Supplementary Information for

**“Fiber aggregation in nanocomposites: aggregation degree and its linear relation with percolation threshold”**

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**Appendix. A Intersecting probability of fibers**



**Fig. A.1.** Schematic diagram for the intersecting probability of two arbitrary fibers

There are three basic unknown functions in Eq..is the probability density function of the angle between two arbitrary fibers. For a fiber system with isotropically distributed angles, it satisfies

|  |  |  |
| --- | --- | --- |
|  | . |  (A.1) |

is the probability density function of center-to-center distance between two arbitrary fibers. To solve, assuming the coordinates of the midpoints of two fibers as, as shown in Fig. A.1 a). Then, the distribution function of the center-to-center distance is

|  |  |  |
| --- | --- | --- |
|  | . |  (A.2) |

By derivation, the probability density function of center-to-center distance can be expressed as

|  |  |  |
| --- | --- | --- |
|  | . |  (A.3) |

 is the intersecting probability of two fibers with given angle  and center-to-center distance *R*. To obtain this probability, the excluded area method is used [1]. The excluded area is the area around an object where the center of another similar shaped object cannot enter if penetration is not permitted. Therefore, a necessary and sufficient condition for the two fibers to intersect is that the midpoint of fiber *i* enter the excluded area of fiber *j*, and vice versa. As shown in Fig. A.1, the gray area is the excluded area of fibers *i* and *j*. When the center of fiber *i* move along a circle with radius and enter into the excluded area, these two fibers must intersect each other. Therefore, the intersecting probability  is the ratio of the arc length inside the excluded area (the blue arcs in Fig. A.1 a) and b)) to the entire cycle circumference with radius *R*.

When the angle between two fibers is fixed, with the radius *R* increases, the analysis of intersecting probability can be divided into four cases, as shown in Fig. A.1c).

Case 1: when, the center of fiber *i* must locate in the excluded area, which means that the two fibers must intersect.

Case 2: when, the circle is cut into eight arcs by the rhombus edges, and four arcs are in the rhombus, as shown in Fig. A.1 b).

Case 3: when, the circle is cut into four arcs by the rhombus edges, and two arcs are in the rhombus, as shown in Fig. A.1 a).

Case 4: when, the two fibers cannot intersect.

Based on geometric analysis,  is half of the long diagonal of the rhombus,  is the half of the short diagonal of the rhombus, is the radius of inscribed circle of rhombus. Therefore, , and can be written as

|  |  |  |
| --- | --- | --- |
|  | . |  (A.4) |

As mentioned above, the intersecting probability  is the ratio of the length of blue arcs to the entire cycle circumference. To measure the length of these blue arcs for case 3 and case 4, a Cartesian coordinate system is introduced with origin located at a vertex of acute angle of rhombus, as shown in Fig. A.1 d) and e). Obviously, the ratios of the arc lengths can be equivalent to the ratios of angles. Therefore, the piecewise intersecting probability is

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| --- | --- | --- |
|  | , |  (A.5) |

where *α*, *β* are the corresponding angles of blue arcs, and can be expressed as

|  |  |  |
| --- | --- | --- |
|  | , |  (A.6) |

where

|  |  |  |
| --- | --- | --- |
|  | . |  (A.7) |

Finally, according to Eqs., (A.1), (A.3) and (A.5), the intersecting probability of arbitrary fibers in an aggregating cluster can be rewritten as

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| --- | --- | --- |
|  | . |  (A.8) |

**Appendix. B Process and size effect of Monte Carlo simulation on percolation threshold**

The process of Monte Carlo simulation on the percolation threshold is carried out as follows.

1. Generation of 2D network models

In a RAE with the size of *L*×*L*, fibers are simplified as line segments with the length *l*f. For a random network without aggregation, the position of nanofiber midpoint (*x*0, *y*0) and the orientation of the fiber *θ* follow uniform distributions in the ranges of [0, *L*), [0, *L*) and [0, π), respectively, and follow the equations as

|  |  |  |
| --- | --- | --- |
|  | , | (B.1) |

where  and *θi* indicate the midpoint position and the orientation angle of the *i*-th fiber in network, respectively, and the “rand” is a random number uniformly distributed in the range of [0,1).

For the network with aggregation, the aggregation degree of the networks can be controlled by the degree of looseness *σ* and fiber number *N*agg f in an aggregating cluster. The midpoint positions of *N*agg aggregating clusters (*x*agg,*y*agg) are assumed to be uniformly distributed in the ranges of [0, *L*) and [0, *L*), respectively. The positions of nanofibers in each aggregating cluster are assumed to follow normal distribution in two perpendicular directions, as

|  |  |  |  |
| --- | --- | --- | --- |
|  | , | (B.2) |  |

where  signifies the midpoint position of the *j*-th aggregating cluster. The “normrnd” refers to a random number that conform to the normal distribution . The orientation of the fibers *θ* still follow uniform distribution in the range of [0, π).

The coordinates of two ends of *i*-th nanofiber can be set as

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| --- | --- | --- |
|  | . | (B.3) |

Assuming the squared RAE is a periodic section in the whole network, the parts of nanofibers outside the area *L*×*L* should be moved to the opposite edge of the RAE boundary, as shown in Fig. B.1, in which the blue line segments are those moved from outside to inside. The 2D network models of RAE with different aggregation degree are shown in Fig. 1(c).



**Fig. B.1.** Schematic diagram of the 2D uniformly random nanofiber network after periodicity process.

2. Search for the connecting path

2.1 Pre-process

(1) Search the fibers intersected with left and right edges of the RAE and put them into two groups, i.e., “input group” and “output group”, respectively, and put all the fibers outside of “input group” into “search group”;

(2) Record intersection relations between fibers, and store them in a “link matrix”;

2.2. Search for the conductive path

(1) Search the fibers in “search group” that are intersected with fibers in “input group” according to the “link matrix”.

If there is no fiber found, the network is not connected. The searching process is stopped.

If there are fibers found, marked these fibers as “fiber temp”.

(2) Check if there exists any fiber in “fiber temp” belongs to “output group”.

If there exists, the network is connected. The searching process is stopped.

If there does not exist, move fibers in “fiber temp” from “search group” to “input group”, and go to step (1) of 2.2.

3. Calculate the connection probability

A total of *N*S models for each set of parameters are generated and calculated. The connection probability of models is the ratio of the number of samples with connecting path *N*P to the total number of samples *N*S,

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| --- | --- | --- |
|  | . | (B.4) |

4. Calculate the percolation threshold using Boltzmann function.

Simulation results show that the connection probability *P* increases with the increase of the combined dimensionless network density *n*f*l*2 f, presenting an “S” shape, as shown in Fig. B.2. This S-shape curve can be described by Boltzmann function, and written as

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| --- | --- | --- |
|  | , | (B.5) |

where *P*1 and *P*2 are the minimum and maximum values of *P* and should be set as 0% and 100%, respectively, *C*0 is the horizontal coordinate of the center of the central symmetrical Boltzmann curve and satisfies the relation , d*x* is the slope at the center point. The network density at connection probability *P*=50% is taken as the percolation threshold.

The dimensionless network density *n*f*l*2 f of uniformly distributed random nanofiber network at connection probability *P*=50% can be predicted by Eq. (B.5) as 5.8. Thus, the relative density at the percolation threshold

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| --- | --- | --- |
|  | . | (B.6) |

It is noted that the process of Monte Carlo simulation on percolation threshold for networks with random and aggregated nanofibers is the same except the modelling process in step 1.

**References**

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