AN EFFECTIVE FLAW MODEL ON ANALYZING NANOFILLER AGGLOMERATION IN NANOCOMPOSITE MATERIALS

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Introduction

Nanocomposite materials have extensive applications in the fields of science, engineering and medicine. In general, mechanical properties of nanocomposites have been found to increase with increasing volume fractions of nanofillers. However, many experimental investigations on nanocomposite materials have indicated a significant decrease in mechanical properties (such as bending strength, fracture toughness etc.) after a critical nanofiller volume fraction. This phenomenon has been widely attributed to the agglomeration of nanofillers [1-5], and has been illustrated by using imaging techniques such as Transmission Electron Microscopy (TEM) [4]. In recent years, reducing agglomeration has be achieved using ultrasonic irradiation, shear mixing, or seeded polymerization, but it is almost impossible to entirely eliminate this effect. For example, large agglomerates can be filtered; but very small agglomerates of two to three nanoparticles might still exist. To ensure reliability in strengths of nanocomposite materials at high volume fractions, a thorough understanding of the nanofiller agglomeration is essential. Although many researchers identify the phenomenon of agglomeration, no attempt has thus far been made to model this problem from a failure mechanics point of view. It becomes crucial to connect nanofiller agglomeration with material failure for further development of nanocomposites with high nanofiller volume fractions. Therefore, the current paper provides a simple effective flaw model to explain the global bending strength reduction due to local nanoparticle agglomeration.

Effective Flaw Modeling

This paper deals with a nanoparticle-reinforced composite material system reported by Soh et al [6]. We consider a square representative volume element (RVE) with a side length of L *2r, where r is the radius of each nanoparticle and L is the number of nanoparticles at the RVE edge. For the sake of simplicity, we assume that the square RVE has N*N agglomerated nanoparticles in the form of an ideal square shape (with a side length N*2r). Additionally, we assume that there are M non-agglomerated nanoparticles within this RVE. Since the initial flaw or failure always stems from the largest agglomerate, our special RVE is focused on the largest agglomerate and other regular nanoparticles without agglomeration. While the presence of complicated agglomerate shapes is acknowledged, this investigation presents the simplest model to understand the agglomeration effect on the mechanical property reduction.

The nanoparticles inside the agglomerate are weakly bonded to each other by van der Waals forces, whereas the nanoparticles on the boundary of the agglomerate are strongly bonded with the matrix. Therefore, we make an assumption that there is one effective flaw inside the agglomerate**,** with a flaw length of $2a_{eff}$ expressed as N*2r-2r. Even in the presence of other effective flaws, this effective flaw is much longer than other flaws, and hence it will lead to the ultimate failure of nanocomposite materials. Now, the volume fraction V_f of the nanofillers inside the square RVE (with total area $4L^2*r^2$) is determined by the total area of agglomerated nanoparticles (number N*N), and the total area of non-agglomerated nanoparticles (number M): $V_f = V_f^A + V_f^{NA} = \frac{N^2\pi r^2}{4L^2r^2} + \frac{M\pi r^2}{4L^2r^2}$

However, final fracture is controlled by the longest flaw inside the largest agglomerate. In this RVE, the non-agglomerated nanoparticles (M) tend to be much lesser than the agglomerated nanoparticles (N*N). Therefore, the nanoparticle volume fraction inside this RVE can be approximated as

$$V_f = V_f^A + V_f^{NA} \approx \frac{N^2\pi r^2}{4L^2r^2} \Rightarrow N \approx 2L\sqrt{V_f/\pi}$$

As expected, the agglomerate size increases with the nanofiller volume fraction. But it should be noted that this relation is an approximation rather than an accurate prediction. When the RVE is subjected to a critical tensile stress, the effective flaw will propagate as a mode-I crack and cause the final failure of the nanocomposite specimen. The detailed process of interaction among mode-I cracks, mixed-mode interface cracks and final failure has been reported. For bending experiments, the final failure occurs when the normal stress inside the bending specimen exceeds a critical level for leading to the effective flaw propagation. Therefore, the bending strength σ_B is related to the mode-I fracture toughness of the agglomerated nanoparticle C_k K_{IC} as [7]: $C_k K_{IC} = \sigma_B \sqrt{\pi a_{eff}} f(a_{eff}/W, E, ..)$ where K_{IC} is the mode-I fracture toughness of the matrix, C_k is a reduction factor for the fracture toughness of the agglomerated nanoparticles, and f is a function of the flaw length a, width of the specimen W, effective elastic modulus E and other parameters. The reduction factor C_k is introduced due to the inability in direct measurement of the mode-I fracture toughness of agglomerated nanoparticles. Finally, we arrive at this formula for the bending strength,

$$\sigma_B = \frac{C_k K_{IC}}{f\sqrt{\pi r\left(2L\sqrt{\frac{V_f}{\pi}}-1\right)}}$$

The variation of bending strengths with the nanoparticle volume fraction, obtained by using different values of C_k is presented in Figure 1.

Results and discussion

The above relationship is valid only for these bending strengths after the critical nanofiller volume fraction, which is obtained from experimental data shown in Figure 1 [6]. It should be noted that this paper only attempts to model the decrease in bending strength beyond the critical volume fraction. The initial increase in bending strength can be explained using a rule of mixtures type relation. Agglomeration of nanofillers does not affect this initial increase in bending strength. The bending strength is shown to decrease with the nanoparticle volume fraction as predicted by our simple effective flaw model. Also, a higher value of C_k, which represents a higher fracture toughness of nanocomposite materials with agglomeration, leads to higher bending strengths after the critical nanofiller volume fraction. Therefore, this simple effective flaw model illustrates the correlation between the bending strengths with nanoparticle agglomeration. There is a lack of experimental data for the fracture toughness in nanocomposites with nanofiller agglomerates. This absence of data has restricted us to choosing a match-up of bending strength and fracture toughness values.

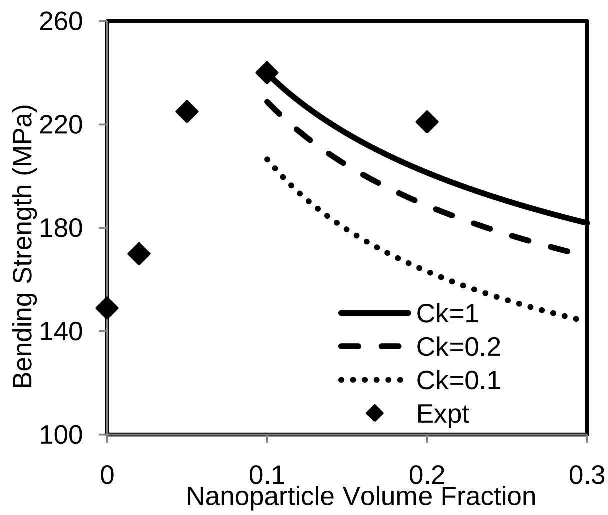

Figure 1. Variation of the nanocomposite bending strength with the nanoparticle volume fraction. Data from Soh et al [6].

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