Two-step multiscale homogenization of polymer nanocomposites for large size RVEs embodying many nanoparticles

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ABSTRACT

In this study, we investigated the effect of nanoparticulate agglomeration on the mechanical behavior of nanocomposites using multiscale analysis. Through parametric studies, we confirmed factors which mainly influence on the elastic modulus of nanocomposites. Comprehensively compiling the mentioned factors, we defined a new index 'clustering density' to represents the degree of agglomeration. Two step homogenization considering the newly defined clustering density contributes to reduce computation time and memory needed for analysis. A new computational approach for analysis of polymer nanocomposites is compared to direct numerical simulations (DNS) to verify accuracy and effectiveness of proposed model.

1. INTRODUCTION

The reinforcing effect of nanoparticles is one of the unique characteristics of polymer nanocomposites and has received much attention over the past years for the design and applications of multifunctional nanostructured materials. However, despite advances in manufacturing technology, non-uniformly distributed nanoparticles often constitute the agglomeration owing to non-bond interaction. This phenomenon limit the obtaining of improved properties by nanoparticles. Many researchers have carried out investigations for the effect of nanoparticulate agglomeration on mechanical properties of polymer nanocomposites. (Pandey 2013) demonstrated that various states of agglomerations can be formed by the interaction between each nanoparticles and influences on the mechanical and thermal properties of nanocomposites. Molecular dynamics (MD) simulations results conducted by Shin (2015) showed that interphase percolation influences on the weak formation of interphase near reinforced fillers, thus, the elastic properties of interphase decrease. In addition, (Shin 2016) propose a novel

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inverse statistical multiscale bridging method to provide guidelines in determining the elastic properties of nanocomposites containing inherent uncertainty. Multiscale research results that as a size of cluster increase, the homogenized elastic properties of nanocomposites monotonically decrease can be found in Shin (2017). Therefore, it is essential to understand the relation between the overall mechanical properties of nanocomposites and nanostructures considering the various states of agglomeration. In order to conduct computational approach for researching this issue, researchers used to set up representative volume element (RVE) reflecting entire behavior of nanostructured materials. Because it takes a lot of computation time and memory to analyze large RVE considering the nanoparticle's clustering, it is valuable to propose efficient multiscale homogenization to improve computational efficiency.

In this study, using a multiscale bridging method in which MD simulations and continuum mechanics are considered, we investigated the effect of nanoparticulate agglomeration on the mechanical properties of nanocomposites. From parametric studies, we confirmed significant factors that affect the elastic modulus of nanocomposites and defined a new index 'clustering density' to represent the degree of agglomeration. To quantitatively evaluate the homogenized Young's modulus of nanocomposites, function formula for the newly defined index is proposed. Then, a new computational approach for analysis of polymer nanocomposites is developed through two-step homogenization process and compared by direct numerical simulations (DNS) for large size RVEs to verify accuracy and effectiveness of proposed model.

2. Model & Methodology

2.1 Brief review of multiscale bridging methodology

Interfacial effect caused by interaction between polymer matrix and nanoparticles significantly affects the mechanical properties of nanocomposites. In order to quantify the interfacial effect, it is essential to determine the interphase characteristics such as thickness and elastic modulus. In this study, a multiscale bridging method proposed by Shin (2015) is applied to determine the elastic modulus and thickness of interphase. Commercial software MATERIALS STUDIO 5.5 and MSC Nastran$^{\circledR}$ were used to construct MD models and homogenized finite element models. At this time, finite element models, which are equivalent with the MD models, consisted of 3 phase (matrix-interphase-nanoparticles). From strain energy-based inverse algorithm method, the Young's modulus and thickness of interphase can be obtained. Additionally, to investigate the effect of interphase percolation on interfacial effect, six models were set up with different distances between nanoparticles. An overlap density which represent the degree of interphase percolation is shown in Eq. (1).

$$\delta_{\text{overlap}} = \frac{V_{\text{overlap}}^{\text{int}}}{V_{\text{total}}^{\text{int}}} \leq 1 \qquad (1)$$

The relation between the elastic modulus of interphase and interphase overlapping is shown in Fig. 1. This figure shows that as the degree of interphase percolation increases, the elastic modulus of interphase diminish. This results imply that

nanoparticulate agglomeration imposes many limitations on obtaining of reinforcing effect which results from adding nanoparticles.
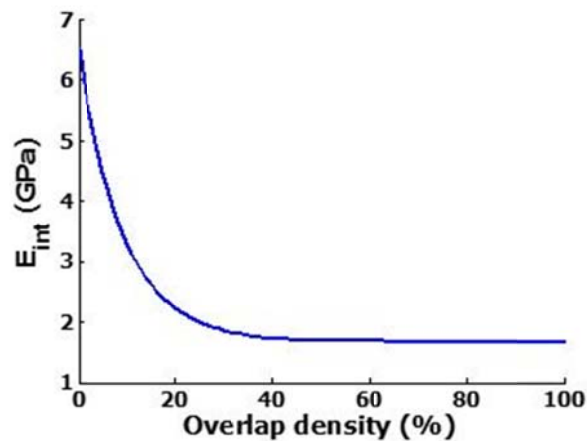

Fig. 1 Elastic modulus of interphase with overlap density of interphase

2.2 Multiscale homogenization

To study the effect of nanoparticle's clustering phenomena on the mechanical properties of nanocomposites, we applied the interphase characteristics which are defined by the multiscale analysis mentioned at 2.1 to continuum models. The continuum model is a finite element model composed of 3 phase (matrix-interphase-nanoparticle). The radius of nanoparticles and thickness of interphase is set to 9Å, 8.1Å respectively. Table. 1 show the type and properties of materials used as matrix and nanoparticle. According to Fig. 1, the Young's modulus of interphase is determined based the overlap density which represent the degree of interphase overlapping. From In-house code guaranteeing randomness, we can obtain the geometric information of non-uniformly located nanoparticles in unit microstructure. The information is transferred to a commercial program Digimat for modeling, and then a commercial software ABAQUS is interlock with it to conduct finite element analysis. Periodic boundary condition in which this unit cell is repeatedly arranged and displacement load condition are given to each model. Using homogenization technique, the stress field on the macroscopic structures is calculated through the stress distribution on the microscopic structures. According to mentioned simulation procedure, parametric studies about various agglomeration situations are carried out to define a new index 'clustering density' representing the degree of nanoparticulate agglomeration. Then, we derive an exponential function for the clustering density to predict the homogenized elastic modulus of nanocomposites.

A schema of two-step multiscale homogenization is shown in Fig. 2. After domain decomposition of a large size RVE, 1st homogenization process is carried out to obtain the homogenized elastic modulus of the local subcell domain using the clustering density of each domain, as shown in Fig. 2. In our exemplary study, 1st homogenization

is proceeded for 8 or 27 subcells. In sequence, global homogenization properties of nanocomposites are obtained by additional 2nd homogenization analysis. Through comparison with DNS model, accuracy and effectiveness of the new computational approach for analysis of polymer nanocomposites are verified.

Table. 1 Mechanical properties of SiC and Polypropylene

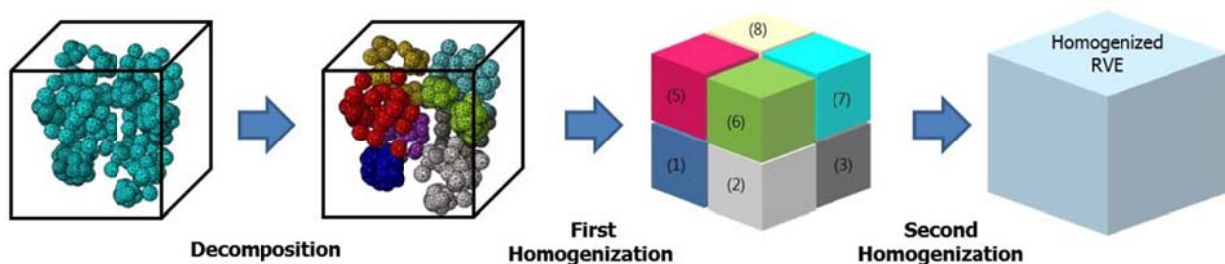| Mechanical Properties	SiC (nanoparticle)	Polypropylene (matrix)
Young's modulus (GPa)	451.6	1.68
Poisson's ratio	0.237	0.424

Fig. 2 Schema of two-step computational homogenization

3. Result & Discussion

3.1 Parametric studies

In order to confirm factors which mainly influence on the mechanical properties of polymer nanocomposites, we conducted parametric studies about the number of clusters, the combination of clusters and the presence of free nanoparticles. Results of the parametric studies are shown in Fig. 3. The influence of cluster's combination on homogenization response are represented in Fig. 3. (a) and (b). When the same number of nanoparticles form the same number of clusters, similar elastic modulus were obtained regardless of the presence of free nanoparticles. In Fig. 3. (c), we can understand that the improvement of properties is suppressed as the agglomeration tendency of the same number of nanoparticles increases. Because, as a size of cluster increase, overlap density of interphase increase and the elastic modulus of interphase decrease. Fig. 4. (d) shows that as the number of free nanoparticles increases, the mechanical properties of the nanocomposites increase. From these results that the number of clusters and free particles are important factors, we derived that the volume fraction of free nanoparticle's interphase and the volume fraction of agglomerated

nanoparticle's interphase play a significant role in determining the mechanical properties of nanocomposites. Therefore, the new index 'clustering density' which comprehensively compiles the above information will be discussed in section 3.2.
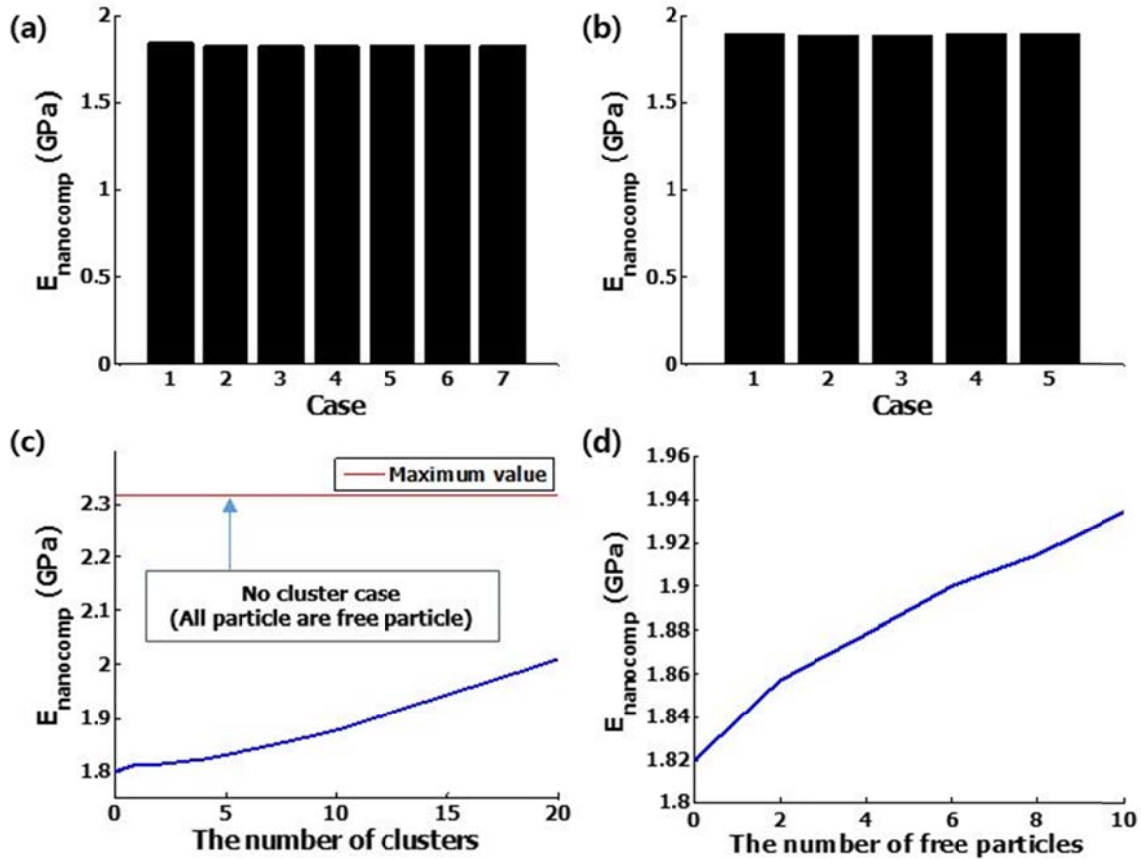

Fig. 3 Elastic modulus of nanocomposites (a) Influence of cluster's combination with non-free nanoparticle, (b) Influence of cluster's combination with 5 free nanoparticles, (c) Influence of the number of clusters, (d) Influence of the number of free nanoparticles.

3.2 Clustering density

We defined the new index clustering density to effectively predict the mechanical properties of nanocomposites in which occur nanoparticles clustering occurs. The clustering density (g) to represent the degree of nanoparticulate agglomeration is defined as below Eq. (2).

$$g = A\left(1 - \frac{\sum f_c + f_{fp}}{f_{max}}\right) \qquad (2)$$

Here, f_c and f_{fp} respectively mean the volume fraction of agglomerated nanoparticle's interphase and the volume fraction of free nanoparticle's interphase. f_{max} is the maximum volume fraction of interphase and A is normalization constants to make the range of clustering density from 0 to 1. When all nanoparticles are free state, the value

of the clustering density would be 0. As the agglomeration phenomenon occurs, the value become closer to 1, and finally, when all nanoparticles in unit cell form one cluster, the value would be 1.

3.3 Elastic modulus of nanocomposites

In order to judge that the mechanical properties of nanocomposites can be predicted using the newly defined clustering density, we made 200 different models with 3% volume fraction of nanoparticles. In this case, the number of nanoparticles contained in the unit cell is from 5 to 50. After homogenization process, the Young's modulus of nanocomposites corresponding each model was obtained. Since we already knew the clustering density corresponding each model before analysis, we could understand the correlation between the elastic properties of nanocomposites and the clustering density. The correlation can be found in Fig. 4.
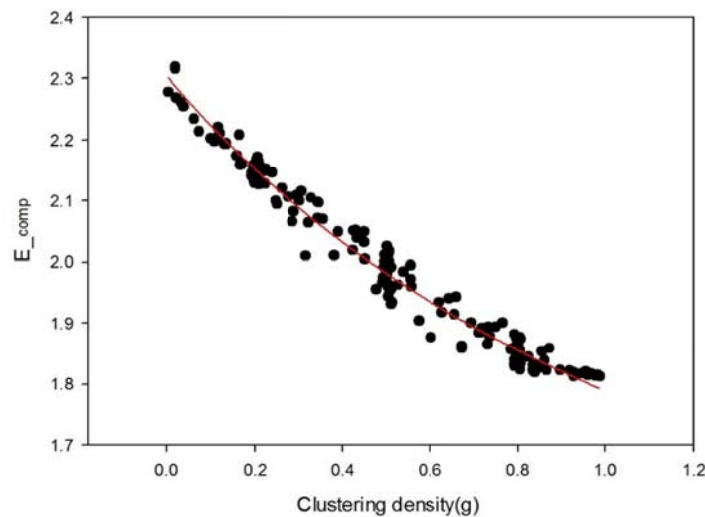

Fig. 4 Young's modulus of nanocomposites with 3% volume fraction

$$E_{comp} = a \times e^{(-b \times g)} + c \text{ [GPa]} \tag{4}$$

Based on these results, the Young's modulus of nanocomposites can be expressed by the Eq. (4) with respect to the clustering density. In this function, g means the clustering density. From comparison with simulation results, we could calculate the mean error and the maximum error which is respectively 0.88 %, 3.45 %. We have also expanded on other volume fraction of nanoparticle because we confirmed that the mechanical properties of nanocomposites can be predicted with great accuracy using clustering

density. Fig. 5. Represents the exponential decay function of the homogenized Young's modulus of nanocomposites including less than 50 nanoparticles for different volume fraction of nanoparticle.
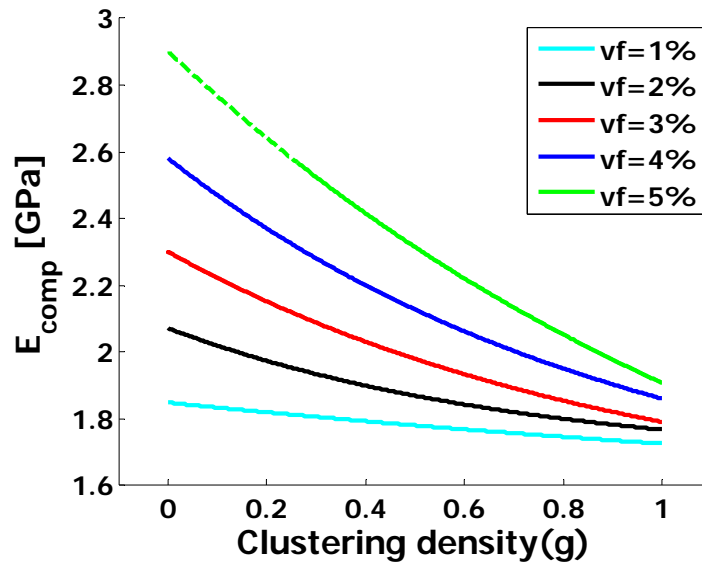

Fig. 5 Young's modulus of nanocomposites with different volume fraction

As can be seen in Fig. 5, when the volume fraction of nanoparticle increase, the nanoparticulate agglomeration phenomenon has more influence on the mechanical behavior of nanocomposites.

3.4 Verification of clustering density

We verified that the newly defined clustering density has sufficient engineering effectiveness. As we mentioned before in the introduction section, it takes a lot of computation time and memory to analyze large size RVEs embodying many non-uniformly located nanoparticles. Therefore, it is very inefficient to homogenize the large size RVEs through the DNS method. (Moore 2014) proposed an efficient multiscale framework for analysis of filled elastomers with complex microstructures. He increased the computational efficiency of the RVE analysis through homogenizing the morphology of sub-RVE scale subcells using micromechanics. Then, the resulting constitutive response acted as inputs to finite element analysis of the RVE. Using a similar procedure, we proposed a new computational approach which contains two-step multiscale homogenization to effectively analyze large size RVEs. Here, the difference is that Moore (2014) use the micromechanics models to obtain the constitutive response of subcell domain, smaller than a RVE, while the new clustering density which represent the state of agglomeration in subcell domain is used. Additionally, the proposed model can compensate for a drawback of micromechanics that does not reflect the various interphase properties in the subcell region. Therefore, this framework

can more accurately analyze large RVEs composed of subcells which are in different agglomeration and volume fraction state. Using the clustering density of each subcell domain obtained by only geometric information of nanoparticles, we conduct the 1st homogenization through Eq. (4) corresponding to volume fraction of each local region. In this process, the complexly nanostructured RVE is equivalently substituted with a simple structure, and finally, the effective properties of the entire structure can be extracted more quickly through additional homogenization. Table. 2 shows the results of the DNS model and proposed model for 3 examples. The Example 1 and 2 is composed of 8 subcell domain, while the third example is composed of 27 subcell domain. Each region in the examples is of various clustering density and volume fraction. The proposed computational approach shows a significant improvement in computation time over DNS which homogenizes the entire structure at once, and allows to accurately predict the mechanical properties of nanocomposites corresponding to the large RVE.

Table. 2 Comparison results between DNS model and proposed model

Example	Total number of Nanoparticles in RVE	Comparison factor	DNS	Proposed
1	240	The number of elements	343150	1000
		Computation time (sec)	943.2	2.74
		E_{comp} (GPa)	2.162	2.169
2	400	The number of elements	577562	1000
		Computation time (sec)	1563	2.32
		E_{comp} (GPa)	1.966	1.965
3	945	The number of elements	1338887	3375
		Computation time (sec)	9510	25.62
		E_{comp} (GPa)	2.1081	2.1143

4. CONCLUSIONS

In this study, we investigated the effect of nanoparticulate agglomeration on mechanical properties of nanocomposites using multiscale analysis. It was confirmed that the mechanical behavior of nanocomposites are mainly dependent on volume fraction of free nanoparticles and the number of clusters. Next, we defined the clustering density as a means to predict the elastic modulus of nanocomposistes. Two-step multiscale homogenization using the newly defined clustering density improves computational effectiveness. Through the application of the proposed method, it is expected that the research can be extended to the viscoelastic or plastic region in the future.

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