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Multiscale Modeling Approach for Prediction the Elastic Modulus of Percolated Cellulose Nanocrystal (CNC) Network

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ABSTRACT

In this study the effective elastic modulus of cellulose nanocrystal (CNC) network is evaluated using multiscale method and micromechanical analysis. For this purpose, the elastic modulus of CNC-water phases are randomly assigned to a two-dimensional (2D) checkerboard structure and the elastic response is evaluated. In addition, the effect of having a different number of phases (CNC, water and interface) is evaluated by assigning a discreet and continuous distribution of elastic modulus to checkerboard structure. When the number of phases increases dramatically, the distribution of phases is continuous and is defined with Weibull distribution. The results show that for two-phase materials (CNC and water) when the microstructure has organized pattern the rule of the mixture and numerical model provide the same effective modulus, however when the microstructure is completely random, the self-consistent micromechanical model should be used. Also, this study suggests 50% volume fraction as the percolation threshold for the CNC network with 10 GPa effective elastic modulus. The results from percolated multiphase network reveal that for microstructures with 4 phases and above, the percolated network converge to 35 GPa.

KEYWORDS: *Cellulose nanocrystal, Elastic modulus, FEM, Percolation, Micromechanics*

INTRODUCTION

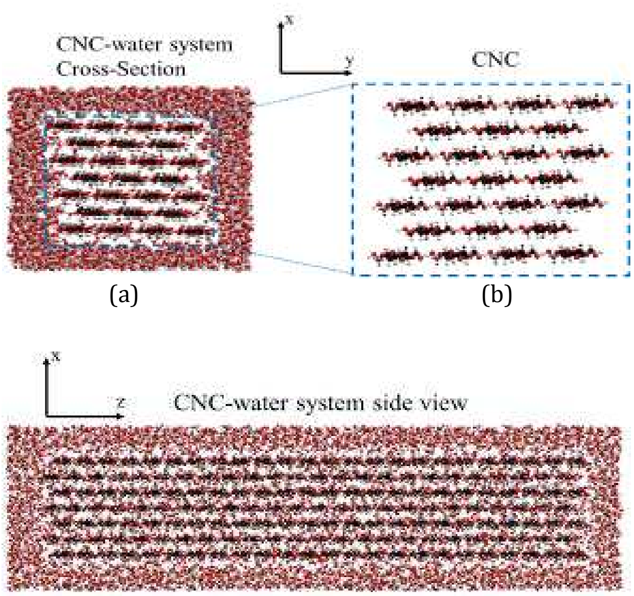
Cellulose is the most abundant polymer on the planet [1,2]. In the past decade new particles of cellulose called crystalline nanocellulose (CNC) with outstanding mechanical properties received tremendous attention for packaging and reinforcement agent [1–3]. Mechanical properties of CNC solutions depends on many factors such as the dispersion and orientation of CNCs in water which can be solved based on percolation theories. When the material reaches the percolation threshold (the minimum volume fraction of the particles that percolation occurs), the microstructure significantly changes and as a result of the macroscopic properties significantly change [4]. Percolated CNC network could be assumed to be a heterogeneous material due to different mechanical properties caused by their density and orientation in the network. Mechanical properties of heterogeneous materials based on their distribution type can be categorized into two general group, (1) materials with lognormal distribution of their mechanical properties found at some length scale of bone, concrete and many other materials and (2) materials with multi-modal distribution found in collagen, rocks and polycrystalline materials [5,6]. Having a different type of distribution for their mechanical properties makes the prediction of their overall mechanical properties challenging. One of the models that have been employed to resemble a simple microstructure for heterogeneous materials is called a checkerboard material [5,7]. This type of microstructure is simply formed by assigning different mechanical properties to each partition of a 2D partitioned square. The benefit of using such structure is that, due to having many partitions in the geometry, by assigning different mechanical properties one can form multi-phase materials [5]. For example, by randomly assigning two elastic modulus one can form randomly distributed two-phased materials. Majority of the research on the checkerboard structure are related to effective conductivity [7–9] and very few on elastic modulus [5]. Dimas et al. (2015), studied how the effective stiffness of 2D checkerboard affected by the size of tiles and modulus contrast between phases and obtained analytical approximations based on the parameters of their study on percolation of two-phases materials [5]. In addition to numerical models, micromechanical models can provide the effective mechanical properties of a complex system such as two-phase randomly distributed or multi-phased materials. There many micromechanical models developed for specific composite materials and may be suitable for a certain case and volume fraction or type of distribution, while they may fail for other cases [9]. In this work, we use numerical checkboard model and two micrometrical model, (1) a simple micromechanical model obtained by a mixture of Voigt and Ruess model and (2) self-consistent method, to characterize the elastic modulus of a percolated CNC network based on randomly two-phase and multi-phase materials.

MATERIALS and METHODS

We use a multiscale framework to obtain the elastic modulus of a percolated CNC network. First, molecular dynamics (MD) simulation is used to find the elastic modulus of a CNC immersed in water. MD simulations as of the major characterizing tools for measuring mechanical, thermal and interfacial properties of materials have been used by many authors before for CNC and other materials [10–12]. Then, we use the finite element method (FEM) and checkboard structure to model a percolated system of CNC and water. Using multiscale framework helps to reduce the computational cost and bridge the scale from nano to macro scale as has been done previously by many authors. Upscaling the mechanical and interfacial properties from Nano to macroscale has been done by many researchers before for CNC [13] and carbon nanotube [14]. For example, Shishehbor et al. (2018), used a novel atomistic to continuum framework for evaluating the role of bonded and non-bonded interactions on the elastic properties of CNCs and showed covalent bond in the main contributor interaction in both bending and tensile loading [13]. We have to mention that, in addition to the multiscale framework, coarse-grained (CG) molecular dynamics have been used extensively to bridge the scale from nano to macro [15–18]. For CNC, there are few promising CG models that can bridge the scale and perhaps can be used for percolation of CNCs. For example, the new CG model developed recently by Shishehbor and Zavattieri, (2019) seems to be very promising for CNC-water and CNC-composite materials [17,19,20]. However, the interfacial energy for CNC and water needs to optimized for the model before usage.

I. CNC-water elastic modulus

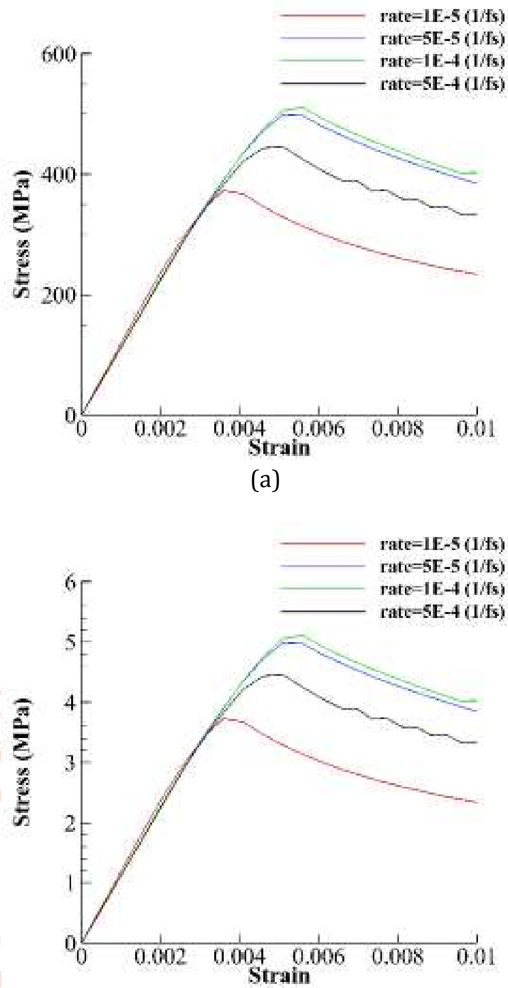
We use MD simulation to find the effective elastic modulus of a CNC in a box of water. A box of water with dimensions of 4.0×4.0×13.5 nm that contains a CNC with dimensions of 2.5×2.5×12 nm in the middle (as shown in Fig. 1) is created using VMD package [21]. The simulation is performed at 300k temperature, 1 atm pressure using NPT ensemble and CHARMM forcefield [22]. All the simulations are performed using LAMMPS package [23].



(a) (b)

(c)

Figure1. Molecular structure of CNC immersed in water.



(a)

(b)

Figure 2. The stress-strain curve at different strain rate for CNC-water. (a) the stress-strain curve in the z (covalent bond direction) and (b) stress-strain curve in the x-direction (van der Waals).

The stress-strain curves obtained for CNC-water is shown in Fig. 2a and Fig.2b in covalent bond (axial) and van der Waals (vdW) direction respectively. The result shows that the elastic modulus is almost independent of the strain rate and equal to 100 GPa and 1GPa for covalent bond and vdW directions respectively. The elastic modulus obtained here is consistent with many MD results obtained previously by other researchers [13,17,24], except that due to immersion in water, the effective elastic modulus is 40-60% lower than 170-200 GPa reported values [17].

II. Finite element and micromechanical models

The microstructure of the problem is a 2D square of length 10, which is meshed with the tile length of 1.0, 0.5 and 0.25 and provides 10x10, 20x20 and 40x40 squares. For the FEM analysis, the nodes on left and bottoms are fixed in the x, y-direction, the displacement is applied on the right nodes, and the nodes on top are free as shown in Figure 3a. The effective elastic modulus of the microstructure from FEM analysis is obtained by dividing the average stresses by average strains calculated in the gauss points of elements.

$$(E_{eff})_{FEM} = \frac{<\sigma_{ave}>}{<\varepsilon_{ave}>} \quad (1)$$

Where $(E_{eff})_{FEM}$ is the effective elastic modulus, σ_{ave} is the average stress and ϵ_{ave} is the average strain. For the micromechanical model, a two-step averaging method is performed. First, the average elastic modulus is obtained in each column, $\overline{E}_1$- $\overline{E}_n$, with Voigt model due to the fact that all the elements (tiles) in the same column have the same strain. Then, the total effective modulus is obtained from Ruess's model for all averaged columns have the same stress.

$$\overline{E}1 = \frac{1}{n}\left[E1 + E2 + \ldots. En\right] \quad (2)$$

$$\left[(Eeff)_{micro}\right]^{-1} = \frac{1}{n}\left[\overline{E}1^{-1} + \overline{E}2^{-1} + \ldots.\overline{E}n^{-1}\right] \quad (3)$$

Where $(E_{eff})_{micro}$ is the effective elastic modulus from the micromechanical model, n is the number of tiles in each column and/or row and $\overline{E}_1$- $\overline{E}_n$ are the effective elastic modulus in each column from simple averaging (Voigt model)? For two-phase materials, the elastic modulus of stiff and soft tiles are $E_1 = 100$ and $E_2 = 1$ (from MD analysis) with equal poison ratio of $\vartheta_1 = \vartheta_2 = 0.3$. Here, first, some microstructures with specific patterns are studied and after verification, the two-phase random microstructure with different volume fraction is evaluated. In order to study the size effect on the effective elastic modulus, random microstructure with different size for tiles (element) is also analyzed.

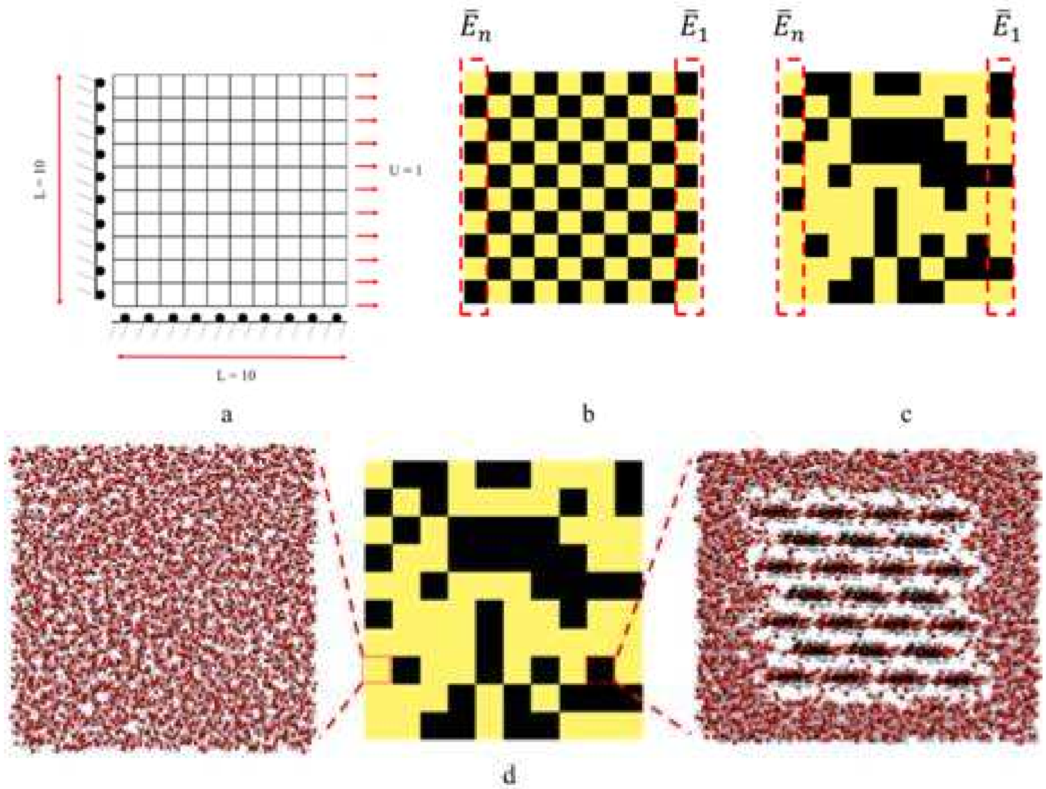


Figure3. The microstructure, FEM and micromechanical model. (a) 10x10 mesh and the FEM setups. The displacement is applied to the right boundary while the nodes on the left and bottom are fixed in x and y direction respectively. (b) Checkerboard microstructure with 50% stiff and 50% soft materials. The average elastic modulus of each column is obtained from the Voigt model and denoted as $\overline{E}_1$- $\overline{E}_n$ (c) Random checkerboard with 50% stiff and 50% soft matrix. The average elastic modulus of each column is obtained from the Voigt model and denoted as $\overline{E}_1$- $\overline{E}_n$.

For multi-phase materials, random distribution of elastic modulus from E_1 to E_2 is assigned to tiles while the number of phases changes from 1 to 10. In addition, a Weibull distribution of elastic modulus with different values for the Weibull slope parameter is studied to evaluate the effect of distribution on the elastic modulus.

RESULTS AND DISCUSSION

III. Random vs organized microstructure

To test the validation of the FEM and micromechanical model, different case studies with different microstructure and volume fraction is tested. Figure 4. shows the different case studies from very simple microstructure to a completely random case where the elastic modulus for black and yellow tile is $E_1 = 100$ and $E_2 = 1$ respectively. The effective modulus from FEM and micromechanical models are shown below each case study in Figure. 4 denoted as FEM and micro respectively. It can be observed that for the cases with certain patterns, the FEM and micromechanical models provide the same results and the slight difference is due to the presence of poison effect in FEM and ignoring that in the micromechanical model. Even for a checkerboard with 50% stiff tile and 50% soft tile, the micromechanical results is very close to FEM with 15% error. However, for a random case study shown in Figure 4.j, the micromechanical model value is 47.5 as opposed to FEM result which is 17.5 and the error is more than 170%.

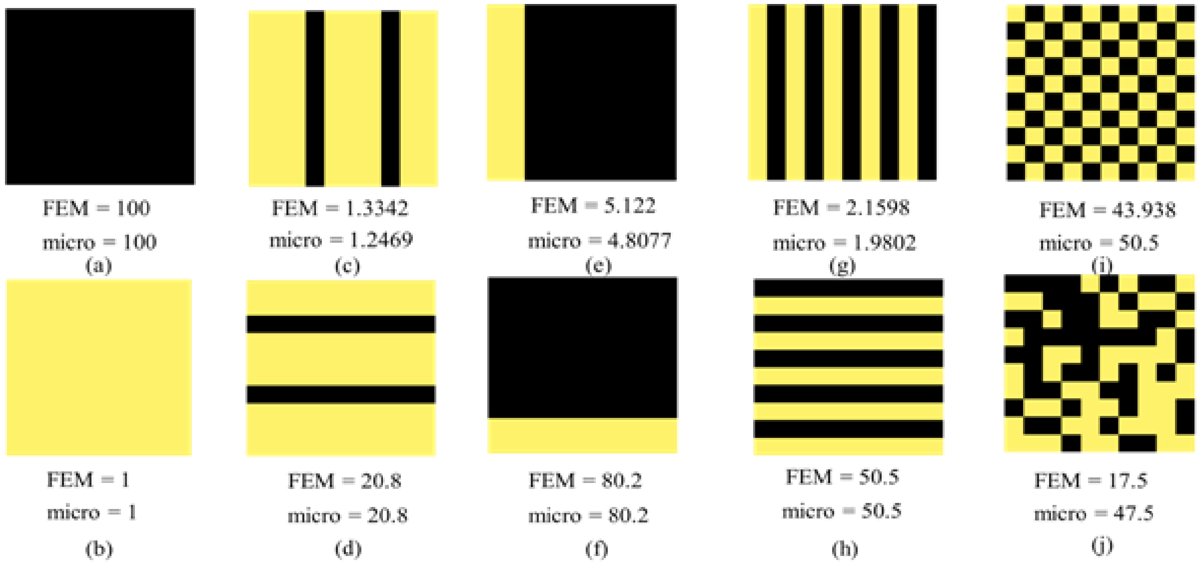


Figure4. Case studies for different microstructure with different volume fraction and patterns. In all cases, the prediction of the micromechanical model is equivalent to FEM results except the random pattern.

IV. Percolated CNC network

To better evaluate the random microstructure, different case studies with different volume fraction and randomness are studied. Figure 5.a displays the variation of effective elastic modulus with volume fraction for 10x10 and 40x40 squares. Each case study was executed 3 times to produce a different random structure. The results indicate that the variation of effective elastic modulus with randomness for smaller microstructure, 10x10, is more than 40x40 microstructure with almost the same average curve. In addition, comparing the micro and FEM results, it can be realized that the simple averaging micromechanical model fails to provide FEM results especially for medium volume fraction (40%-60%). Figure 5b. compares the effective elastic modulus from FEM, averaging micromechanical model and self-consistent approach. The results indicate that the self-consistent approach provides very accurate results for all range of volume fraction for two-phase random checkerboard microstructure. Also, the result shows a sa udden change in effective elastic modulus for 50% volume fraction and therefore, it seems that 50% volume fraction with associated 10 GPa effective elastic modulus is the percolation threshold for CNC network. Indeed, many studies have estimated the elastic modulus of CNC nanofilm to be around 5-20 GPa depending on the alignment and therefore the result shows that this value is in a reasonable range [25].

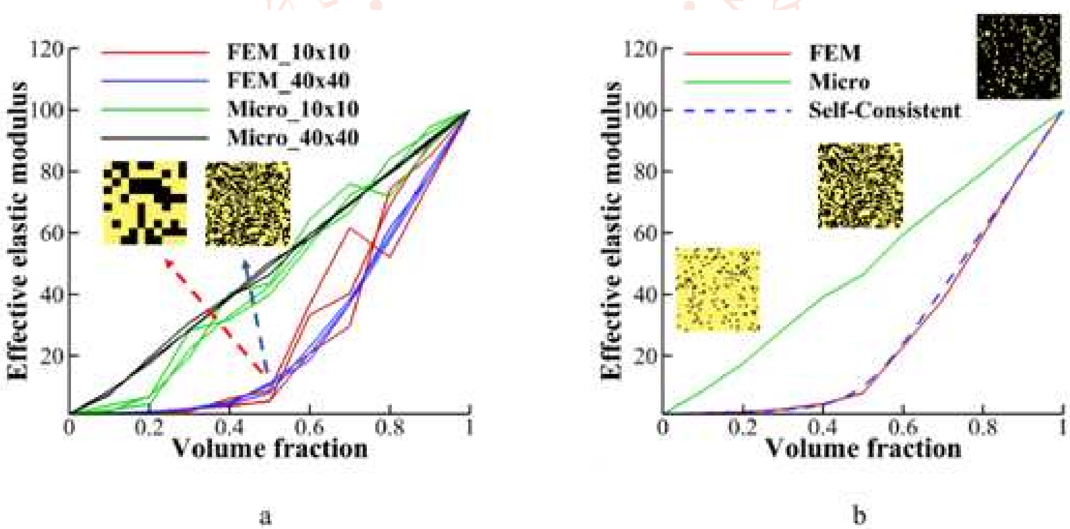


Figure5. Variation of effective elastic modulus with volume fraction. (a) comparing the effect of size of the microstructure and randomness on the results. (b) Comparing the effective elastic modulus from FEM, averaging micromechanical model and self-consistent approach.

Two-phase vs multiphase percolated network

In the previous section, the percolated CNC network was modeled as a two-phase material with E=100 GPa and E=1 GPA. However, due to the orientation of CNC particles, each checkboard could take elastic modulus between 1-100 GPa. For multi-phase materials, the elastic modulus in a range of E1-E2 is randomly assigned to tiles and by controlling the number of phases involved in the microstructure, by controlling how many different elastic moduli is provided, the variation of the effective elastic modulus with respect to the number of phases can be obtained as shown in Figure 6. When the number of phases increases sufficiently, the discrete distribution could be approximated by a continuous one as shown in Figure 6.c.

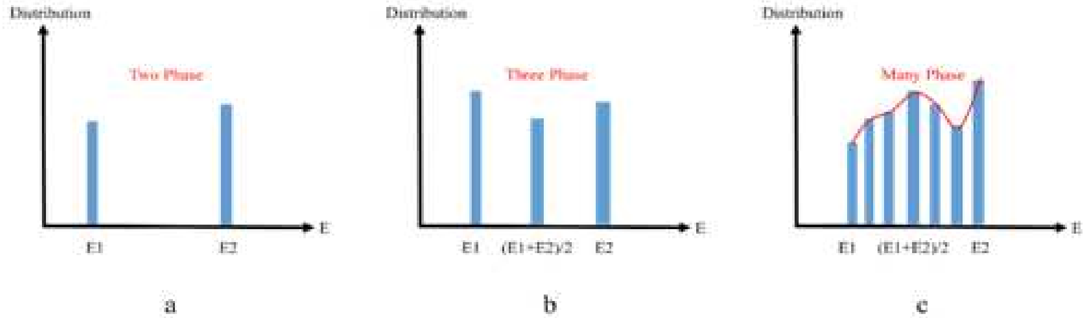


Figure6. Discrete distribution of elastic modulus for having multi-phase materials. (a) Two-phase materials. (b) Three phase-materials and (c) Multi-phase materials which can be approximated with continuous distribution.

Figure.7a displays the variation of effective elastic modulus with a number of phases and its comparison with the micromechanical model. It is interesting to see that by increasing the number of phases, the FEM results have an asymptotic value. In other words, the effective elastic modulus for having 10 different phases and 5 different phases are almost the same. Note that each case study has been performed 4 times to also see the variation of curves with randomness. In addition to having a discrete number of phases, having a continuous distribution of elastic modulus provides continuous variation of a number of phases. Here, Weibull distribution is used to provide such a variation to the elastic modulus. The equation for the probability distribution function of Weibull is:

$$f(x)=\frac{\beta}{\lambda}\left(\frac{x}{\lambda}\right)^{(\beta-1)}e^{-\left(\frac{x}{\lambda}\right)^{\beta}} \qquad (4)$$

Where β is the scale parameter and λ is the mean value. The effect of Weibull scale parameter, β, which controls the diversity of the number of phases is also studied as shown in Figure 7b. For β=1 the FEM and micromechanical model show very different results and although the micromechanical value is very close to the average elastic modulus in the Weibull, a=E=50, the FEM results are around 30. Comparing the discrete and continuous distribution number of phases shows that when the variation of elastic modulus is large, β=1, the continues distribution is the asymptotic value of discrete number of phases, here around 35, but as the β parameter increases, even though there are many phases involved in the microstructure due to having continuous distribution, the FEM and micro results are close to the average value (around 45).

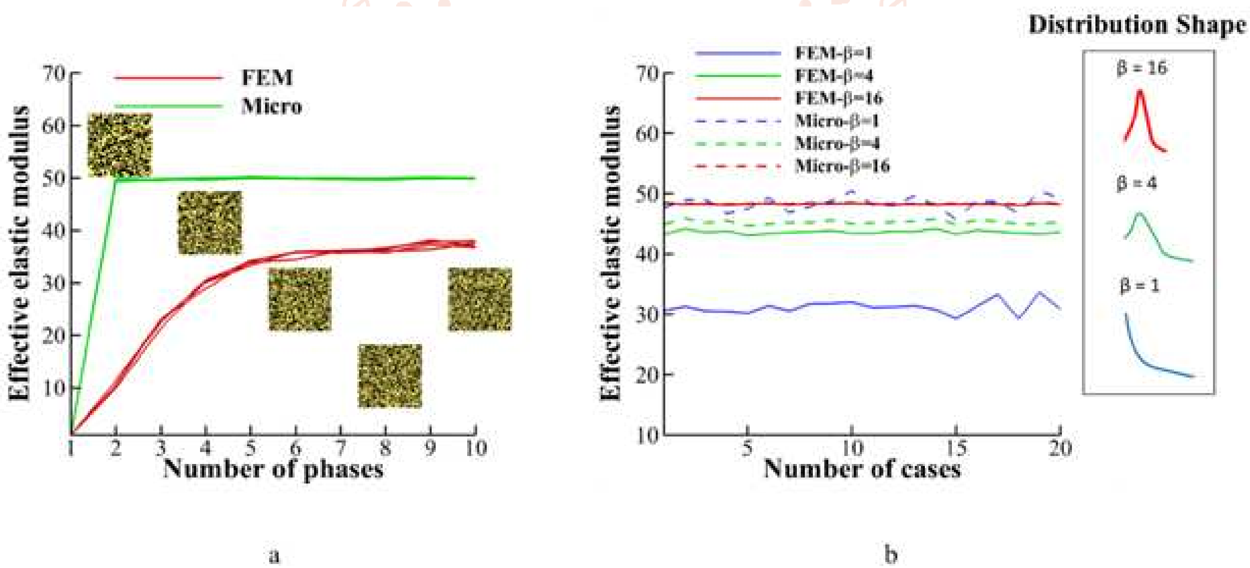


Figure7. The discrete and continuous distribution of a number of phases in the microstructure. (a) The variation of effective elastic modulus with respect to a number of phases. (b) The effective elastic modulus for the different scale parameter of Weibull distribution.

CONCLUSION

In this paper the effective elastic modulus of two-phase and multi-phase percolated CNC network was estimated using FEM and two different micromechanical models (a mixed Voigt-Ruess micromechanical and self-consistent model). The microstructure is produced by randomly assigning elastic modulus to a 2D checkerboard structure. The results show that for two-phase materials when the microstructure has a certain pattern the micromechanical model and FEM provide the same effective modulus, however when the microstructure is completely random, the micromechanical model fails to produce FEM results, although using self-consistent model shows a great match with FEM results for different volume fraction. For random multiphase materials, the effect of a number of phases on the effective elastic modulus was studied by discreetly controlling the number of phases and randomly assigning them to checkerboard tiles.

In addition, the effect of a continuous distribution of elastic modulus, continuous phases, were studied with Weibull distribution of elastic modulus. The results show that by increasing the number of phases, the effective modulus for discrete distribution has an asymptotic value which is equal to Weibull scale parameter $\beta=1$. By increasing the β, the effective elastic modulus gets closer to the single-phase with average elastic modulus in the Weibull distribution. In other words, having a continuous distribution only provides two sides of the discrete distribution, one for two-phase materials and one for many phases which provides asymptotic effective modulus. Finally, this study suggests 50% volume fraction as the percolation threshold for CNC network with 10 GPa effective elastic modulus. The results from percolated multiphase network reveal that for microstructures with 4 phases and above, the percolated network converge to 35 GPa effective elastic modulus.

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