Quantitative evaluation of inclusion homogeneity in composites and the applications

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**ABSTRACT**

Microstructures are critical for designing composite materials with admirable properties required by various applications. However, desired inclusion arrangements are pre-required and have to be reached by appropriate processing as well as quantitative evaluation. Up to date, visual characterization like transmission electron microscope is still the “golden rule” for measuring inclusion arrangement, together with qualitative descriptions in most studies. In order to establish structure-property relationship, optimize processing parameters and even predict composite performances, quantitative evaluation of inclusion arrangement becomes a must. This review focuses on the numerous developed mainstream quantitative approaches and their recent advances. Methods, including ASTM index (American Society of Testing Materials), Morishita’s index, quadrat method, linear intercept distance, free-path spacing, nearest neighbor distance, inter-particle distance, free-space length, functional analysis, Delaunay triangulation and Dirichlet tessellation, are classified into three categories: methods based on inclusion features, methods based on inclusion position and methods based on inclusion position and inter-distance, which are introduced in the manuscript. Definition, advantages, updated progress and recent application examples of specific method are included. The differences between each methods and their limitations are summarized.

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1. Introduction

Composites containing numerous kinds of inclusions are ubiquitous in civil, automobile, aviation, electrical, electronics, and military industries [1–4]. Composites offer satisfactory structural properties and additional functionalities at reduced weight. Besides the matrix materials, the final properties of the composites also highly depend on the species, size and shape, concentration, interaction with matrix, and distribution of the inclusions. Up to date, most of the applied inclusions are micro- and nano-scale particulates (low aspect ratio) or filaments and sheets (high aspect ratio), which have been artificially introduced into various matrices [5–8]. The inclusion features and loading amounts can be well-controlled, and the surfaces of the inclusions can be tailored to adjust interactions with matrix [9–11].

Until now, intensive researches have been contributed to construct the morphology-property relationship in order to achieve the ability to predict properties based on microstructures. Friedrich and Almajid [12] concluded that the contributions of matrix and fibers to the final properties of the composite are diverse. Some properties like stiffness, strength and fatigue are heavily determined by fibers while other properties such as thermal and chemical resistances are almost determined by matrix solely. Correlations between fiber species and diameter on the mechanical properties have been concluded by Karaduman et al. [13]. Kenny and Opalicki [14] studied the effect of calcium carbonate particulates and glass fibers on the curing kinetics through differential scanning calorimetry and rheometry and proposed a numerical model to foresee the dynamic curing process [15]. Francis et al. [16] studied the morphology of homogenous particle size distribution of an epoxy/poly(ether ether ketone) blend and the curing kinetics. Kalaprasad et al. [17] developed theoretical model to predict the tensile properties of fiber-reinforced polyethylene composite. Factors including fiber loading, orientation and length had been taken into consideration. Composite models including Hirsch, Cox, Halpin-Tsai and modified Bowyer and Bader were applied to analyze the experimental data. Thomas et al. [18] focused on the epoxy/carboxyl-terminated (butadiene-co-acrylonitrile) (CTBN) blend. Two-phase morphology was observed and CTBN loading and size were correlated with thermal and mechanical properties of the materials, such as $T_g$, impact strength and fracture toughness.

Ponnamma et al. [19] did a comprehensive overview on carbon nanotubes based elastomer composites. Numerous fabrication methods such as solvent casting, freeze drying and spray drying were introduced and the dispersion quality was emphasized. The relationship with mechanical, viscoelastic, thermal and electrical properties are systematically studied. Hollister and Kikuchi [20] noticed that homogenization theory is more effective to estimate the elastic behaviors of periodic porous composites than standard mechanics approaches. Later on, Vieville et al. [21] reported the limitation of traditional self-consistent scheme in mechanics, and proposed using incremental method to determine strain concentration in composites with inclusions. Meanwhile, Zhou and Meschke [22] developed a strength homogenization model based on linear comparison composite approach to analyze the stress distribution in composites. Karger-Kocsis et al. [23,24] contributed a lot researches on the relationship between morphology of polymer blend and composites with mechanical properties, in both macroscopic and microscopic scales.

Meanwhile, inclusion arrangement has to be considered, which is capable to strongly influence or even dominate numerous properties of composites as well. However, comparing with the aforementioned inclusion parameters, achieving desired inclusion arrangement is much more difficult, and often regarded as one of the major challenges for composites manufacturing [25,26]. In most cases, like enhancing mechanical modulus and strength [27], friction and wear [28], dielectrics and electrical breakdown strength [29], and optical transparency [30,31], homogeneity or uniformity is the ideal inclusion arrangement, although specific inclusion arrangements are preferred in specific applications like thermal/electric conductive materials [32,33]. Gawdzińska et al. [34] noticed the importance of structure homogeneity and provide clear definition to it, including homogeneity scale and homogeneity feature. Notably, rather than a primary parameter, homogeneity actually involves two parts, which are usually described as dispersion and distribution. These two terminologies have been mixed used in many researches although they are not identical. In brief, dispersion emphasizes on describing local arrangement while distribution mostly focuses on global arrangement [35]. In practice, good homogeneity allows certain degree of randomness, rather than ideal lattice microstructures, although the latter is often considered as the standard to facilitate comparison. A figure (Fig. 1) is provided here to help understanding the relation and differences between them. Up to date, approaches for tailoring inclusion arrangement, such as melt processing, solution processing, ultra-sonication and centrifugation, have been completed so far [36], but estimating inclusion arrangement is usually qualitative. Descriptions like “well-dispersed” or “serious agglomerated” are stuffed in research during the past, which would possibly lead to ambiguous discussion and conclusions. In many times, composite with inclusion arrangement A and B are both concluded as “well-dispersed”, however, material properties of arrangement A can be varied from arrangement B. Such differences are unable to be explained through qualitative evaluation. To compare
material properties, establish structure-property relationship, optimize processing parameters and even predict composite properties, quantitative evaluation is demanded and urgently required. A quantitative result, or even a numerical value is preferred to support systematic comparison objectively, especially for composites with similar components but distinctive arrangements of inclusions [37].

However, quantitative evaluation of inclusion arrangement is not a topic solely considered by composite researchers temporarily. In fact, this topic is an interdisciplinary field, constituting universal applicability in numerous subjects. It demands the skimming of several other independent areas, including astronomy [38], ecology [39], archaeology [40] and computer science [41], which have provided parallel methods for different purposes. Moreover, many of these methods have reached high mathematical complexity while still advance continuously. A good example is quadrat method, which had been applied in ecology for analyzing spatial distribution of bird nests even before a century [42]. However, modified quadrat method based on Shannon’s entropy was developed only several years ago [43]. Till now, there are numerous related methods have been reported based on different theoretical foundation and algorithms. Although brief classification of the developed methods for uniform arrangement analysis has been carried out before [37], comprehensive overview on mainstream and recent advances is lacking. Considering of their extensive applications in material science as well as other disciplines, it is of extremely important to exhibit their advantages and disadvantages and show their differences and specialized application situation, so that to promote the development of related areas. To achieve these, this review focuses on the advances of inclusion quantification methods. Representative approaches like particle size method, linear intercept distance method, quadrat method, inter-particle distance method, nearest neighbor distance method, free space length method and Delaunay tessellation method as well as their variations are involved, together with their strength and weakness. Kernel definition, boundary condition, algorithm and index will be described and compared. Summary is given along with the perspective on further development in this area.

2. Overview of characterizations for homogeneity analysis

Before quantitative analyzing the homogeneity of inclusions, characterization of the composite is necessary to provide indispensable microstructural information. Various characterization methods have been applied so far for related analysis. X-ray diffraction (XRD) is one of the most common methods to elucidate the nanostructures of composites, especially for layered-silicate nanocomposites [44]. Analysis is based on the measurement of interlayer d-spacing (distance between basal layers of any layered material). The method is able to present the dispersion quality of layered inclusions rather than distribution quality, but usually inappropriate for characterizing composites containing particulate inclusions without exfoliation capability. Characterization based on solid-state nuclear magnetic resonance (NMR) faces similar difficulties [45]. Yoon et al. [46] studied the dispersion state of single-walled carbon nanotubes (CNTs) using Raman spectroscopy, by using peak intensity at 267 cm$^{-1}$ to evaluate agglomeration degree. Selimov et al. [47] measured the photoluminescence of chromium impurity to estimate the arrangement of alumina in carbon fiber reinforced composite. Only dispersion information could be achieved by the spectral methods while no distribution performance was reflected directly. Kim et al. [48] described the application of differential scanning calorimetry (DSC) for assessing dispersion of CNTs in epoxy, based on the variation in curing kinetics and reduction in curing enthalpy. This method reveals the overall dispersion of the inclusions in sample, but is only appropriate for reactive matrix. Rheological technique was also investigated in a PET based nanocomposite to correlate dispersion and characteristic rheological response [49]. Zhang and Park [50] reported the Payne effect of non-linear elasticity, providing information of interfacial interaction and filler network. Method based on rheology is able to provide overall dispersion, and sensitive to filler loading, shape etc. Lively et al. [51] proposed the “equivalent circuit model”, which assumed that inclusion and matrix have high conductivity differences, thus their resistance-capacitance performances under AC/DC condition are divergent. Macro-dispersion is able to be figured out when their AC and DC
features are characterized. Unfortunately, this method is only workable for inclusion above percolation threshold. Methods like thermal diffusivity mapping were more recently developed by Greis et al. [54] based on the relationship between thermal conductivity and dispersion, while interface thermal resistance was not considered.

Although indirect methods are developing, visual observation based on optical microscope (OM) [55], scanning electron microscope (SEM) [56] and transmission electron microscope (TEM) [57] are still the "golden rule" and remain the most extensive characterizations for composite analysis in most research efforts. To minimize the error caused by scaling, distributions at several magnitude levels are analyzed. On the other hand, other visualized methods like X-ray microtomography (μCT) have been developed as well in order to achieve more comprehensive visualization [58]. Materials with thickness up to 200 μm can be characterized completely with 3-D information rather than conventional 2-D images. As reliable data and interpretation are provided, inclusion homogeneity assessment through visualization has been favored by most researchers to date. Notably, image capture is the very initial step for quantitative assessment of inclusion homogeneity, the whole process mainly involves three steps [59], which are:

1. Capturing the images representing the microstructures of composite through microscope;
2. Identifying inclusions from the obtained images;
3. Conducting statistical analysis to describe the level of homogeneity by numerical indicators.

This review focuses on the third step and composites with both particulate inclusions and filament inclusions are involved, while the former is emphasized. The statistical analysis methods have been proposed in some brief introductions during the past [60,61]. In this review, these methods are classified into three categories, as a combination of the advantages of past classification while emphasis on their differences.

3. Method based on inclusion features

3.1. ASTM index

The ASTM D2663 standard [62] provides several quantification methods of carbon dispersion in matrix. Among them, method B is often applied to quantify carbon inclusions in polymer composites. Captured figures are divided into nine sections and further segmented into 90,000 cells. Five of the nine sections are selected and the cells within the sections are counted (U), if half of the cell is filled by carbon inclusions (Fig. 2). The ASTM index D is expressed as

\[ D = 100 - \frac{SU}{L} \]  \hspace{1cm} (1)

where L is the volume percentage of carbon inclusions in composite and S is the swelling factor of the composite (only composite with rubber matrix is considered). Perfect dispersion is corresponding to a D value of 100 while a value of 0 indicates strong agglomeration (D value can be negative but artificially set as 0).

Krause et al. [63] used a modified algorithm to calculate the ASTM index of CNT in polyamide composites so that swelling factor is bypassed

\[ D = \left( 1 - \frac{\bar{A}/A_0}{V} \right) \times 100\% \]  \hspace{1cm} (2)

where \( \bar{A} \) is the effective volume of filler in agglomerate, \( A_0 \) is the ratio of agglomerate area to the total area while V is the filler volume. They figured out that higher index value D could be achieved if higher mixing energy is selected. At a mixing energy higher than 25,000 J/cm³, perfect dispersion was able to be obtained. Meanwhile, continuous increase in electrical volume resistivity was found if higher D value was reached.

3.2. Inclusion size, density and Morisita’s index

Inclusion size measurement provides quantitative statistical values of inclusion size and size distribution, which are useful for evaluating the composites with large agglomerates, so that dispersion quality of particulate, filament and platelet inclusions can be effectively estimated. However, when inclusions are well dispersed, these parameters become constants and cannot reflect the distribution of the inclusions.

Later on, Dennis et al. [64] and Fornes et al. [65] proposed “TEM dispersion” and “TEM particle density” to describe the inclusion density, focusing on mean particle number per TEM image and per micrometer square, respectively. Morisita’s Index (Iₘ) can be obtained from the data of inclusion density, which is defined as

\[ Iₘ = \frac{\sum_{i=1}^{Q} n_i (n_i - 1)}{N (N - 1)} \]  \hspace{1cm} (3)

where N is the total inclusion number, \( n_i \) is the inclusion number in section i, and Q is the total section number. Iₘ is smaller than 1 for random and dispersed system while larger than 1 for agglomerated system. Modification was done by Kashiwagi et al. [66], who proposed “relative dispersion index” to indicate the inclusion homogeneity by the deviation of actual inclusion counts from ideal inclusion counts. Murugiah et al. [67] analyzed the dispersion degree of carbon nanofiber and graphene oxide in a polymer based membrane by counting the inclusion numbers and inclusion area fraction, which is essentially, a variant of density measurement. More recently, You et al. [68] studied silica enhanced PMMA nanocomposites and proposed the number density of particle clusters \( P(N_{Agg}) \) to illustrate dispersion of inclusions

\[ P(N_{Agg}) \sim N_{Agg}^\tau \]  \hspace{1cm} (4)

where \( N_{Agg} \) is the inclusion number in cluster and \( \tau \) is the Fisher exponent. The critical distance between inclusions is defined as \( 2R_0 \) (\( R_0 \) the gyration radius of polymer matrix). Small agglomerates are corresponding to larger \( \tau \) value, thus better dispersion is observed.
Approaches based on inclusion density are applicable for composites with different inclusion size. However, since density is related to filler loading, comparison can only be made at the same loading ratio. Moreover, internal spacing is generally not considered based on this method. Kim et al. [69] found that analysis based on Morisita’s Index could not well-distinguish the degree of mixing so that optimal condition for processing alumina/PET composite by two-screw extruder was unable to be figured out.

3.3. Stereology method

To be precise, more than a method for analyzing inclusion homogeneity, stereology is a science of art to quantitatively analyze 3-D composite structures from lower-dimensional data [70]. This is carried out based on the rigorously dedicated Delesse–Rosiwal law, which can be extended to composites with arbitrary phase numbers. For classical two-phase composites containing inclusions and matrix, it can be simplified as

\[ \phi = V_V = A_A = L_L = P_P \]  

where \( V, A, L \) and \( P \) represent volume, area, interface length and points, respectively. Parameters with subscripts indicate the corresponding inclusion ratios in composites. For analyzing composite microstructures, methods involving stereology would provide 3-D information although only 2-D optical or electro-microscopic images were at hand (Fig. 3).

Basu et al. [71] proposed two independent indicators, exfoliation number (\( \xi \)) and inter-particle distance (\( \lambda \)) for quantifying inclusion in polymer-clay nanocomposites. The former is evaluated by the percentage of clay interfacial area exposed to polymer matrix, within the interval \([0, 100]\). The latter is measured following the stereological relation

\[ \xi = \frac{100(S_V)_p-C}{(S_V)_{total}} \]  

and

\[ \lambda = \frac{4(1 - V_V)}{(S_V)_{p-c}} \]

where \( V_V \) is the volume fraction estimated from Cavalieri principle by measuring the area fraction of inclusions in image. Meanwhile, \((S_V)_{total}\) and \((S_V)_{p-c}\) are the total interfacial area and polymer-clay interfacial area per unit volume, estimating from particle line traces. This method is mathematically rigorous but small agglomerates dispersion is not included. To overcome this, two corresponding parameters, degree of dispersion (\( \chi \)) and mean inter-particle distance per unit volume of clay (\( \lambda_V \)), complementing to the aforementioned indicators were proposed by Xie et al. [72]

\[ \chi = \xi \left( 1 - \frac{\psi_{agg}}{\psi_C} \right) \times 100\% \]  

and

\[ \lambda_V = \frac{\lambda}{100V_V} \]  

where \( \psi_{agg} \) and \( \psi_C \) are the volume fraction of agglomerates and all inclusions factors like inclusion aspect ratio and orientation are involved. This modified approach was applied to a polypropylene-clay nanocomposite to compare influences of biaxial stretching condition at macro- and microscopic levels. It is able to distinguish different inclusion homogeneity and obtain optimal processing parameters.

Lively et al. [51] studied carbon nanofiber-filled polycarbonate composite. Bulk macro-dispersion was estimated by agglomerate numbers, sizes and size distribution functions. Worse dispersion would lead to smaller agglomerate numbers but large mean and deviation of agglomerate sizes. By employing Wicksell’s corpuscle problem, agglomeration size distribution data was improved in poor and medium dispersed microstructures while comparable to the microstructures with good dispersions. As industrial composites are mostly fabricated with low or medium dispersion quality, this method can effectively enhance the accuracy of quantitative estimation.

Fu et al. [52,53] proposed a stereological-energy method based on composites containing inclusions with only regular shapes. They suggested the dispersion index (\( D \)) can be represented by the surface energy, which can be calculated based on the stereology principle. For simplification, system with filling amount of 1% dispersion index can be expressed as

\[ D = \frac{S_V}{V_V} \]
This method had been applied to analyze the silica-epoxy nanocomposite and compared with free-path spacing method (will be introduced later). It was found that stereological-energy method was able to distinguish systems containing agglomerates or dispersion inclusions with different sizes. Unfortunately, strong assumption was made that global randomness is identical to local randomness, so that distribution of inclusion was not considered in these studies.

4. Methods based on inclusion position

4.1. Linear intercept distance method

Eckel et al. [73] conducted linear intercept measurement by placing an array of parallel lines with identical gaps in-between over the cross-sectional images of organo-clay reinforced olefin nanocomposite. The lines intersect the clay and the length of the lines (L) are divided by the intersection number (n). Better dispersion is indicated by smaller linear intercept distance. The calculated results were compared with the flexural modulus of the composite with specific composition (Fig. 4). Better flexural modulus was shown for samples with smaller line intercept distance, which indicated better dispersion. A modification is settled by Bertmer et al. [74] where further considering the influence of platelet thickness (d)

\[ D_{TEM} = \frac{L - nd}{n} \]  \hspace{1cm} (11)

Linear intercept distance was verified by a montmorillonite filled nylon nanocomposite and compared with the analysis based on the spin-lattice relaxation of protons.

Comparing with classical particle density measurement, the advantage of linear intercept distance is that it is not affected by the length of the filling inclusions while the disadvantage is the estimation relies on orientation (Fig. 4). Clays with random orientation show larger linear-intercept distance than orientation with better in-plane arrangement. Moreover, similar to quadrat method, selecting gaps between parallel lines is critical and will influence the obtained result. For a specific composite image, \( D_{TEM} \) would be changed if line arrays with different gaps are selected, which is related to clay loading level. In other words, \( D_{TEM} \) is dependent on inclusion loading. Unfortunately, this method generally fails to give a distribution of spacing between inclusions. This is further adverse to distinguish agglomerates from dispersed inclusions [75].

4.2. Quadrat method

Quadrat method has a history of more than a century and was originally developed in the field of ecology for statistically analyzing the spatial distribution of plants and animals, and was later introduced into material science [76]. Typically, quadrat method is carried out by using a grid of square cells named quadrats, to divide the composite image (Fig. 5). The inclusions in the quadrat are isolated by selecting appropriate threshold and their centroids are figured out. Then the inclusion number \( N_q \) within each quadrat is counted. For inclusions across quadrats, the centroid position determines their located quadrat. Because quadrat method also involves the spatial arrangement of inclusions, it is able to simultaneously evaluate the dispersion and distribution quality. For a composite with complete spatial randomness, it would lead to quadrats with similar \( N_q \) values, leading to a bell-shaped structure for a \( N_q \) plot. On contrary, extensive agglomerates would lead to quadrats disparity, some of which are empty while the others have large \( N_q \) values, resulting in an asymmetric \( N_q \) plot.

A classical parameter to quantify inclusion homogeneity in composite based on quadrat method is the index of dispersion (ID), which is defined as

\[ ID = \frac{(k - 1)s^2}{\bar{x}} \]  \hspace{1cm} (12)

where \( k \) is the quadrat number, \( s \) and \( \bar{x} \) are the variance and mean of inclusion numbers in quadrat. Typically, \( ID \) follows the \( \chi^2 \) distribution while lower \( ID \) is corresponding to less clustering.

4.2.1. Quadrat skewness

As a consequence of complete spatial randomness, a symmetric shape of distribution function of inclusion number in quadrat can be obtained. Meanwhile, variation in distribution leads to asymmetry of the function, which is defined as skew-
ness ($\beta$) and is one of the classical indices for quadrat method. The skewness ($\beta$) is defined as:

$$\beta = \frac{q}{(q-1)(q-2)} \sum_{i=1}^{q} \left( \frac{N_{qi} - \bar{N}_q}{\sigma} \right)^3$$  \hspace{1cm} (13)

where $q$ is the total number of quadrat, $N_{qi}$ is the inclusion amount in $i$th quadrat, $\bar{N}_q$ is the average inclusion amount per quadrat and $\sigma$ is the standard deviation of $N_q$ distribution. The value of skewness ($\beta$) varies from inﬁnities while small $\beta$ is corresponding to better homogeneity of the inclusions in composites. In addition, if inclusions are simpliﬁed as centroids, inclusion distribution is able to be expressed by binomial model, negative binomial model and Poisson model \cite{77,78}. Rezaei et al. \cite{79} studied the effect of consolidation temperature on the microstructure and mechanical properties of metallic glass reinforced aluminum composite. By estimating distribution symmetry through quadrat method, they figured out the optimal processing temperature to achieve composites with smallest grain size and best yield strength.

4.2.2. Composite index

Taking into account of both dispersion and agglomeration, new techniques are developed by Haslam et al. \cite{80}, partially based on quadrat method. The new method was demonstrated in a CNT-polymer nanocomposite and compared with classical ASTM D2663 standard \cite{81}. This method proposed a composite index, $\text{compindex}$, which includes the dispersion distribution index $\text{dindex}$ and size distribution index $\text{sindex}$. These two indices are corresponding to spatial location and CNT cluster size. Besides, each index includes two components relating to the shape and range of distribution, respectively. The dispersion distribution index $\text{dindex}$ is

$$\text{compindex} = \frac{1}{2} (\text{dindex} + \text{sindex})$$  \hspace{1cm} (14)

where

$$\text{dindex} = \frac{1}{2} \left[ 1 - \frac{s(b)}{0.5222} + \frac{\bar{b}}{\max(b)} \right]$$  \hspace{1cm} (15)

and

$$\text{sindex} = \frac{1}{2} \left[ 1 - \frac{\max(a)}{\sum_{i=1}^{n} a_i + n \bar{N}} \right]$$  \hspace{1cm} (16)

Herein, $b$ is the carbon content percentage observed in each quadrat, $s(b)$, $\bar{b}$ and $\max(b)$ are standard deviation, arithmetic average value and maximum value of $b$. 0.5222 is the largest possible standard deviation for a $3 \times 4$ grid, which varies if other grids are selected. Generally, higher $s(b)$ represents larger variation of inclusions in quadrat, corresponding to poorer distribution and lower $\text{dindex}$ value. Distribution range is defined by $\bar{b}/\max(b)$. Higher agglomerates lead to larger $\max(b)$ value, similarly indicated by lower $\text{dindex}$ value. The two terms can vary solely but are not completely independent. The numerical range of $\text{dindex}$ is 0 to 1. When $\text{dindex}$ equals to 1, desired distribution of inclusions is achieved without considering agglomerates. As supplementary, $\text{sindex}$ is proposed regardless of grid, conceptually similar to “TEM particle density”, where $a_i$ is the area of each agglomerates, $\bar{N}$ is the number of agglomerates and $n$ is the number of agglomerates smaller

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than 100 pixels. The value is maximum size of a randomly dispersion with high inclusion amount (20 vol% herein). Similarly, $s$ index ranges from 0 to 1. A value of 1 represents no apparent agglomerates.

Comparing with ASTM index, $compl\;index$ can well indicate the homogeneity change of different CNT loading with small index deviation while the ASTM index shows surprising deviation. On the other hand, although agglomerates are taken into consideration, the disadvantage of the index is also obvious. The weights of the two sub-indices, as well as the components within them are given equally, which seems arbitrary. In addition, the index value is highly based on the maximum value while regardless of other factors, which would cause severe deviation.

4.2.3. Shannon’s entropy

Offering an inherent objective theoretical foundation, Shannon’s entropy was introduced to characterize inclusion homogeneity in composite, using quadrat data for probability determination [82]. For $N$ species of inclusions in a space of $M$ quadrats, the overall Shannon’s entropy can be written as

$$S = \sum_{j=1}^{M} \left[ p_j S_j (N) \right] + S (M) \quad (17)$$

where

$$S_j (N) = - \sum_{n=1}^{N} \left[ p_{nj} \ln p_{nj} \right] \quad (18)$$

and

$$S (M) = - \sum_{j=1}^{M} \left[ p_j \ln p_j \right] \quad (19)$$

Herein, $p_{nj}$ is the probability of an inclusion of species $n$ in quadrant $j$ and $p_j$ is the probability of quadrant $j$. The effectiveness of the method was evidenced by Alemany et al. [82], through evaluating the mixing quality of acrylonitrile butadiene styrene (ABS) resin with different colors. They figured out that both distribution and dispersion can be quantified by using a single metric. Moreover, a mixing index considering the effect of original inclusions with different sizes associated with weight average of entropy was constructed.

To compare the homogeneity of a state $P$ and a state $Q$, Pfeifer and Bandaru [83] proposed the usage of relative entropy $d(P||Q)$

$$d(P||Q) = \frac{1}{2} \left[ D(P||Q) + D(Q||P) \right] \geq 0 \quad (20)$$

where

$$D(P||Q) = S (P) - S (Q) \quad (21)$$

Herein, $S(P)$ and $S(Q)$ define the entropies of inclusion-matrix ensembles $P$ and $Q$, respectively. If $Q$ is the targeted homogeneity, $D(P||Q)$ indicates the relative ‘insufficiency’ between the two ensembles. The method is verified by CNTs-epoxy composites with pristine CNTs as well as surface-functionalized CNTs and deviation in homogeneity was clearly evidenced. Huo and Ren [84] tried to simplify the past methods based on Shannon’s entropy by proposing a mixing index ($\gamma$) to illustrate mixing homogeneity of inclusions

$$\gamma = \frac{S(P)}{\ln N} + \frac{d}{D_c} \quad (22)$$

where $S(P)/\ln N$ is the relative Shannon’s entropy, $D_c$ is the size of maximum agglomerate and $d$ is the single inclusion size. Therefore, both dispersion and distribution of inclusions in composite are evaluated. Apparently, ideal homogeneity can be achieved when mixing index ($\gamma$) reaches 2. This indicator was verified in CaCO$_3$-polyethylene based composites and samples with better homogeneity quality was found to have better flexural and tensile strength.

The major difficulty of quadrat method is to obtain optimal quadrat size, which is normally selected as squares. The importance can be interpreted as: a small quadrat size results in numerous cells without containing any inclusions, while a large quadrat size leads to similar number of particles in each quadrat, thus unable to figure out agglomerates. Therefore, change in quadrat size would lead to different result. The optimal size may be achieved by trial-and-error, but imperially, a quadrat size with approximately twice the main area of the inclusions is appropriate, although adjusting quadrat size based on the inclusion distribution was made as well [85]. Meanwhile, the spatial information within quadrat is lost, so that the distribution of inclusions cannot be well presented [61]. These two points should always be aware when applying this method.

5. Methods based on inclusion position and inter-distance

5.1. Free-path spacing

Luo and Koo [86] proposed a quantitative method based on the principle of stereology and performed random lines to intercept particles, resulted in a free-path spacing ensemble between inclusions $X=(x_i, i=1...N)$. The first process is similar to linear intercept distance method but differences exist: 1. Free-path spacing measures the spacing between single layers while linear intercept distance characterizes spacing between stacks; 2. Unlike linear intercept distance, free-path spacing indicator is independent to the inclusion loading level (Fig. 6). After collecting spacing data, the dispersion $(\delta)$ is calculated based on $\mu$ (mean value) and a standard deviation $\sigma$. For a dispersion range of $\mu \pm 0.1 \mu$, dispersion $D_{0.1}$ is expressed as

$$D_{0.1} = \int_{0.9 \mu}^{1.1 \mu} f (x) \; dx \quad (23)$$

while the frequency density $f_i$ is defined as

$$f_i = \frac{n_i}{N \cdot \Delta x} \quad (24)$$
where \( n_i \) is the number of data within interval \( \Delta x \) and \( N \) is the total number measured. Apparently, higher \( D \) value is corresponding to higher homogeneity of inclusions. Meanwhile, other deviation ranges such as \( 0.2\mu \) or \( 0.3\mu \) could be chosen as well for specific dispersion analysis, and the corresponding dispersion \( D \) is monotonous increasing with \( \mu/\sigma \). To verify this method, regular and clustered inclusion arrangements models are selected and their dispersion indicators \( D \) are compared based on their spacing frequency functions. Interestingly, to obtain \( \mu \) and \( \sigma \) values, the fitting distribution species (like normal distribution or lognormal distribution) would not cause apparent variation in calculated dispersion values.

Orientation is also considered in their another related study [87]. Two perpendicular arrays of parallel lines are applied to composites with isotropic while one array of lines is required for anisotropic samples. However, the purpose is mainly to enhance the accuracy of \( D \) indicator. Based on statistical homogeneity theory, Luo [88] introduced additional orientation indicator \( H_0 \) to measure the angular data concentration. For 2-D circular and 3-D spherical distributions, the corresponding indicators are integration of probability density functions within the range of \( 0.1\pi \) (\( H_{0,1} \)) are

\[
H_{0,1} = \int_{-0.1\pi}^{0.1\pi} f(\theta) \, d\theta
\]

and

\[
H_{0,1} = \int_{-0.1\pi}^{0.1\pi} \int_0^{0.1\pi} f(\theta, \phi) \sin \phi \, d\phi \, d\theta
\]

Practical examples are carried out by measuring the dispersion of carbon nanofiber-reinforced polymer composites based on TEM images and microstructures with small-size tactoids are managed to be identified. However, this method is scale and typically inappropriate for systems with significant tactoids [87] and systems with potential nanoscale reinforcement [89].

To address the disadvantages of aforementioned methods on characterizing inclusion agglomeration, Tyson et al. [75] proposed a dispersion parameter \( D \) together with an agglomeration quantity \( A \), which are determined by the inter-particle distance and the inclusion size, respectively. Herein, dispersion parameter \( D \) is estimated through the algorithm similar as the aforementioned method while the additional agglomeration quantity \( A \), within a certain interval \( \mu \pm 0.3\mu \), is related to the integral of lognormal distribution function, as evidenced by Luo [88].

\[
A_{0.3} = 1 - \int_{0.7\mu}^{1.3\mu} f(x_\mu) \, dx
\]

Verification was carried out by quantifying the arrangement of CNFs in aqueous solution. They figured out that bundled CNFs had smaller dispersion parameter value (\( D_{0.2} = 10.38\% \)) and larger agglomeration quantity (\( A_{0.3} = 73.29\% \)) than dispersed CNFs (\( D_{0.2} = 15.82\% \) and \( A_{0.3} = 66.77\% \)) at a loading of 0.5 wt\%. This method was proved to be equally efficient with optical and electrical visualization. However, some parts can be further improved. The bounds of agglomeration integral are better to be determined by fiber diameter rather than statistical mean and the distribution function may not always follow lognormal distribution.

Meanwhile, Glaskova et al. [90] noticed the technical difficulty in separation of inclusions and quantification of the inter-particle distance. In this way, they proposed the dispersion parameter \( D \) as the probability to fall in a certain range (area with radius \( R \)) of particle area distribution. For a probability density function following Gaussian distribution, we have

\[
D_b = \int_{0}^{\mu[1+k]} f(a) \, da = \frac{2k \mu}{\sqrt{2\pi} \sigma}
\]

where \( k \) is the coefficient for selected interval and \( f(a) \) is the probability density function within

\[
R = \sqrt{\frac{K_j}{l_{min}^2}}
\]

Herein, \( K_j \) is the selected particles in clusters and \( l_{min}^2 \) is the radius of space around particle. The proposed analysis was applied to evaluating model composite. At a specific filler content with different filler fraction for generating clusters, decrease of dispersion parameter \( D \) was observed accompanied with the increase of radius \( R \), because of larger filler fraction for forming clusters. Meanwhile, increase of filler loading led to the decrease of dispersion parameter \( D \), as
more fillers would facilitate clusters formation). Meanwhile, dispersion parameter $D$ was also applied to exhibit the time-dependent evolution of filler agglomerates with different loading concentration. System with larger filler concentration (1.0 wt%) required longer time to reach the optimal dispersion condition than that with lower amount (0.2 wt%). This parameter was also applied to estimate the influence of processing conditions on a MWCNT/epoxy composite system [91]. They figured out that ultra-sonication duration and temperature dominated the dispersion process rather than ultra-sonication power level.

5.2. Nearest neighbor distance

Nearest neighbor distance belongs to the methods based on microstructural features. The coordinate positions of inclusions, especially their centroid are recorded to measure the distances of them and their nearest neighbors (Fig. 7). Mathematically, the distances of a random inclusion set in composite have been proven to follow the Poisson’s distribution [37]. Clark and Evans [92] provided a classical example for using $R$ as a randomness indicator to quantify randomness by statistical analysis based on nearest neighbor distance:

$$R = \frac{\bar{r}_A}{\bar{r}_E}$$  \hspace{1cm} (30)

where $\bar{r}_A$ is the mean nearest neighbor distance of the sample while $\bar{r}_E$ is the mean nearest neighbor distance of the standard with ideal randomness arrangement. For a composite with inclusion population $N$ and density $\rho$, $\bar{r}_A$ and $\bar{r}_E$ can be further expressed as

$$\bar{r}_A = \frac{\sum r}{N}$$  \hspace{1cm} (31)

and

$$\bar{r}_E = \frac{1}{2\sqrt{\rho}}$$  \hspace{1cm} (32)

Therefore, indicator $R$ approaches 1 for ideal randomness and reaches 0 for complete aggregation. In addition, when inclusion arrangement is close to perfect lattice structure, such as repeating hexagon, $R$ would become larger than 1 and reaches an upper boundary of 2.1491. To distinguish clusters from background and evaluate significant parameters, additional variance indicator $R'$ was introduced

$$R' = \frac{s_A}{s_E}$$  \hspace{1cm} (33)

where $s_A$ and $s_E$ are the mean variance of nearest neighbor distance of the sample and random patterns. In this way, inclusion patterns are described by both $R$ and $R'$.

Bakshi et al. [93] proposed two complementary parameters and demonstrated in a CNT reinforced aluminum nanocomposite. Dispersion parameter ($DP$) is obtained by image analysis technique to characterize CNT cluster size, which we have already introduced in Section 3. Meanwhile, clustering parameter ($CP$) is based on nearest neighbor distance. For measuring nearest neighbor distance, the centers of CNTs were picked out and their positions in coordinates were recorded. Contour maps are introduced for better illustration (Fig. 8). Clustering parameter ($CP$) defines the degree of clustering, which is obtained by the following equation based on the fact that larger CNT fraction would facilitate CNT packing and leading to an increase in $CP$

$$CP = \frac{\text{Cumulative fraction of distances less than or equal to } 5D_{CNT}}{\text{Overall CNT fraction}}$$  \hspace{1cm} (34)

where $D_{CNT}$ is the mean diameter of CNT. The DP and CP values obtained from analyzing specific cross-section images were applied to analyze the elastic modulus by Halpin-Tsai relation, and compared with modulus measured by nano-indentation. This method was found to predict the high elastic modulus of the composite at low CNT fraction. However, the selection of $5D_{CNT}$ is arbitrary and more often based on experience or trial-and-error.

The aforementioned methods are based on distances between different inclusion elements, instead, Yourudkhani and Hubert [94] developed a quantitative approach relies on distances between inclusion elements and matrix elements. They proposed a new dispersion index ($DI$) as

$$DI = \frac{\mu}{\mu_u}$$  \hspace{1cm} (35)

and

$$\mu = \frac{\sum_{i=1}^{N_m} d_i}{N_m}$$  \hspace{1cm} (36)

where $\mu$ is the mean nearest neighbor distance and $\mu_u$ is the $\mu$ of an ideal homogeneous state. The number of matrix elements is represented by $N_m$ while $d_i$ indicates the inclusion-matrix distances. Other than ideal and random dispersion, other factors such as particle clustering, particle size and cluster distribution had been considered to verify the method’s sensitivity. Application was carried out based on MWCNT/epoxy composites treated at numerous temperatures. $DI$ value was evidenced to show good consistency with visual estimation. Besides, Zhang et al. [95] applied this method to study the re-agglomeration network of PMMA/epoxy/SWCNT systems. They found that $DI$ of CNT in the composite was small when mixed at room temperature but became larger at 100 °C. They found re-agglomeration would lead to enhancement in flexural modulus and strength caused by effective loading transfer.

5.3. Inter-particle distance

Unlike nearest neighbor distance method which only considers the closest gaps of an inclusion couple, inter-particle distance takes into account of gaps between all inclusions (Fig. 9). Hamming et al. [97] studied effect of inclusion distribution on $T_g$ shift by inter-particle distance method. 2-D geometrical distance was directly calculated based on the coordinates of inclusion centroids and numerically averaged.
to achieve mean distance between agglomerates $\bar{D}$ and average distance between agglomerates $\bar{A}$

$$\bar{A} = \frac{\sum \bar{D}}{N} = \frac{\sum (\bar{D}/n)}{N}$$

(37)

where $n$ is the number of inclusions in $N$ images, $\bar{D}$ is the mean distances between centroid of an inclusion, expressed as

$$\bar{D} = \frac{\sum \sqrt{(x_i-x_c)^2 + (y_i-y_c)^2}}{n-1}$$

(38)

Correlation between $\bar{A}$ and $T_g$ was evidenced by TiO$_2$ reinforced polymethylmethacrylate (PMMA) nanocomposites at 3 wt% loading. Sample with $\bar{A} = 4.16 \mu m$ has a smaller $T_g$ value ($110.5 \, ^\circ C$) than sample with $\bar{A} = 4.60 \mu m$ ($T_g = 116.6 \, ^\circ C$). Smaller $\bar{A}$ indicates larger contact area between inclusions and matrix. For a repulsive/de-wetting system like TiO$_2$-PMMA, increasing in surface area leads to decrease in $T_g$.

Focusing on inclusion arrangement in nanofibers, Blazer et al. [96] proposed a dispersion factor ($\beta$) considering both inclusion loading and fiber aspect ratio, which is the ratio of average to standard deviation of inter-particle distance

$$\beta = \frac{\mu}{\sigma}$$

(39)

where

$$\mu = \lambda \Gamma \left( 1 + \frac{1}{\kappa} \right)$$

(40)

and

$$\sigma^2 = \lambda^2 \left( r \left( 1 + \frac{2}{\kappa} \right) - \left( r \left( 1 + \frac{1}{\kappa} \right) \right)^2 \right)$$

(41)

Herein, $\lambda$ and $\kappa$ are the shape and scale parameters, respectively. Generally, larger dispersion factor indicates better homogeneity along the fiber direction. They introduced empirical model to scan the optimal condition and figured out best arrangement could be reached at a loading of 0.20 and D/d of 2.40 (Fig. 10).

Yazdanabaksh et al. [37] proposed dispersive work as a new concept to quantify arrangement of inclusions in composite, based on the fact that work is required to separate agglomer-

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Discrete permission calculation composite maximum.

Fig. 10 – Dispersion factor $\beta$ over the range of $D/d$ from 0 to 10 and $\phi$ from 1 to 20%. Reproduced from Ref. [96] with the permission from American Chemical Society.

5.4. Functional characteristics

For functional characteristics, complete spatial randomness (CSR) is typically regarded as the ideal inclusion arrangement. The empty space function $F(r)$ is the cumulative distribution function of distances between selected points and the nearest inclusions. Meanwhile, the nearest neighbor distance function $G(r)$ is the cumulative distribution function of nearest neighbor distance. Lieshout and Baddeley [100] proposed $J(r)$ function, based on the ratio of the former functions

$$J(r) = \frac{1 - G(r)}{1 - F(r)}$$

At CSR state, inclusions exhibit a Poisson distribution, of which $F(r) = G(r)$, and $J(r) = 1$. On the other hand, clustering and regularity are corresponding to $J(r) < 1$ and $J(r) > 1$, respectively. Meanwhile, the reduced second moment function $K(r)$ is able to describe spatial inclusion distribution as well, which is defined as the expected number of inclusions (simplified as points) within radius $r$ of a typical random point. Better statistical properties can be interpreted by using below variance function $L(r)$ and pair correlation function $g(r)$ [61]

$$L(r) = \sqrt{\frac{K(r)}{\pi}}$$

and

$$g(r) = \frac{1}{2\pi r} \frac{dK(r)}{dr}$$

Zhou et al. [61] tested the corrected detection probability and clustering degree of these functional algorithms. Comparing with other methods like quadrat method and Dirichlet tessellation, functional algorithm shows 100% corrected detection probability on boundary effect, however, they are feeble in quantifying single cluster patterns, especially $J(r)$ function.

Rempe et al. [101] applied 3D pair-correlation function to quantify the homogeneity of inclusions by average inter-particle distance. Rapley’s K-function $(K(r))$ in 3D form was applied for analyzing points within sphere $4/3\pi r^3$ with an overall inclusion density $\lambda = n/V$

$$K(r) = \frac{1}{\lambda n} \sum_{i=1}^{n} \sum_{j=1}^{n} I_r(d_{ij})$$

with $i \neq j$

and

$$I_r(d_{ij}) = \begin{cases} 1 & \text{if } d_{ij} \leq r \\ 0 & \text{otherwise} \end{cases}$$

Fig. 11 – Dispersive works of a random inclusion arrangement (left) and an agglomerated inclusion arrangement (right).
where \( n \) is the number of inclusions and \( V \) is the related volume. Ideal inclusion randomness gives \( K(r) = 4/3\pi r^3 \). When agglomeration takes place, the value of \( K(r) \) becomes higher. This method is verified to differentiate the states from agglomeration, randomness and homogeneity, based on epoxy nanocomposites filled with numerous silica nanoparticles.

5.5. Free-space length/gap statistics

Khare and Burris [102] found that inter-particle distance method is quite sensitive to inclusion numbers rather than inclusion distribution, because distances within agglomerates are larger than distances between agglomerates. To overcome this, they proposed a new concept called free-space length (\( L_f \)). Instead of measuring distances between particles, the size of unreinforced matrix domain with \( L_f^2 \) is characterized (Fig. 12). Smaller \( L_f \) could be obtained if inclusion arrangement becomes more homogenous. The appropriate \( L_f \) is corresponding to the largest square size of randomly square with the most probable number of covered inclusions is zero.

The calculation of unreinforced matrix domain is based on the assumption that they have the highest possibility for failure occurrence. However, agglomerates with larger size, they are more probable to be the failure initiator and pathway. In this way, effective free-space length (\( L_f^* \)) was further suggested

\[
L_f^* = L_f \left[1 + \left( \frac{1}{\alpha} \right)^n \right]
\]

(48)

where \( L_a \) is the agglomeration length, \( n \) is a sensitivity exponent and \( \alpha \) is the critical ratio. This modified method was applied to explain the variation of tensile modulus and elongation at break of \( \text{Al}_2\text{O}_3 \)-epoxy nanocomposites with different filler loading. At 1 phr, the small modulus (1415 MPa) and elongation (7%) are attributed to the unreinforced domain, which is indicated by a large \( L_a \) (415 nm) but small \( L_f \) (13 nm). Increasing in filler loading leads to enhancement in modulus (1680 MPa) and elongation (9.4%) simultaneously, due to appropriate filler distribution (\( L_t = 211 \text{ nm} \)) and dispersion (\( L_a = 78 \text{ nm} \)). However, further introducing fillers leads to severe agglomeration (\( L_t = 89 \text{ nm} \), \( L_a = 200 \text{ nm} \)), thus causes deterioration in both modulus (1491 MPa) and elongation (3.4%). The practical application verified the effectiveness of the method, which is sensitive to the dispersion state, density and length-scale [103]. However, it may be more suitable for particulate inclusions rather than fillers with large aspect ratios and the determination of \( n \) and \( \alpha \) is not convenient.

Suchitra et al. [103] applied the free-space length method for analyzing epoxy based nanocomposites reinforced by glass fibers, nano-alumina, nano-silica and micro-alumina trihydrate. They figured out that with smaller free-space length, nanocomposites with larger contact angle could be achieved and better surface tracking reliability was obtained. More recently, Rempe et al. [101] extended this method toward three-dimension and verified it by an epoxy-based nanocomposite. The 3D free-space length provides real 3D inclusion distribution in the matrix. Besides, it leads to the independence of the thickness of TEM slice.

Meanwhile, Anane-Fenin et al. [104] proposed the Dispersion Quantity (D) founded on the gap method for clustering analysis. \( D \) involves a gap factor (\( G_0 \)), particle spacing dispersity (\( \text{PSD}_1 \)) and particle size dispersity (\( \text{PSD}_2 \)), expressed as

\[
D = \left( \frac{3}{D_0} \right) \times 100\% \quad \text{where} \quad \frac{3}{G_0 + \text{PSD}_1 + \text{PSD}_2} \times 100\%
\]

(49)

where

\[
G_0 = \left[ \int_{x=1}^{b} f(x) \, dx \right] - \left[ \int_{a=1}^{b} f(x) \, dx \right]
\]

(50)

and

\[
\text{PSD} = \left[ \frac{\sum x_i^2}{N} \right] / \left[ \frac{\sum x_i}{N} \right]
\]

(51)

Herein, \( G_0 \) is the gap factor and the area between expected curve \( f(x) \) and observed curve \( f(x) \) while \( a \) and \( b \) are the inspected values. Determination of \( \text{PSD}_1 \) follows the inter-particle distance approach. This method was verified on real images while all the effect of distribution, inclusion spacing and size were able to be reflected. Larger agglomeration led to \( D \) value close to 0 while \( D \) equals to 1 for ideal lattice microstructure.

5.6. Delaunay triangulation and Dirichlet tessellation

In order to construct Delaunay triangulation, inclusions within characterization images are simplified as their centroids and the locations are recorded in coordinates. The inter-spacing of the centroids is scribed to generate an ensemble containing adjacent but non-overlapping triangles. Notably, generation of these triangles is not arbitrary. Two guidelines have to be followed in order to obtain the optimal triangulation [105], which are “empty circle”, minimum angle maximization and “empty circle criterion”. No fourth vertex exists in the circumcircle formed by three triangle vertices.

Meanwhile, Dirichlet tessellation, also known as Voronoi tessellation, has been re-invented several times in various disciplines for different applications, like Rogers in mathematics, Rhynsburger in geography, Gilber in crystallography, etc., together with numerous names [106]. Definitely, the distances between each vertex of Dirichlet tessellation and the vertices of the locating triangle are the same. In other words, the vertices of Dirichlet tessellation are the circumcenters of Delaunay triangles. Therefore, a Dirichlet tessellation is corresponding to a unique Delaunay triangulation (Fig. 13) [107], Dirichlet tessellation goes to infinity if not limited by the captured images. However, practical analysis should be carried out within a sample window. Mathematically, centroids of inclusions in the window \( W \) are considered as an ensemble \( P = \{ p_i \mid i = 1 \ldots N \} \), the polygon \( T_m \) of \( p_m \) is defined as

\[
T_m = \left\{ x \in W : d(x, \text{p}_m) < d(x, \text{p}_n) \quad \forall \text{m} \neq n, \text{p}_n \in W \right\}
\]

(52)

where \( d \) is the geometrical distance. The vertexes of the polygons are recorded to calculate their area \( A \) and the variation
coefficient $DT$ is used to quantify the homogeneity of inclusions, which can be calculated as

$$DT = \frac{\sigma_A}{A}$$  \hspace{1cm} (53)

where $\sigma_A$ is the standard deviation of polygon area $A$. Obviously, a larger average $DT$ value $DT$ indicates poor homogeneity and clustering. Zhou et al. [61] applied Dirichlet tessellation and used $DT$ to calculate metal matrix nanocomposites and can effectively detect clusters while unable to provide satisfactory result on clustering level. Sun et al. [108] proposed an improved Delaunay triangulation algorithm by convex hull calculation with Graham method and optimization.

Marcelpoil et al. [109] proposed area disorder $AD$ as an alternative to measure area heterogeneity of Dirichlet tessellation and defined within $[0,1]$ interval. Moreover, roundness factor homogeneity $RFH$ to describe the disorder of the geometrical properties. These parameters are defined as

$$AD = 1 - \left( 1 + \frac{\sigma_A}{A} \right)^{-1}$$  \hspace{1cm} (54)

and

$$RFH = 1 - \left( 1 + \frac{\sigma_{RF}}{RF} \right)^{-1}$$  \hspace{1cm} (55)

where

$$RF = \frac{1}{N} \sum_{i=1}^{N} \frac{4\pi A_i}{L_i^2}$$  \hspace{1cm} (56)

Herein, $RF$ is the average roundness factor, $A_i$ is the polygon area while $L_i$ is the polygon perimeter. Perfect order is indicated by both $AD$ and $RFH$ values ($AD = 0$, $RFH = 1$). In this way, centroids with aggregates or barren islets can be distinguished. This method is developed for theoretical biology analysis, but also adaptable to material science. Interestingly, Al-Ostaz et al. [107] discovered the strong correlation between Dirichlet tessellation and nearest neighbor distance method. As distance between nearest neighbors increases, the area of Voronoi polygon becomes larger. Therefore, stress concentration of the composite will decrease as the size of Voronoi cell increases.

Unlike the aforementioned statistical analysis based on Dirichlet tessellation, Bray et al. [110] developed measurement directly based on Delaunay triangulation. They defined a dimensionless value, named as Area Disorder of the Delaunay network ($AD_{del}$), which is a modification of area disorder ($AD$) proposed by Marcelpoil et al. [109].

$$AD_{del} = 1 - \left( 1 + \frac{2Ns_D}{L^2} \right)^{-1}$$  \hspace{1cm} (57)

where $N$ is the inclusion centroids number, $s_D$ is the standard deviation of Delaunay triangle’s area and $L^2$ indicates the area of the selected square window. $AD_{del}$ is applied to estimate the homogeneity of the inclusions in composites. Smaller $AD_{del}$ implies better homogeneity, when $AD_{del}$ reaches zero, perfect homogeneity is obtained with inclusion centroids arranged as crystal lattice. Meanwhile, random inclusion arrangement leads to a mean $AD_{del} < 0.478$. This method was verified by a random hard-core model as well as silica nanoparticle modified composite. However, for silica-rubber particle modified composite which contained clusters, selection of appropriate cluster is critical for determining $AD_{del}$ value. The minimum size for the window containing a cluster is

$$L \geq \sqrt{\frac{\pi \left( \frac{4s_{RF}}{2} \right)^2}{A_f}}$$  \hspace{1cm} (58)
where $A_f$ is the area fraction covered by inclusions and $l_{clus}$ is the cluster size. Jiang et al. [111] applied the aforementioned method to describe the spatial distribution of $B_3C$ inclusions in $Al$ matrix. They figured out that distribution of $B_3C$ inclusions is highly related to the size. Inclusions with large size generally located at the granular interface while small nano-inclusions preferred to stay within the grains.

Other than quantifying inclusion homogeneity based on the polygon or triangle area, Sul et al. [112] proposed a positional randomness index (dispersity index) which is used to show the homogeneity of inclusion arrangement in composite by virtual inter-particle potential. Delaunay triangulation was employed in scenarios with different arrangement states, including poor dispersion and distribution, poor dispersion but well distribution, well dispersion but poor distribution and well distribution and distributions (Fig. 1). Physical background was endowed for calculation, by applying Lennard-Jones potential to estimate dispersity index

$$\text{Dispersity index} = \sum N V(r) = \sum_{N} 4\epsilon \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6$$

where $\epsilon$ is the potential well depth, $\sigma$ is the distance to potential-zero position and $r$ is the inter-particle distance. The Lennard-Jones potential becomes larger as inclusions agglomerate. Meanwhile, modification of the expression was done as it becomes invalid if $r$ approaches zero (inclusion contact). This method was verified by a CNT-filled polymer based composite and considered variances in both dispersion and distribution levels. It was found that quantification of homogeneity through dispersity index facilitated the understanding of mechanical behaviors. Tensile strength of the composite was highly related to the dispersity index. Higher tensile strength could be achieved by lower dispersity index, which was corresponding to better dispersion state. By employing stereology, this method is able to be extended to 3-D analysis.

In general, Dirichlet tessellation/Delaunay triangulation is able to identify clustering, but had been proved to be insufficient for characterizing small variation of inhomogeneity [113].

## 6. Conclusions and perspectives

Although qualitative estimation based on visual observations remains the major way to evaluate inclusion arrangement in composites, increasing researchers have attempted to apply quantification methods to establish structure-property relationship, find optimal processing conditions and even predict material properties. Till now, numerous quantification methods have been developed over the past decades and advanced approaches to quantify inclusion homogeneity are emerged continuously, but no general approach is available to measure all types of microstructures. Methods based on inclusion features are able to evaluate dispersion quality rather than distribution quality. Methods based on inclusion position, such as quadrat method, can reflect global distribution, but local distribution within quadrat is ignored. Methods based on inclusion position and inter-distance are especially effective in certain inclusion arrangement, but inappropriate for other types. One example is inter-particle distance method, which is sensitive to inclusion loading but insensitive to dispersion quality [89]. Some methods require ideal microstructure as standard, but ideal state may not be unique [107]. Some methods propose multiple indicators to cover all the parameters as much, but making comparison between samples becomes difficult. Grouping them together would also lead to another problem, which is the determination of their weight factors.

The aforementioned methods are mostly related to quantify the homogeneity level of practical state, which is preferred in applications focusing on mechanical, rheological and optical performances. Meanwhile, for thermal and electric applications, such as thermal/electric conductive materials, inclusion arrangement in certain conductive network rather than homogeneity is preferred, but corresponding quantification method is rare, which is likely to have active development in the near future.

## Author contributions

L. Zhang and Z. Chen contributed equally.

## Conflicts of interest

The authors declare no conflicts of interest.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2020.01.067.

## References


[70] Zhang Y, Park SJ. Influence of the nanoscaled hybrid based on nanodiamond@graphene oxide architecture on the rheological and thermo-physical performances of carboxylated-polymeric composites. Compos A 2018;112:356-64.


