
5. M. STERNITZKE, M. KLATT, P. TWIGG and B. DERBY, *Silicates Industriels* **63** (1998) 129.
6. H. Z. WANG, L. GAO and J. K. GUO, *J. Inorganic Mater.* **14** (1999) 679.
7. *Idem.*, *J. Adv. Mater.* **33** (2000) 60.
8. S. J. AHMADI, Y. D. HUANG and W. LI, *J. Mater. Sci.* **39** (2004) 1919.
9. Y. KOJIMA, A. USUKI, M. KAWASUMI, A. OKADA, Y. FUKUSHIMA, T. KURAUCHI and O. KAMIGAITO, *J. Mater. Res.* **8** (1993) 1185.
10. F. L. GONG, C. G. ZHAO, M. FENG, H. L. QIN and M. S. YANG, *J. Mater. Sci.* **39** (2004) 293.
11. C. H. CHO, M. S. CHO, J. H. SUNG, H. J. CHOI and M. S. JHON, *ibid.* **39** (2004) 3151.
12. J. H. WEI, J. SHI, J. G. GUAN and R. Z. YUAN, *ibid.* **39** (2004) 3457.
13. Y. TIAN, H. YU, S. WU, G. JI and J. SHEN, *ibid.* **39** (2004) 4301.
14. P. NI, J. LI, J. SUO and S. LI, *ibid.* **39** (2004) 4671.
15. D. A. BRUNE and J. BICERANO, *Polymer* **43** (2002) 369.
16. T. D. FORNES and D. R. PAUL, *ibid.* **44** (2003) 4993.
17. R. C. CAMMARATA, *Prog. Surf. Sci.* **46** (1994) 1.
18. J. R. RICE and T. J. CHANG, *J. Amer. Ceram. Soc.* **64** (1981) 46.
19. R. E. MILLER and V. B. SHENOY, *Nanotechnology* **11** (2000) 139.
20. Y. LI, J. YU and Z. X. GUO, *Polym. Int.* **52** (2003) 981.
21. J. J. LUO and I. M. DANIEL, *Compos. Sci. Technol.* **63** (2003) 1607.
22. T. C. LIM, *J. Math. Chem.* **33** (2003) 29.
23. *Idem.*, *ibid.* **34** (2003) 151.
24. *Idem.*, *J. Mater. Sci. Lett.* **22** (2003) 1783.
25. C. F. FAN and S. L. HSU, *Macromolecules* **25** (1992) 266.
26. T. C. LIM, *J. Mater. Sci.* **39** (2004) 4965.
27. *Idem.*, *J. Thermoplast. Compos. Mater.* **16** (2003) 385.
28. *Idem.*, *Adv. Compos. Lett.* **10** (2001) 53.
29. *Idem.*, *Mater. Lett.* **54** (2002) 152.
30. *Idem.*, *J. Reinf. Plast. Compos.* **22** (2003) 301.
31. *Idem.*, *ibid.* **23** (2004) 549.
32. M. GRUJICIC, G. CAO and W. N. ROY, *J. Mater. Sci.* **39** (2004) 4441.
33. K. Q. XIAO and L. C. ZHANG, *ibid.* **39** (2004) 4481.
34. W. ZHANG and M. J. YANG, *ibid.* **39** (2004) 4921.

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