

Research Article

A Simple Effective Flaw Model on Analyzing the Nanofiller Agglomeration Effect of Nanocomposite Materials

Arun Krishnan¹ and L. Roy Xu²

¹Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, TN 37235, USA

²Department of Mechanical Engineering, University of Texas, El Paso, TX 79968, USA

Correspondence should be addressed to L. Roy Xu, luoyu.r.xu@gmail.com

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A special mechanics/material phenomenon involving nanocomposites is the agglomeration of nanofillers at high volume fractions of nanofillers. Numerous experimental investigations on nanocomposites have indicated a significant decrease in mechanical properties, due to the agglomeration of nanofillers. This paper describes a simple effective flaw model to correlate the local mechanical behavior of agglomerated nanoparticles with the change in global strengths of nanocomposites. The estimated bending strength reduction from our model is shown to be similar to experimental results reported by previous researchers. These results can be used as a guide for future nanocomposite design and development. Future nanomaterial manufacturing should be focused on eliminating the largest agglomerates, rather than limiting the nanofiller volume fraction. Meanwhile, by reducing the nanofiller agglomerate size, we expect that a high critical nanofiller volume fraction could be obtained to delay the mechanical property reduction.

1. Introduction

Nanocomposite materials have extensive applications in the fields of science, engineering, and medicine [1–8]. 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 and fracture toughness) after a critical nanofiller volume fraction, as illustrated in Figure 1. This phenomenon has been widely attributed to the agglomeration of nanofillers [9–18], and has been illustrated by using imaging techniques such as transmission electron microscopy (TEM). As shown in Figure 1, agglomeration of carbon nanofibers was severe and had a stark effect on the mechanical properties of nanocomposite materials in addition to their low interfacial load transfer [18].

Agglomeration in nanocomposites is the sticking together of nanofillers inside the matrix during the mixing process [19–22], and it is well known that this phenomenon is

certainly detrimental to the strength and fracture toughness of nanocomposites. In recent years, reducing agglomeration has been achieved using ultrasonic irradiation [23], shear mixing [24], or seeded polymerization [25], 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. Unlike stiffness, which is based on volumetric averaging, strength and fracture toughness are very sensitive to minor local defects like nanoparticle agglomeration.

To ensure reliability in strengths of nanocomposite materials at higher volume fractions, a thorough understanding of the nanofiller agglomeration is essential. However, previous work has mainly focused on changes in nanocomposite stiffness due to agglomeration [16, 26]. Berhan and Sastry have developed a model for a similar problem albeit with different objectives [27] (percolation in nanocomposites). 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

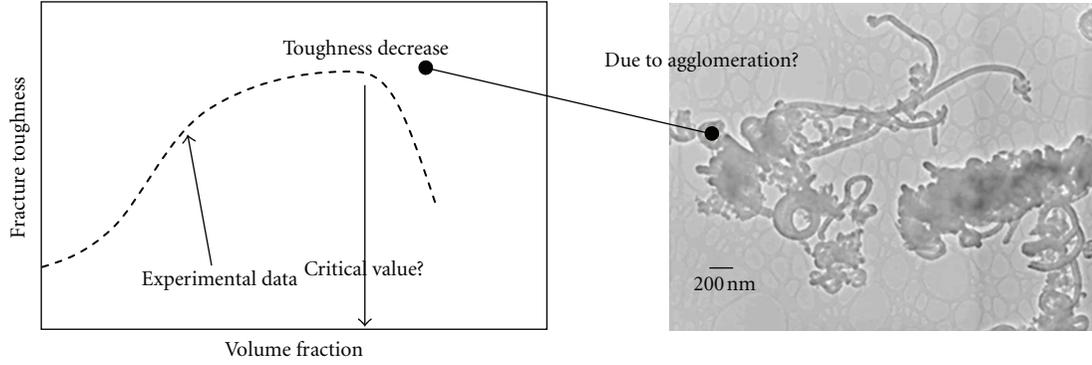


FIGURE 1: Nanocomposite fracture toughness as a function of nanofiller volume fractions. After a critical volume fraction, fracture toughness will decrease, probably due to agglomeration as seen in a TEM image [18].

failure for further development of nanocomposites with high (close to critical) 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. We attempt to model the reduction in global bending strength of the nanocomposite with increasing the nanofiller volume fraction.

2. Effective Flaw Modeling

This paper deals with a nanoparticle-reinforced composite material system reported by Soh et al. [28]. 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 $N * 2r$) as shown in Figure 2. Additionally, we assume that there are M nonagglomerated nanoparticles within this RVE, and that no more agglomerates exist inside this RVE. Since the initial flaw or failure always stems from the largest agglomerate, our special RVE is focused on the largest agglomerate, although it is acknowledged that other smaller agglomerates exist outside this RVE. This modeling process is similar to a TEM image recording some severe agglomeration as seen in Figure 1, that is, although other small agglomerates were recorded but they were less important to the strength and fracture toughness of nanocomposite materials so they were not reported. Meanwhile, “large or small” agglomerate is always relative to the single nanofiller; but we do not know the size of the smallest agglomerate which cannot be filtered as mentioned. Therefore, the large agglomerate refers to the one agglomerate whose size is larger than other agglomerates in the same specimen for mechanics modeling purpose and not an absolute size. 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

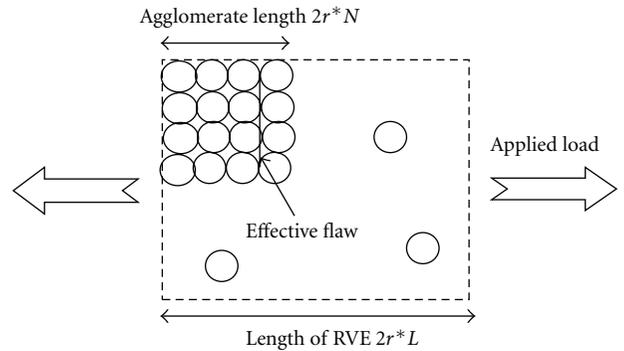


FIGURE 2: Schematic diagram depicting an effective flaw inside a nanoparticle agglomerate within a square RVE.

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 $2a_{\text{eff}}$ expressed as

$$2a_{\text{eff}} = N \cdot 2r - 2r. \quad (1)$$

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 nonagglomerated nanoparticles (number M):

$$V_f = V_f^A + V_f^{NA} = \frac{N^2 \pi r^2}{4L^2 r^2} + \frac{M \pi r^2}{4L^2 r^2}. \quad (2)$$

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

$$V_f = V_f^A + V_f^{NA} \approx \frac{N^2 \pi r^2}{4L^2 r^2} \implies N \approx 2L \sqrt{\frac{V_f}{\pi}}. \quad (3)$$

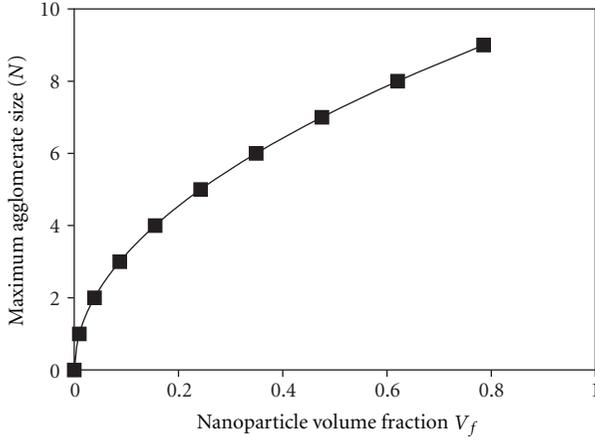


FIGURE 3: Estimated variation of the maximum agglomerate size (in terms of the agglomerated nanoparticle number N) with the nanoparticle volume fraction (V_f).

This relationship between the side length of the square agglomerate (N) and the volume fraction of nanoparticles (V_f) is expressed for an RVE with a size of 9×9 ($L = 9$) nanoparticles as shown in Figure 3. As expected, the agglomerate number 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 in references [29, 30]. 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 [31]:

$$C_k K_{IC} = \sigma_B \sqrt{\pi a_{\text{eff}}} f\left(\frac{a_{\text{eff}}}{W}, E, \dots\right), \quad (4)$$

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_{eff} , 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. The bending strength σ_B is related to the effective flaw size by

$$\sigma_B = \frac{C_k K_{IC}}{f \sqrt{\pi a_{\text{eff}}}}. \quad (5)$$

To illustrate our model, we choose a C_k value of 1 to match the experimental data point with the critical volume fraction.

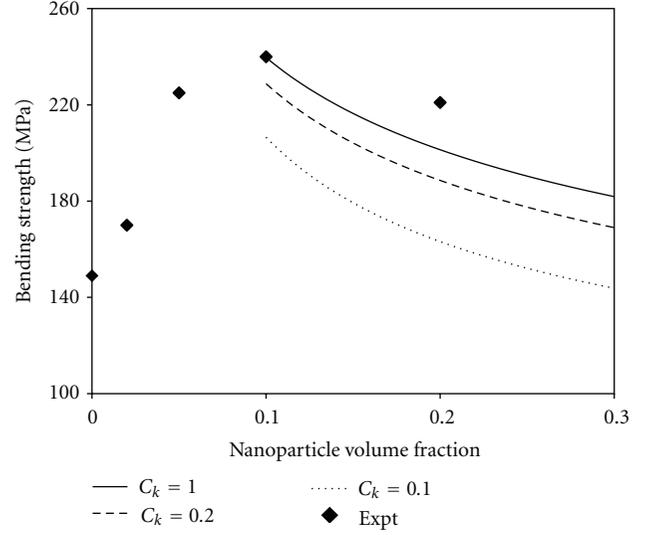


FIGURE 4: Variation of the nanocomposite bending strength with the nanoparticle volume fraction. Data from Soh et al. [28].

Substituting (3) into (5), we arrive at this formula for the bending strength:

$$\sigma_B = \frac{C_k K_{IC}}{f \sqrt{\pi r (2L \sqrt{V_f/\pi} - 1)}}. \quad (6)$$

The variation of bending strengths with the nanoparticle volume fraction, obtained by using different values of C_k , is presented in Figure 4.

3. Results and Discussion

The relationship in (6) is valid only for these bending strengths after the critical nanofiller volume fraction, which is obtained from experimental data shown in Figure 4 [28]. 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 matchup of bending strength and fracture toughness values.

The above results can be used as a guide for future nanocomposite designs and development. For example, in case of two nanocomposite systems with the same volume fraction of agglomerated particles, the nanocomposite with one large

agglomerate of 100 nanoparticles will fail first in bending before a nanocomposite with 50 small agglomerates of two nanoparticles inside each agglomerate. Therefore, future material processing should be focused on eliminating the largest agglomerates, rather than limiting the nanofiller volume fraction. Meanwhile, small nanofiller agglomerates will lead to high critical nanofiller volume fractions to show mechanical property reduction. In summary, this is an original attempt in understanding the relationship between the nanoparticle agglomeration at a local scale and the corresponding decrease in strengths at a global scale. Sophisticated models considering agglomerate geometries, nanofiller shapes should be developed after this issue receives greater attention.

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