On the Determination of the Threshold Content of Fibrous Nanomodifier

SMIRNOV Vladimir Alexeevich[1, a *], KOROLEV Engenij Valerjevich[1, b] and EVSTIGNEEV Alexandr Viktorovich[1, c]

[1]26 Yaroslavl hw., Moscow, Russian Federation

[a]smirnov@nocnt.ru, [b]korolev@nocnt.ru, [c]evstigneev@nocnt.ru

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Abstract. Currently, numerous specific methods directed to the improvement of the building materials are developed. Many of such methods are intrinsically the implementations of the nanotechnology; the random reinforcement by nanoscale fibers is a well known way for the enhancement of operational properties. The later can be achieved if the fibers form the continuous percolation lattice. In the present work we have offered the simple algorithm for the assessment of the threshold content of fibers that correspond to the formation of such lattice. The algorithm couples simple geometry-based stochastic modeling with the regression analysis. Several numerical experiments are carried out; it is shown that for high aspect ratios (about 10^2) the percolation lattice can be formed even if the volumetric ratio of the fibers is relatively small (less than 1%).

Introduction

There are permanent demands in modern construction for new materials of enhanced operational properties. Currently, numerous specific methods directed to the improvement of the materials are developed. Many of such methods are intrinsically the implementations of the nanotechnology; applications of nanotechnology in constructional material science and civil engineering are numerous, ranging from the admixture of carbon nanotubes into the concrete composites [1] to the molecular design of the binders [2] and hyperplasicizers [3]. At present, the principles are also formulated that are general enough to allow implementation of the nanotechnology in construction in sound, consistent manner [4]. In particular, the mentioned principles dictate the necessity to move from the experimental studies and regression analysis (statistical modeling) towards the approach that involves extensive use of numerical experiments. The later approach allows to reduce the resource consumption significantly during research and development of the so-called nanomodified building materials; such materials can be enhanced by separately synthesized fibrous nanoscale agents (nanomodifiers). Thus, it is beneficial to carry out numerical experiments for the determination of the volumetric content of such nanomodifiers.

Estimates of structural parameters of multiphase materials can be obtained on the basis of ideas about the topology of a percolation lattice [5]. If the short fibers are used for the improvement of operational properties of composite (so-called random reinforcement), the analysis of topological features becomes more complicated. It is well known that percolation threshold for random graphs can be found exactly. But unfortunately modeling the distribution of fibers in composition by random graph is not adequate in most cases. It was also stated [6] that sophisticated nature of many numerical approaches leads to fallibility in application, and consumes excessive resources by providing information irrelevant to the current problem.

Thus, to estimate number of inter-particle contacts we propose the simple stochastic modeling (Monte-Carlo) method that can also be combined with regression analysis.

Modeling Procedure

We assume that all structural units of the modifier, which are distributed in the volume of the dispersion medium, are of linear conformation and can be presented as cylinders of diameter *d* and length *l*. Both length and diameter can either be fixed of are subject to some probability distributions.

The proposed simulation method operates on the volume *V* that should satisfy the condition $l << \sqrt[3]{V}$ (in case of fixed length *l*) or $M[l] << \sqrt[3]{V}$ (where $M[l]$ is the mean of the respective probability density). If the model volume is the parallelepiped with dimensions s_k, $k = \overline{1,3}$, than for every dimension one of the conditions $l << s_k$ or $M[l] << s_k$ has also be met. Assume the modeling volume to be parallelepiped $a_k \le x_k \le (a_k + s_k) = b_k$ that is bounded by coordinate-aligned planes $x_k = a_k$ and $x_k = b_k$. We propose the following modeling algorithm.

1. Select the next point $\mathbf{r}_i = (x_{ik})$, $i = \overline{1,N}$ that is uniformly distributed in a parallelepiped; here *N* is the preliminary unknown number of filaments (fibers of nanomodifier).

2. Select the vector $\mathbf{p}_i$ that is uniformly distributed on the unit sphere. To select the appropriate vector the following subroutine may be used:

2.1. Generate three normally distributed values p_k of means equal to zero and dispersions equal to 1/3. Interpret such numbers as coordinates of the $\mathbf{p} = (p_k)$.

2.2. If the point **p** is out of the spherical shell $0.8 < \sqrt{\sum_{k=1}^{3} p_k^2} < 1$, then proceed back to step 2.1.

2.3. Normalize the vector **p** and use it as the sought-for vector $\mathbf{p}_i$.

3. From the point $\mathbf{r}_i$ in the direction of the unit vector $\mathbf{p}_i$ draw the cylinder of selected length *l* and diameter *d*.

4. Repeat steps from 1 to 3 until the predefined volumetric content of the filler is reached (obviously, it is possible to compute number *N* of fibers directly, but not in case if the radius and length are subject to some probability distributions).

5. Calculate the $(N^2 - N)/2$ "distances" between the fibers. The length of common perpendicular can be used as the sought-for distance [7], Fig. 1, as we have described earlier [8]. Considering the finite length of the fiber, the distance is also considered finite only if the foots of the perpendicular lies on the fibers to which it was drawn (Fig. 2 and 3).

6. Compute number N_C of contacts as number of cases where the distance between fibers is less than the sum of the fiber's radiuses.

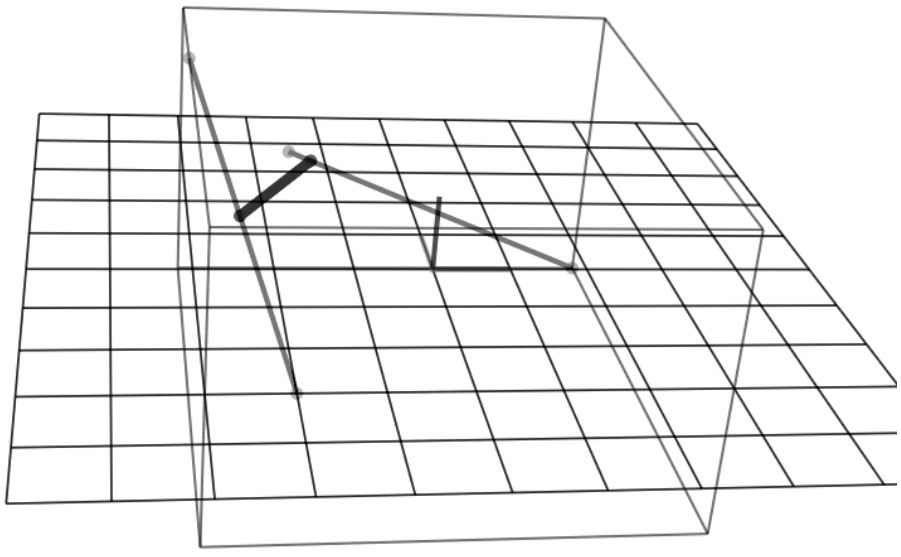

Fig. 1 Common perpendicular that is drawn to the axes of filaments [8].

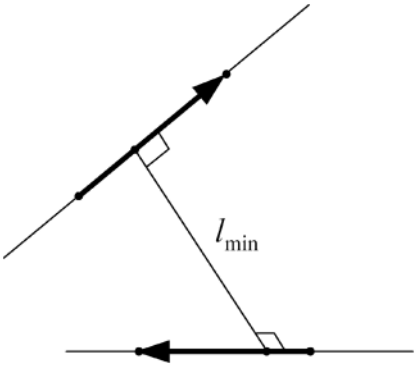

Fig. 2. The length of the common perpendicular is considered as a distance between fibers

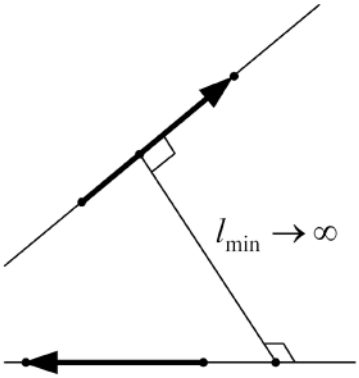

Fig. 3. The case when the distance is considered to be infinite

Steps 1 and 2 involve the algorithm for generation of uniformly distributed random numbers. Our current implementation is based on an algorithm described in [9].

Results and Discussion

Simulation was carried out for fibers of diameter d_f of 2 and 10 nm, with length l_f of 100 and 200 nm (full factorial design – also not for the real experiment, but for the numerical simulation). For each point in the factor space (d_f, l_f) the dependence between number of fibers and number of contacts was found (number of fibers during simulation was up to 10^5).

Dependencies between the relative number of contacts (ratio N_c/N, where N_c is number of contacts, N is the number of fibers) and the volume content v_f of disperse phase are shown in Fig. 4-7.

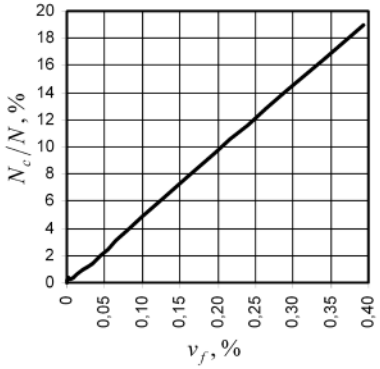

Fig. 4. The relative number of contacts for *lf* = 100 nm, *df* = 2 nm

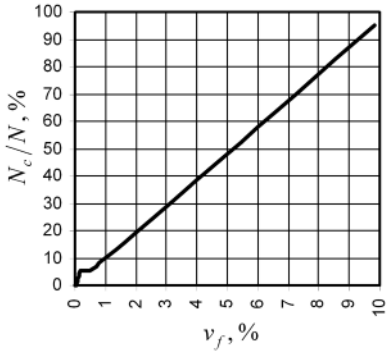

Fig. 5. The relative number of contacts for *lf* = 100 nm, *df* = 10 nm

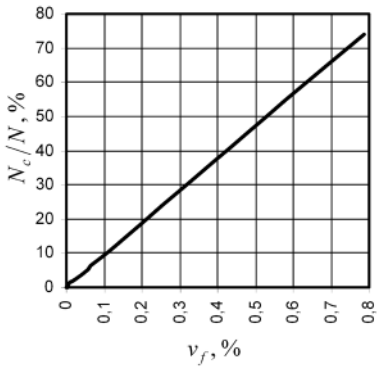

Fig. 6. The relative number of contacts for *lf* = 200 nm, *df* = 2 nm

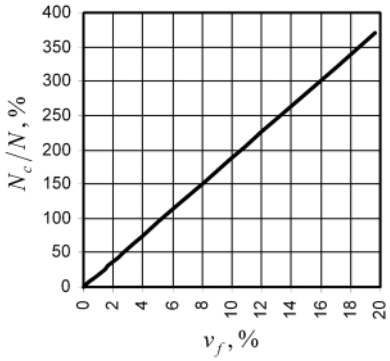

Fig. 7. The relative number of contacts for *lf* = 200 nm, *df* = 10 nm

As it can be seen from the Fig. 4-7, there is an almost linear dependence between the volume content of dispersed phase (fibers) and the relative number of contacts between the fibers. Comparison of Fig. 4 and 5 also shows that with an equal volume degree of filler the possibility of formation of percolation lattice is increasing with the increase of form factor (length to diameter ratio).

Slopes of the straight lines approximating the dependencies shown on the Fig. 4-7 determine the predicted percolation threshold; the later correspond to the point of equality $N_c=N$. On the base of the simulation results (the full description of regression procedure is given in [10]) the regression model is constructed:

$$v_{f,crit} = 4.7–1.5x_1+3.1x_2–x_1x_2\ \%, \quad (1)$$

where, x_1 and x_2 are normalized length and diameter of the fiber, respectively.

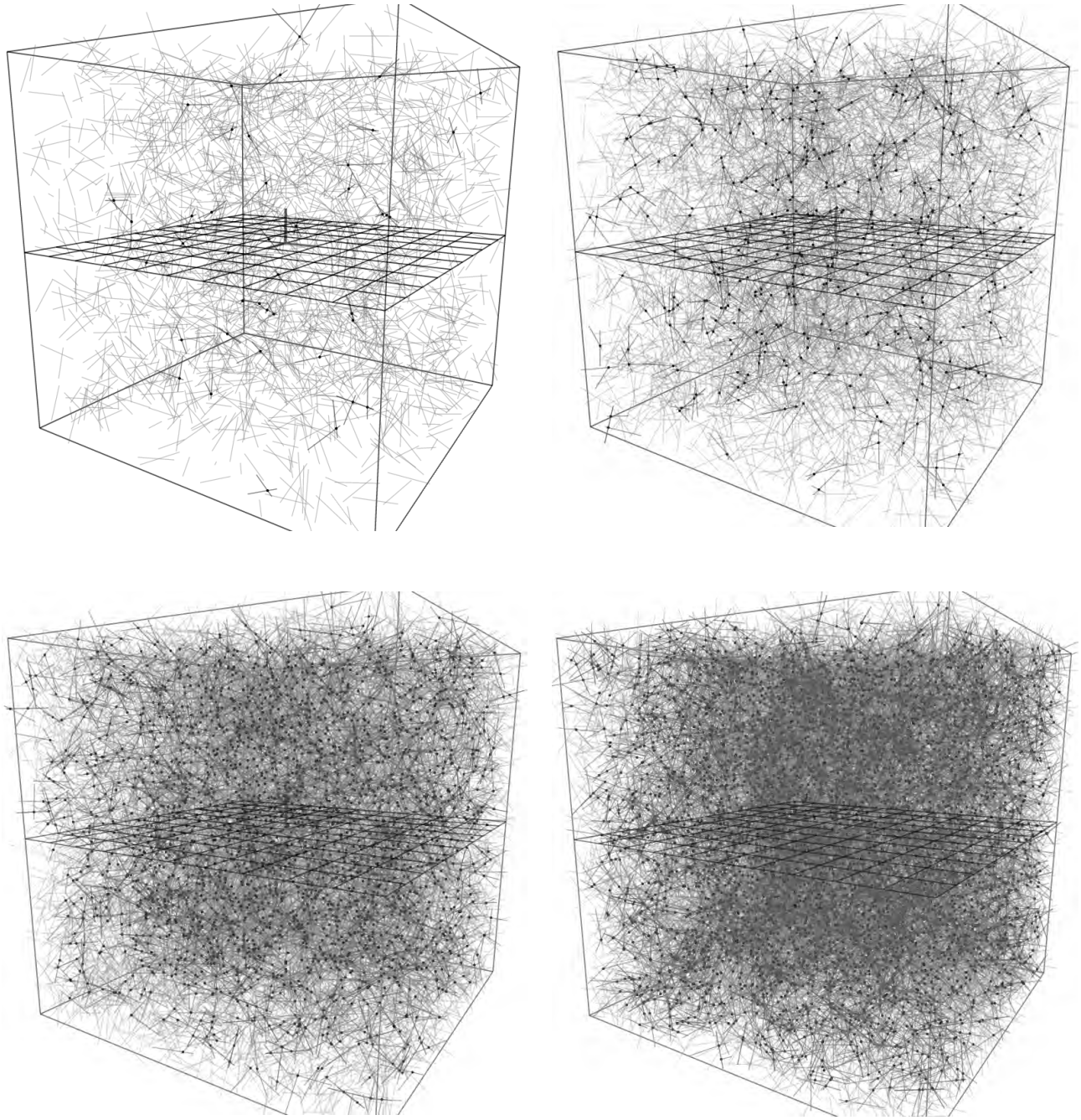

Fig. 8. Visualization of the systems of different N_c/N ratio

The constant term in Eq. 1 determines the average value of the percolation threshold for all investigated systems. It must be noted that value of the term 4.7% is much smaller than the well-known value of 16% for the percolation threshold for the lattice formed by spheres. Sign of the second term indicates that with the increase of the fiber length (and, therefore, the aspect ratio) the volume fraction corresponding to the threshold becomes smaller. This is obviously due to an increased probability of contact for the longer fibers.

Some modeled systems were also visualized (Fig. 8).

The points on the Fig. 8. represent the contacts between filaments. The last image on the Fig. 8 corresponds to the $N_c/N = 0.2$.

It should be noted that the proposed algorithm is rather computation intensive. However, it can easily be parallelized. Moreover, the most resource demanding stage (fifth one) can be readily implemented on GPU, thus reducing the total computation time in orders of magnitude. The serial implementation is available in source code [9].

Summary

By means of using the stochastic modeling it is possible to estimate some properties of composite filled with nanoscale fibers. The results of such estimation can be used for the initial mixture design.

We have proposed the simple algorithm that allows the assessment of the volumetric content that corresponds to the formation of the continuous percolation lattice. The serial implementation of the algorithm is made; the code is available as open source.

With the developed software we have performed several numerical experiments. During the experiments the primary attention is made to the ratio of number of contacts to the number of nanoscale objects. The condition when such ratio is near the unit value is considered essential for the formation of the continuous lattice.

It is shown that for high aspect ratios (about 10^2) the percolation lattice can be formed even if the volumetric ratio of the fibers is relatively small (less than 1%).

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