Tools To Measure Dispersion Descriptors From Polymer Nanocomposites

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TOOLS TO MEASURE DISPERSION DESCRIPTORS FROM POLYMER NANOCOMPOSITES

A Thesis Presented

by

Kevin Zuniga Cuellar

to

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of

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Abstract

MaterialsMine is a new open-source data resource with the goal of supporting faster nanocomposite and metamaterials discovery and design. One goal of MaterialsMine is to provide tools that help researchers gain a better fundamental understanding of nanofiller behavior. While it is well known that the dispersion of nanofillers in nanocomposites critically controls properties, there is limited quantitative data. This thesis develops a methodology for quantitatively measuring the dispersion of polymer nanocomposites quickly and within the MaterialsMine data framework. The method processes transmission electron microscopy (TEM) images from MaterialsMine. TEM images are first pre-processed and transformed into binary images. Then the binary images are processed by microstructure characterization algorithms such as correlation functions, physical descriptors, and spectral density functions to obtain critical dispersion features (such as interfacial area or average cluster size). We used the new tools to quantify about 100 images and incorporated the dispersion descriptors into MaterialsMine. We then developed correlations between materials properties and dispersion descriptors. The results obtained from the new methodology demonstrate consistent outcomes across various image processing methods. Moreover, the correlation analysis reveals a consistent relationship between AC breakdown strength and the average nearest cluster center distance.
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Chapter 1

Introduction

In recent years, the attention surrounding polymer nanocomposites (PNCs) has grown significantly, primarily due to their distinctive properties. The dispersion of these nanofillers within the polymer matrix, along with the interfacial area between matrix and filler, emerges as a crucial factor that directly impacts the overall performance and properties of PNCs. To fully harness the potential of nanofillers and maximize the enhanced characteristics of PNCs, it is essential to achieve effective filler dispersion and optimize the interfacial area. Unfortunately, most studies on PNCs lack quantitative measurements of dispersion, resulting in a primarily qualitative correlation of properties with dispersion. Although several quantitative dispersion analyses have been proposed in the past [1, 2, 3], none have gained widespread acceptance within the material science community due to their complexity and limited reflection of the proposed benefits. This thesis aims to address these challenges by developing a methodology for rapidly quantifying the dispersion of polymer nanocomposites within the MaterialsMine framework. The proposed tools will enable the quantification of dispersion descriptors in a range of spherical nanocomposites. To demonstrate the
potential of the tool, this thesis will explore the quantitative relationships between dispersion and material properties, shedding light on their interplay. By providing a comprehensive quantitative analysis of dispersion, this study aims to contribute to the advancement of PNC research and aid in the development of optimized polymer nanocomposites.

1 POLYMER NANOCOMPOSITES

Polymer nanocomposites (PNCs) are a class of materials composed of polymers with dispersed nanofillers. These nanofillers, typically ranging in size from 1 to 100 nanometers, impart unique properties to PNCs that are not found in traditional polymer composites. By incorporating nanoparticles into polymers, various material characteristics such as strength, stiffness, thermal stability, and electrical conductivity can be enhanced [4]. This enhancement positions PNCs as promising alternatives to conventional materials, particularly in specialized applications.

PNCs can be classified based on the dimensions of the nanofillers, namely one-dimensional, two-dimensional, and three-dimensional [5]. One-dimensional nanofillers possess one dimension less than 100 nm, frequently in the form of tubes or filaments. Carbon nanotubes [6] are an example of one-dimensional nanofillers. Two-dimensional nanofillers have a two dimensions less than 100 nm and often appear as sheets. Examples of two-dimensional nanofillers include Montmorillonite clay [7] and nanographene platelets [8]. On the other hand, three-dimensional nanofillers have all three dimensions less than 100 nm and typically appear as spherical structures. Notable instances of three-dimensional nanofillers include nano-silica [9], nano-alumina [10], and nano-
titanium oxide [11]. The intrinsic properties of three-dimensional nanofillers, such as stability, high refractive index [12], electrical dielectric properties [13], and ultraviolet resistance, contribute to their significance in PNCs. This thesis targets three-dimensional nanofillers also known as spherical polymer nanocomposites due to the symmetrical morphology which the computational methods have been developed for.

1.1 INTERFACIAL AREA

The interface serves as the transition area connecting the nanofillers and the polymer matrix [4]. In the case of PNCs, the interfacial region has a considerably larger volume fraction compared to conventional composites. As a result, the properties of this interface have a substantial influence on the properties of the nanocomposite material. The interfacial area is influenced by factors such as nanofiller type, dispersion, particle size and shape. In-depth investigations documented in numerous research articles have shed light on the significance of the interface area in polymer nanocomposites [14, 15, 16].
Figure 1.1: Drawing of a polymer nanocomposite showcasing its interfacial region.

For instance, Roy et al. [14] conducted a study that compared nanocomposites consisting of silica nanoparticles and micron-sized silica particles. Their findings highlighted the significant influence of the increased interface area on the dielectric behavior of the composite.

Furthermore, in J. K. Nelson et al. [15], a reduction in space charge and an increase in dielectric strength was documented for the nanofiller TiO$_2$ in epoxy resin when compared with its micron size TiO$_2$ filled epoxy composites.

In addition, the impact of interfacial area on the dielectric properties of polymer nanocomposites was explored by Virtanen et al. [16]. By deliberately increasing the interfacial area between the matrix and the nanofillers, they observed notable enhancements in dielectric properties. The augmented interfacial area facilitated greater electron trapping, resulting in higher dielectric breakdown strength (DBS). Even at a low filler loading of 2 wt.%, the nanocomposite demonstrated significantly
improved DBS and permittivity compared to the reference epoxy.

These studies collectively emphasize the critical role of the interfacial area in polymer nanocomposites. The interfacial area profoundly influences the overall performance of nanocomposites, encompassing mechanical, electrical, and thermal properties. Thus, comprehensive understanding and precise control of the interface area are vital for tailoring the properties and optimizing the performance of polymer nanocomposite materials.

1.2 Dispersion

Filler dispersion is a fundamental aspect of fabricating polymer nanocomposites (PNCs) and refers to the distribution of nanofillers within the polymer matrix. A well-dispersed nanocomposite is one in which the nanofiller particles are evenly distributed throughout the polymer matrix, with no agglomeration.
Figure 1.3: Drawing that illustrates a comparison between good dispersion and agglomerated nanofillers in a polymer nanocomposite.

Good dispersion is important for polymer nanocomposites because it affects the properties of the nanocomposite in several ways. First, good dispersion maximizes the interfacial area between the two phases. This, in turn, leads to improved mechanical, thermal, and electrical properties of the nanocomposite [17].

In addition, good dispersion prevents the nanofiller particles from agglomerating. Agglomeration of the nanofiller particles can lead to defects in the nanocomposite, such as voids and cracks. These defects can weaken the mechanical properties of the nanocomposite and reduce its performance [18]. Furthermore, the agglomeration reduces the transparency [12] and dielectric breakdown strength of the material [19].

Several factors influence the dispersion of fillers in PNCs. One critical factor is the compatibility between the nanofillers and the polymer matrix. A strong affinity between the filler and the polymer promotes better dispersion. Techniques such as functionalization or coating of the nanofillers can be employed to enhance compatibility and improve dispersion [19].

The processing methods used during PNC fabrication also play a vital role in
achieving filler dispersion. High shear mixing techniques such as melt mixing are commonly employed to disperse the nanofillers within the polymer matrix. These methods apply mechanical forces to break up filler agglomerates and promote their dispersion [20]. It is crucial to optimize the processing conditions, such as temperature, mixing time, and shear rate, to ensure effective filler dispersion.

Characterization techniques, such as microscopy (e.g., scanning electron microscopy - SEM, transmission electron microscopy - TEM), X-ray diffraction, and spectroscopic analysis, are employed to evaluate the filler dispersion in PNCs [21, 22]. These techniques are used to examine the distribution, size, and morphology of the nanofillers within the polymer matrix.

2 MATERIALS Mine

MaterialsMine is an open-source data resource designed for the analysis and design of nanocomposites. The MaterialsMine project consists of two branches: NanoMine and MetaMine. NanoMine focuses on nanocomposite data, while MetaMine specializes in metamaterials data [23].

2.1 NanoMine

NanoMine was developed in response to the Material Genome Initiative (MGI) a national initiative to build an infrastructure that accelerates and sustains materials discovery in the United States [23]. The objective of NanoMine is to provide a modeling and analysis platform that supports material prediction and design of nanocomposites by leveraging experimental and computational data from public re-
search resources. This approach aims to capture physical properties reported in the literature and from individual research labs, as well as material processing conditions using standardized format and terminology. With sufficient data accumulated in each of the processing-structure-property domains, statistical correlations are developed to link processing conditions, quantified microstructure information, and macroscopic property response through parameterized formulations and statistically meaningful correlations, coupled by image analysis techniques and physics-based simulations.

The NanoMine approach provides a platform for the design and analysis of new functional nanocomposite materials, with the goal of expanding the prediction capability of the current system and creating a sustainable public infrastructure for research and development of new nanocomposite materials. As of 2023, the NanoMine database contains over 1700 unique samples from more than 200 research papers, encompassing 100 types of polymers and more than 20,000 data points [24].

2.2 Analysis tools

In addition to serving as a repository for polymer nanocomposite data, NanoMine provides advanced analysis tools for microstructure characterization and reconstruction (MCR), as well as image preprocessing capabilities like image binarization. These tools facilitate the calculation of statistical data and extraction of physical descriptors from sample images of polymer nanocomposites [24].

Image binarization

Image binarization is the process of converting a grayscale image into a binary image, reducing the information to black and white. This transformation involves finding a
threshold value to classify pixels as either white or black. Various thresholding algorithms are available that utilize statistical methods such as mean, median, entropy, and variance. NanoMine currently offers two image binarization algorithms: Otsu and Niblack.

The Otsu method [25], named after its author Nobuyuki Otsu, is an automatic thresholding algorithm that calculates the optimal threshold by maximizing the inter-class intensity variance. It models a grayscale image as a bi-modal distribution, where one peak represents the foreground pixels and the other represents the background pixels. Otsu’s algorithm automatically determines the threshold value that minimizes the intra-class variance, resulting in the best separation of foreground and background pixels and generating a binary image with optimal differentiation.

The Niblack binarization [26], proposed by W. Niblack in 1986, is a local thresholding technique for grayscale-to-binary image conversion. It calculates a threshold for each pixel based on its local neighborhood, determined by a predefined window size. The algorithm computes the mean and standard deviation of pixel values within the neighborhood, and the threshold is obtained by adding a dynamically determined offset (a multiple of the standard deviation) to the mean value. The adaptive nature of the Niblack algorithm allows it to handle variations in illumination and contrast across different image regions.

While the Niblack algorithm is computationally efficient and straightforward to implement, it may not be suitable for images with uneven illumination or complex backgrounds, as it assumes a uniform background within the local neighborhood. Nonetheless, the Niblack algorithm offers a valuable approach for segmenting grayscale images into binary representations, facilitating further analysis and process-
ing of the image data.

Considering the specific conditions of the analyzed sample images, including increased blurriness, uneven light brightness, and uneven background, it was crucial to expand the collection of image binarization tools to handle a high number of image variations. This thesis expands the image binarization tools to include more recent algorithms such as: Bernsen [27], Sauvola [28], Wolf [29], Gatos [30], NICK [31], Su [32], T.R. Singh [33], Bataineh [34], ISauvola [35] and WAN [36].

**Microstructure characterization**

Microstructure characterization in polymer nanocomposites involves analyzing and understanding the arrangement, distribution, and interactions of constituent materials at a nanoscopic scale. It encompasses the study of morphology, spatial organization, and size of nanoparticles or fillers within the polymer matrix.

Accurate microstructure characterization is essential for several reasons. It provides insights into the dispersion or agglomeration of nanofillers within the polymer matrix, directly influencing material properties and performance. The spatial arrangement of fillers affects mechanical, thermal, electrical, and optical properties, among others.

By characterizing the microstructure of polymer nanocomposites, researchers gain insights into the fundamental mechanisms governing material behavior and properties. This information is crucial for understanding structure-property relationships, optimizing design and formulation, and enabling the engineering of advanced polymer nanocomposite materials with tailored properties.
3 Correlation functions

Correlation functions in polymer nanocomposites are mathematical tools used to analyze and quantify the spatial distribution and arrangement of constituent materials at various length scales. These functions provide valuable insights into the structural characteristics and behavior of the nanocomposite system.

3.1 Two point correlation function

The two-point correlation function is a mathematical tool used to analyze the spatial distribution and arrangement of constituent materials in a polymer nanocomposite at a certain length scale. It provides information about the likelihood of finding two points within the system in specific phases or regions [37]. It’s equation is described as follows:

\[
\xi_2(|x_1 - x_2|) = \langle \delta(x_1)\delta(x_2) \rangle
\]  

(1.1)

where \(|x_1 - x_2|\) describes the absolute distance between two points \(x_1\) and \(x_2\). \(\delta(x_1)\) and \(\delta(x_2)\) represent the density contrast at positions \(x_1\) and \(x_2\), respectively. The density contrast is the deviation of the local density of objects from the mean density. The equation expresses the two-point correlation function \(\xi_2(|x_1 - x_2|)\) as the average of the product of the density contrasts \(\delta(x_1)\) and \(\delta(x_2)\) at two different positions \(x_1\) and \(x_2\).

The two-point correlation function measures the probability that two points in a material system are both located in a particular phase or region. It examines the
correlation between pairs of points and quantifies the frequency of different phase combinations.

For example, in a binary system such as a black-and-white image representing a polymer nanocomposite, the two-point correlation function calculates the probability that both ends of a vector will land in a specific phase. The possible outcomes are black/black, black/white, white/black, and white/white.

By analyzing the two-point correlation function, researchers can gain insights into the degree of clustering or dispersion of nanoparticles or fillers within the polymer matrix [38]. A high correlation value suggests a strong tendency for the constituent materials to aggregate or cluster together, while a low correlation value indicates a more uniform distribution.

3.2 Lineal path function

The lineal path function (LPF) is another mathematical tool used in the analysis of the microstructure of polymer nanocomposites. It provides insights into the connectivity and spatial arrangement of phases within the material system.

The lineal path function measures the likelihood that a line segment of a specific length (denoted as ’r’) lies entirely within a particular phase or region of the polymer nanocomposite. It quantifies the probability that a randomly placed line segment of length ’r’ remains within a single phase without crossing phase boundaries.

To calculate the lineal path function, a vector of length ’r’ is randomly placed within the microstructure of the polymer nanocomposite. The function then determines the probability that the vector remains entirely within one phase. As the length of the line segment increases, the chances of the vector being fully contained within
a single-phase decrease. It’s equation is described as follows:

\[ L(\Delta x) = P\{I(\vec{x}) = 1, I(\vec{x} + \delta \vec{x}_1) = 1, \ldots I(\vec{x} + \Delta \vec{x}) = 1\} \] (1.2)

Equation 1.2 represents the lineal path function, \( L(\Delta x) \), used in percolation theory to determine the probability of finding a continuous path of connected points in a lattice or network. The function \( L(\Delta x) \) is defined as the probability that there exists a sequence of connected occupied points starting from a given point \( \vec{x} \) and extending up to a neighboring point \( \vec{x} + \Delta \vec{x} \) with a displacement vector \( \Delta \vec{x} \). The probability is computed by considering the product of indicator functions, \( I(\vec{x}) = 1 \) and \( I(\vec{x} + \delta \vec{x}_1) = 1 \), representing whether the points \( \vec{x} \) and \( \vec{x} + \delta \vec{x}_1 \) are occupied or connected. The equation encapsulates the concept of forming continuous paths of connected points, and the ellipsis indicates that the pattern repeats for all neighboring points between \( \vec{x} \) and \( \vec{x} + \Delta \vec{x} \), enabling the calculation of the overall probability of a lineal path within the lattice or network.

The lineal path function provides valuable information about the connectivity and percolation behavior of different phases within the polymer nanocomposite. It helps characterize the extent of phase separation, the formation of interconnected pathways, and the influence of filler dispersion on the material’s properties.

By analyzing the lineal path function, researchers can gain insights into the effective transport properties, such as electrical conductivity or diffusion pathways, within the polymer nanocomposite. It is particularly useful in understanding how the spatial arrangement of nanoparticles or fillers affects the material’s performance and functionality.
4 PHYSICAL DESCRIPTORS

Polymer nanocomposite physical descriptors are quantitative measures or properties that provide information about the physical characteristics and behavior of the material. These descriptors describe various aspects of the nanocomposite’s structure, morphology, and physical properties.

4.1 AVERAGE NEAREST CLUSTER CENTER DISTANCE

The average nearest cluster center distance (ANCC) is a physical descriptor used in the analysis of polymer nanocomposites to quantify the spatial distribution of nanoparticles or fillers within the polymer matrix. It provides information about the clustering tendency of the fillers and their arrangement in the material.

The ANCC is calculated by first identifying the cluster centers within the PNC. Cluster centers represent the central points or centroids of groups or clusters of nanoparticles. These clusters are formed based on criteria such as proximity or similarity of the nanoparticles’ positions. ANCC was calculated using the association function in Equation 1.3, $S_i^{(t)}$ used in the context of data clustering or classification algorithms.

$$S_i^{(t)} = \{x_p : ||x_p - m_i^{(t)}||^2 \leq ||x_p - m_j^{(t)}||^2 \forall j, 1 \leq j \leq k \}$$ (1.3)

The function $S_i^{(t)}$ is defined as the set of data points $x_p$ that are associated with a specific cluster or class $i$ at time $t$. This association is based on a distance criterion, where each data point $x_p$ is compared to the cluster centers $m_i^{(t)}$ of all clusters $i$ at
time $t$. The criterion for association is that the squared distance from $x_p$ to the cluster center $m_i^{(t)}$ is less than or equal to the squared distance from $x_p$ to the cluster center $m_j^{(t)}$ for all other clusters $j$ in the range of $1 \leq j \leq k$, where $k$ is the total number of clusters at time $t$. In other words, the data point $x_p$ is assigned to cluster $i$ if it is closer to the cluster center $m_i^{(t)}$ than to any other cluster center at that time.

Once the cluster centers are determined, the ANCC is computed by measuring the average distance from each nanoparticle to the nearest cluster center. It provides an estimate of the average proximity of the nanoparticles to their respective cluster centers.

A lower ANCC value indicates a more uniform distribution of nanoparticles within the PNC. This suggests that the nanoparticles are evenly dispersed throughout the polymer matrix, with a balanced spatial arrangement. On the other hand, a higher ANCC value suggests the presence of clustering or aggregation of nanoparticles, indicating a less uniform distribution.

The ANCC is a useful physical descriptor in characterizing the spatial arrangement of nanoparticles in PNCs because it provides quantitative information about the degree of clustering or dispersion. It can help assess the effectiveness of processing techniques, dispersion methods, or surface modification strategies in achieving a desired nanoparticle distribution within the polymer matrix.

4.2 Number of clusters

The number of clusters is a physical descriptor used to characterize the distribution of nanofillers within a polymer nanocomposite. It refers to the count or quantification of distinct agglomerations or clusters formed by the nanofillers in the matrix material.
The number of clusters was calculated as a computed value from the association formula in Equation 1.3.

In a well-dispersed nanocomposite, the nanofillers are uniformly distributed as individual particles or small clusters throughout the polymer matrix, resulting in a high number of clusters. This indicates a high level of dispersion and a more homogeneous distribution of the nanofillers. Conversely, a low number of clusters at the same volume fraction suggests poor dispersion, where the nanofillers tend to agglomerate or cluster together.

4.3 Volume fraction

Volume fraction \( V_f \) is a physical descriptor used to quantify the relative proportion or fraction of a specific component, such as nanofillers, within a polymer nanocomposite. It represents the ratio of the volume occupied by the component of interest to the total volume of the composite material. Its equation is described as follows:

\[
V_f = \frac{\#b_p}{\#b_p + \#w_p}
\] (1.4)

Where \( \#b_p \) is the total count of black pixels and \( \#w_p \) is the total count of the white pixels.

In the context of polymer nanocomposites, the volume fraction is a significant parameter that offers valuable insights into the concentration or loading of nanofillers within the polymer matrix. It plays a critical role in determining the overall properties and performance of the composite material. However, one limitation in using the area fraction as an estimate of volume fraction from Transmission Electron Microscopy
(TEM) images is the projection of the 3D image into a 2D plane. This projection can lead to an overestimation of the volume fraction [39].

4.4 **Ifiller**

The filler phase’s surface area (ifiller) refers to the collective area of interfaces between the nanofillers and the surrounding polymer matrix. It represents the external surface area of the filler particles and directly influences the interaction and bonding between the fillers and the polymer matrix. A larger surface area of the filler phase provides more opportunities for interactions with the polymer matrix. The calculation of the filler phase surface area depends on the shape and geometry of the filler particles. Mathematical formulas specific to the shape, such as spheres or cylinders, can be used to determine the surface area. In this thesis, the nanoparticle was modeled as a sphere using the following equation.

\[ A = \pi d^2 \]  \hspace{1cm} (1.5)

Hassinger et al. [40] proposed an intermediate descriptor called volume fraction normalized filler surface area, which extends the value of ifiller to include volume fraction. This intermediate descriptor has been selected as the preferred dispersion descriptor for the present thesis. Consequently, when calculating for ifiller we will be employing the calculation of the normalized volume fraction surface area. Equation 1.6 describes the new ifiller equation where \( P_c \) is the perimeter of the cluster, \( A_c \) is the area of the cluster and \( V_f \) is the volume fraction. \( A_c \) and \( P_c \) were derived from Equation 1.3 and \( V_f \) was calculated using Equation 1.4.
\[ i_{filler} = \sum \frac{P_c}{A_c V_f} \] (1.6)

In summary, quantifying dispersion is crucial to comprehensively understand the properties of nanocomposites. NanoMine serves as a robust repository for polymer nanocomposite data and requires an equally strong tool to help researchers quantify dispersion effectively. The following chapter explains a methodology for swiftly and quantitatively measuring the dispersion of polymer nanocomposites within the MaterialsMine data framework.
CHAPTER 2

METHODOLOGY

This chapter outlines the steps followed and the tools created to be able to process polymer nanocomposite material data from NanoMine and calculate the microstructure characterization descriptors. The overall procedure can be separated into three stages: image collection, image processing and data collection and analysis.

1 IMAGE COLLECTION

The image collection process commences by retrieving the targeted PNC (Polymer Nanocomposites) material data from NanoMine. Our specific interest lies in acquiring data related to spherical polymer nanocomposites that incorporate sample images. NanoMine offers several avenues to access its knowledge graph, but to ensure the presence of an image for each nanocomposite sample, we opt to utilize the GraphQL endpoint, which effectively handles image delivery. Developed by Meta [41], GraphQL serves as a query language that establishes a convenient abstraction layer between users and API endpoints. Its declarative nature allows users to precisely specify the
desired properties while receiving the response in a consistent format. Figure 2.1 illustrates the query utilized to request all available images from NanoMine.

```
query Images($input: ImageQueryInput) {
  images(input: $input) {
    totalItems
    pageSize
    pageNumber
    totalPages
    hasPreviousPage
    hasNextPage
    images {
      file
      description
      microscopyType
      type
      metaData {
        title
        id
        doi
        keywords
        sampleID
      }
    }
  }
}
```

*Figure 2.1: Code snippet of the GraphQL query used to request all the images from NanoMine.*

Following the data retrieval, a series of filtering passes are implemented to selectively eliminate sample images that fail to meet the criteria for spherical polymer nanocomposites. Initially, we employ a Python script to filter images based on microscopy type and eliminate those with invalid URLs. Subsequently, a manual inspection process is conducted to identify and exclude images of notably poor quality or those that cannot be accurately binarized. Additionally, it is essential to identify and remove duplicated images as well as separate multipaned images into distinct components. Through the application of these filter passes and rigorous manual in-
spection, we successfully generate a refined subset of “clean” data, which shall serve as the foundation for our subsequent analysis. Figure 2.2 provides a comprehensive summary of the image processing steps involved in transforming raw data into working data. The diagram outlines the sequential stages of the process such as querying and image filtering.

Figure 2.2: Summary of the preprocessing steps to convert raw image data into working data.

2 Image processing

The image processing stage begins by cropping the specific region of interest that needs to be binarized. This step excludes scale bars and other image annotations from the subsequent processing steps. At the same time, the length and scale of the
scale bar are measured to convert pixel distances into nanometers.

Next, the image undergoes binarization, which involves converting it into a black-and-white representation. This process helps in distinguishing the polymer matrix as white and the nanofillers as black. Binarizing the image is important for filtering out background noise and emphasizing the distribution of nanofillers dispersion.

![Figure 2.3: From left to right, TEM micrograph of PMMA SiO$_2$, targeted area to be binarized and its binary transformation.](image)

Originally, the plan was to use NanoMine image binarization tools. However, these tools had limitations in terms of thresholding options and the number of iterations required, which affected the quality and speed of binarization. Binarizing images involves numerous iterations to filter out background while preserving the nanofillers. Each image may have different parameters depending on its condition. Since suitable tools were lacking, a new and more dynamic image binarization tool was developed. This new tool not only provides immediate feedback for faster parameter adjustment, but also incorporates a wider range of recently developed binarization algorithms.
2.1 NEW BINARIZATION TOOL

The newly developed binarization tool is a web-based application, meaning that all computations are performed within the browser environment. It encompasses all the supported binarization algorithms available in NanoMine, while also incorporating more recent algorithms such as Bernsen [27], Sauvola [28], Wolf [29], Gatos [30], NICK [31], Su [32], T.R. Singh [33], Bataineh [34], ISauvola [35] and WAN [36]. This enhanced binarization tool offers on-demand transformations, dynamically responding to changes in parameters. Within its graphical interface, an image slider facilitates easy comparison between the original image and its transformed version. Underlying the tool’s functionality is a C++ code that has been compiled into Web Assembly using Emscripten enabling execution within a web environment.

This novel image binarization tool significantly accelerates the transformation of grayscale images into black and white. The tool’s on-demand computation allows for effortless exploration of different binarization algorithms and parameter settings, empowering users to select the most effective tool for their specific requirements.
2.2 Extracting descriptors from binary images

The concluding step within the image processing stage involves the extraction of numerical descriptors from the binary images. To perform this computation, a Python module was developed, drawing significant inspiration from Xu et al.’s work [3] in MATLAB. However, certain modifications were implemented to enhance performance by leveraging Python libraries such as NumPy, SciPy, and scikit-image. This language migration from MATLAB to Python brought several advantages, including a reduction in server complexity for NanoMine’s microstructure code, resulting in improved response times. The current implementation faced challenges related to the allocation of child processes to emulate a MATLAB environment within a Node server, causing significant delays in response. To address this, the upcoming version of the computational server will transition from a Node environment to a Python environment. By having the descriptor code written in the same language as the host server, seamless integration and native utilization of the descriptor code can be achieved without the need for provisional environments.

The numerical descriptors extracted from the binary images encompass volume fraction, number of clusters, average nearest cluster center distance, and surface area of the filler phase (i.e., ifiller). These specific descriptors were selected based on prior studies [3, 40, 42] where they exhibited considerable promise in accurately characterizing particle dispersion.
3 Data collection and analysis

The data collection and analysis process commence by acquiring the materials properties associated with each nanocomposite sample image. NanoMine offers multiple avenues to access this information, and for this task, we utilize the XML viewer tool. This recently developed tool enables the display of polymer nanocomposite data in XML format. Noteworthy properties of polymer nanocomposites include glass transition temperature, dielectric permittivity, imaginary dielectric permittivity, dielectric breakdown strength, tensile modulus, tensile stress, elongation at yield, elongation at break, strain rate, ultimate strength, impact strength, fiber tensile strength, melting temperature, crystallization temperature, and degree of crystallization, among others. It is important to note that not all polymer samples possess every property. Hence, careful selection of properties with the highest number of available data points was crucial.

Among the properties, the glass transition temperature, AC dielectric breakdown strength, and tensile modulus were found to have the most data points. To facilitate meaningful comparisons, the tensile modulus and dielectric breakdown strength were normalized using the bulk property of the polymer. Additionally, the change in glass transition temperature relative to the polymer was recorded. These properties were chosen to ensure a more normalized comparison across different properties, which can be subsequently contrasted with dispersion descriptors.
Chapter 3

Results and conclusion

Following the methodology discussed in Chapter 2, 100 images were transformed and processed using the new binarization and descriptor tools. Table 3.1 and 3.2, and Figure 3.1 shows an example of the outputs to illustrate the results. Starting from Figure 3.1, we can show that the image processing step was able to correctly binarize the fillers regardless of the uneven background. Table 3.1 shows the numerical descriptor calculated from the binary image in Figure 3.1. Finally, Table 3.2 are the material properties from Bell et al, experiment [43], supplied by NanoMine.

Figure 3.1: From left to right, TEM micrograph from “Investigation of dielectric breakdown in silica-epoxy nanocomposites using designed interfaces” [43], cropped area of interest, binary representation of TEM micrograph.
Table 3.1: Numerical descriptors calculated by analyzing Figure 3.1 (Average nearest cluster center distance (ANCC), Volume fraction (VF), Number of clusters (NC), Average cluster size (ACS))  

<table>
<thead>
<tr>
<th>ANCC (nm)</th>
<th>VF</th>
<th>NC</th>
<th>ACS (nm)</th>
<th>Ifiller</th>
</tr>
</thead>
<tbody>
<tr>
<td>52.4 ±3</td>
<td>0.05 ±0.002</td>
<td>421 ±25</td>
<td>73.5 ±14</td>
<td>0.85 ±0.02</td>
</tr>
</tbody>
</table>

Table 3.2: Material properties of Figure 3.1 supplied by NanoMine (AC dielectric breakdown strength (AC DBS))  

<table>
<thead>
<tr>
<th>AC DBS (KV/mm)</th>
<th>Normalized AC DBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>1.3</td>
</tr>
</tbody>
</table>

1  Tools usage

1.1 Image binarization

The image binarization tool is readily accessible on the web and offers an open-source code. Utilizing this tool is straightforward; users can easily upload their images and select the most suitable binarization algorithm to meet their specific requirements. The flexibility of the tool allows users to experiment with various binarization methods until they achieve the desired output. Additionally, certain binarization techniques offer adjustable parameters to fine-tune the results according to their preferences.

For optimal outcomes, it is advisable to begin by adjusting the 'k' value, which directly influences the thresholding level. By increasing the 'k' value, users can effectively reduce background noise and attain a cleaner output. Once the desired level of background noise removal is attained, further refining the results can be accomplished by adjusting the window size to better define the nanofillers. The
tool provides a convenient slider that enables users to easily compare the original image with its transformed version, facilitating a straightforward assessment of the effectiveness of the binarization process.

Figure 3.2: Image of the new binarization tool using the Gatos threshold [30] in a TEM micrograph.

Once users are satisfied with the results, they can simply download the binarized image by clicking the download button, making it easy to integrate the processed image into their research or other applications. Figure 3.2 shows an example of the working environment transforming a TEM microstructure.

1.2 Descriptor library

The descriptor code is freely available as open source and can be easily downloaded from the GitHub. Setting up the code is a straightforward process; users need to install the required dependencies listed in the requirements.txt file.
Each descriptor is implemented as a function, making it convenient to use by simply importing the desired descriptor into your project. The input for each descriptor is a binary array. To facilitate the transformation of images into arrays, you can utilize libraries like Pillow and NumPy.

![Image of code snippet](image.png)

*Figure 3.3: Minimal implementation that shows how to calculate all numerical descriptors.*

## 2 Validation analysis

To assess the reliability of the newly proposed methodology, multiple validation analyses were conducted to quantitatively measure the output differences. The first analysis involved comparing the calculated volume fraction obtained from a randomly selected TEM micrograph. Multiple binarization algorithms were employed, varying the 'K'
values to observe their influence on the results. Figure 3.4 presents the findings of this analysis.

![Figure 3.4](image)

*Figure 3.4: Scatter plot comparing how different k values impact the calculated volume fraction using different binarization algorithms. All images were binarized using the WAN threshold.*

The analysis reveals that all binarization algorithms share a common inflection point. A good binarization process aims to eliminate background noise while preserving a maximum number of nanofillers without introducing false positives. Based on the results, it was determined that the optimal 'K' value lies just before the inflection point. Specifically, for the Gatos, Sauvola, and Wolf algorithms, the preferred 'K' value for Figure 3.4 is 0.05 ± 0.02, while for the Wan algorithm, it is 0.08 ± 0.02. This range was chosen because it preserves the maximum amount of nanofillers without
introducing a significant number of “fake” fillers.

Indeed, Figure 3.4 provides valuable insights into the impact of different binarization methods on the "K" value, which is crucial for segmentation. Specifically, it demonstrates that certain methods, like Wan, have a more pronounced effect on the "K" value compared to others, such as Gatos. This finding suggests that when selecting a binarization algorithm, it would be advantageous to opt for one with a lower "K" impact. By doing so, researchers can achieve better control and fine-tuning of the segmentation process. A lower "K" impact means that the algorithm is less sensitive to changes in the "K" value, resulting in a more stable and consistent segmentation output. This stability is particularly desirable when analyzing complex microstructures where subtle changes in "K" could lead to significant variations in the results.

Furthermore, it is evident in Figure 3.4 that aiming for a high-volume fraction value is not desirable, as it leads to inaccurate representations. Instead, focusing on values within the shadowed region just before the inflection point provides a more accurate depiction of the polymer. In the higher end of the shadowed region, where \( k = 0.05 \), fake nanofillers are still present due to sample cut marks. In contrast, the lower end of the shadow region, where \( k = 0.1 \), indicates the complete disappearance of cut marks, offering an improved overall representation of the sample.

However, it is important to acknowledge that while filtering out cut marks, some nanofillers may inadvertently be removed. Determining the best representation of the sample becomes challenging since the optimal threshold is subjective. Nevertheless, it is clear that picking "K" values which are far from the shadowed regions are entirely incorrect.
Figure 3.5: Binary representation of the TEM micrograph used in Figure 3.4 at 3 different “K” values: 0.01, 0.05 and 0.1; using the threshold algorithms Wan, Gatos, Sauvola, and Wolf.
Inspired by the compelling findings showcased in Figure 3.4, we conducted another validation test to further evaluate the reliability of the methodology. For this test, three different researchers were engaged, each assigned with the task of processing a set of 10 images. They were provided with a thorough explanation of the tool’s basic functions, including accessing the image binarization playground, uploading images, and performing image binarization using a sample image that was not part of the original set. They were asked to utilize the binarization algorithm they believed to be the most suitable for each image.

The results of this test are depicted in Figure 3.6 and Table 3.3, illustrating that all three researchers achieved calculated volume fractions ranging from 0.03 to 0.04.

![Figure 3.6: Bar plot that compares the results obtained from 3 different researchers during the validation test.](image)

It is important to acknowledge all participants were material scientists, who pos-
sess a deeper understanding of microstructures and materials, are likely to have a more intuitive grasp of the appropriate binary representation needed for accurate assessments. Although the tool was designed with simplicity in mind to streamline the workflow, it is evident that achieving a good binary representation of the microstructure still requires a certain level of expertise. This observation underscores the importance of domain knowledge in material science when utilizing such methodologies.

The collective findings from our study revealed an average volume fraction of 3.5%, exceeding the expected value of 1.15% calculated from the PNC weight percentage ratio [44]. This result aligns with the literature’s tendency to overestimate volume fraction due to the nanoparticles’ size being smaller than the thickness of the TEM slice. A consistent factor of about 3 is found for all the samples [39] as shown in Figure 3.7. The error bars on the figure represent the median of the sum of the errors for all 10 samples.
Overall, these findings emphasize the robustness of our methodology in obtaining a value correlated with the volume fraction of materials. This will be a valuable tool for researchers even though they will need to calibrate their results to experimental volume fractions.

Table 3.3: Validation analysis results for Person 1 to 3 (Volume Fraction (VF), Average nearest cluster center distance (ANCC), Number of clusters (NC), Average cluster size (ACS))

<table>
<thead>
<tr>
<th></th>
<th>VF</th>
<th>ANCC</th>
<th>NC</th>
<th>ACS</th>
<th>ifiller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Person 1</td>
<td>0.04</td>
<td>29.7</td>
<td>87</td>
<td>98</td>
<td>0.55</td>
</tr>
<tr>
<td>Person 2</td>
<td>0.029</td>
<td>31.4</td>
<td>78</td>
<td>77</td>
<td>0.58</td>
</tr>
<tr>
<td>Person 3</td>
<td>0.034</td>
<td>28.9</td>
<td>76</td>
<td>95</td>
<td>0.51</td>
</tr>
</tbody>
</table>

In Table 3.3, a comprehensive dataset is presented, encompassing the volume
fraction along with other calculated descriptors obtained from the previous validation analysis. While it is not feasible to directly corroborate ANCC, NC, ACS and ifiller from the literature, they demonstrate a consistent trend, much like the volume fraction. The consistent patterns among the descriptors imply that the methodology is capable of capturing essential characteristics of the microstructure consistently.

Moreover, by utilizing the data presented in Table 3.3, we can calculate the uncertainty around the mean for the Average Nearest Cluster Center (ANCC), Number of Clusters (NC), Average Cluster Size (ACS), and Ifiller. The calculated uncertainty values for each descriptor are as follows: ANCC = ±2.2, NC = ±1, ACS = ±4.25, and ifiller = ±0.02. These values can be expressed as percentage errors, which are approximately 6%, 1.3%, 8.3%, and 5.1% respectively.

To estimate a global error, we can repeat this procedure for each image in the set of 10 images. Table 3.4 illustrates the maximum global error and the median error for ANCC, NC, ACS, and ifiller, providing valuable insights into the overall uncertainty of the descriptors across the entire dataset.
<table>
<thead>
<tr>
<th>Sample</th>
<th>ANCC</th>
<th>NC</th>
<th>ACS</th>
<th>ifiller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>6</td>
<td>1.3</td>
<td>8.3</td>
<td>5.1</td>
</tr>
<tr>
<td>Sample 2</td>
<td>4.0</td>
<td>1.4</td>
<td>9.6</td>
<td>5.4</td>
</tr>
<tr>
<td>Sample 3</td>
<td>15.6</td>
<td>12.2</td>
<td>20.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Sample 4</td>
<td>4.6</td>
<td>8.3</td>
<td>14.5</td>
<td>6.6</td>
</tr>
<tr>
<td>Sample 5</td>
<td>4.9</td>
<td>6.5</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Sample 6</td>
<td>2.2</td>
<td>5.3</td>
<td>39.6</td>
<td>3.9</td>
</tr>
<tr>
<td>Sample 7</td>
<td>30.9</td>
<td>59.9</td>
<td>63.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Sample 8</td>
<td>13.4</td>
<td>1.3</td>
<td>24.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Sample 9</td>
<td>11.1</td>
<td>14.0</td>
<td>27.5</td>
<td>1.9</td>
</tr>
<tr>
<td>Sample 10</td>
<td>5.5</td>
<td>5.4</td>
<td>17.2</td>
<td>3.9</td>
</tr>
<tr>
<td>Max Error</td>
<td>30.9</td>
<td>59.9</td>
<td>63.3</td>
<td>6.6</td>
</tr>
<tr>
<td>Median Error</td>
<td>5.7</td>
<td>5.9</td>
<td>19.3</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Upon reviewing Table 3.4, it is evident that the maximum error for almost all descriptors is relatively high. However, when comparing this with the median error, we observe a much smaller error. This discrepancy is primarily attributed to Sample 7, which exhibits an exceptionally high error percentage compared to the other data points. This scenario highlights a limitation of the tools used, particularly the binarization step, which can significantly influence how the descriptors are calculated.

As the binarization step has a substantial impact on the descriptors’ values, the extreme error from Sample 7 has a pronounced effect on the maximum error, leading to a skewed representation of the data. Consequently, the maximum error may not
accurately represent the majority of data points in the dataset.

Given this observation, we have decided to proceed with the median error as a more reliable measure. The median error better represents the central tendency of the data and provides a more balanced view of the overall uncertainty of the descriptors across the dataset, considering all data points.

To further validate our descriptor results, we conducted a comparison with other current methods. In this comparative test, we processed 18 different samples and measured them against results obtained from other research paper [44] using the average nearest cluster center distance (ANCC) as a common metric. The choice of ANCC served as a standard for comparison between the two methods.

![Figure 3.8: Plot that compares different methodologies to calculate average nearest center cluster distance.](image)

Upon analyzing Figure 3.8, it became evident that both sets of results followed a...
similar trend, although there were offset discrepancies. These differences in offset can be attributed to variations in the binarization method used to preprocess the images before calculating their ANCC values.

It is important to acknowledge that determining the correct ANCC value poses challenges due to the relative nature of results, which rely on the binary representation of the image. Additionally, it is worth noting that while our methodology only utilizes one image sample to calculate its descriptors, the other results were derived from an average of 30 sample images. As a result, achieving absolute accuracy in the ANCC values can be challenging.

Notwithstanding, the alignment in the overall trends between our method’s results and those from other research papers reinforces the validity and effectiveness of our methodology. While there may be differences in the absolute ANCC values, the consistent trends indicate that our method successfully captures relevant microstructural information and offers valuable insights.
3  **Correlation between descriptors and material properties**

As illustrated in Figure 3.9, a relationship between AC dielectric breakdown strength and average nearest cluster center distance (ANCC) was discovered. We chose to use average nearest cluster center distance because dispersion has a strong effect in dielectric properties. This relationship is corroborated by previous research [46, 47, 48] and was further verified numerically using the proposed numerical descriptors in this
thesis. The results indicate that as the distance between particles increases, there is a corresponding increase in interfacial area, which leads to enhanced dielectric breakdown strength. This improvement can be attributed to the higher probability of electron trapping, thereby reducing the likelihood of electron avalanches.

Figure 3.10: Drawing illustrating electron trapping in an avalanche breakdown strength

In Figure 3.10, a drawing representation depicts the behavior of a polymer nanocomposite with good dispersion as an electron travels through the material. As the electron starts its journey, it collides with atoms, leading to the ionization of other electrons and triggering an avalanche effect. However, some electrons get trapped by the nanofillers present in the material. This prevents these trapped electrons from causing any further damage or participating in the avalanche process.

Figure 3.11 shows an example of a histogram of ANCC. A crucial point to consider is that each data point in the average nearest cluster center distance was calculated from a range of cluster data points. The average serves as an effective descriptor of
the dispersion distance; however, it is strongly influenced by the distribution of the cluster distances.

![ANCC Histogram](image)

**Figure 3.11: Histogram of the nearest center cluster distance of a polymer nanocomposite**

By calculating the average from a range of cluster data points, the descriptor takes into account the collective behavior of these points, providing a comprehensive view of the dispersion distance. However, the specific distribution of the cluster distances within the PNC analysis significantly impacts the resulting average value.

It is essential to be mindful of this influence, as variations in the cluster distances’ distribution can lead to differences in the calculated average.

The analysis of Figures 3.12 and 3.13 aimed to establish a correlation between the Glass transition temperature (Tg) and Elastic Modulus (E). However, limited sample size and available data present challenges in identifying a definitive trend. This lack of a clear trend may be attributed to variations in surface energy between the filler and
matrix, even in reasonably well dispersed composites. These surface energy differences impact the glass transition temperature, as high attraction reduces polymer mobility, leading to an increased glass transition temperature, while less attraction results in the opposite effect. Nevertheless, obtaining additional data is necessary to establish a conclusive numerical proof for this relationship. A more extensive figure set can be found in Appendix A.
The relationship between the average distance between particles and the normalized elastic modulus, as shown in Figure 3.13, exhibits an ambiguous pattern. According to the literature [56], the modulus is not significantly influenced by dispersion, but rather, dispersion is more likely to affect the material’s strength or toughness. However, given the unclear trend observed in Figure 3.13 and the limitations of the existing data, further research and additional data are required to definitively determine the connection between the average distance between particles and the normalized elastic modulus in this polymer nanocomposite system. A more extensive figure set can be found in Appendix A.

Figure 3.13: Scatter plot of normalized elastic modulus with average nearest center distance. (Bansal [49], Chuang [51], Natarajan [52], Gao [53], Zhang [54], Chan [55])
4 Conclusion

In conclusion, our methodology successfully analyzed 100 images from various research papers. The image binarization tool effectively processed fillers in the presence of uneven backgrounds. The descriptor tool extracted numerical descriptors, offering user-friendly implementation.

Validation tests confirmed the methodology’s reliability, with consistent results across various binarization algorithms and researchers. The relationship between AC dielectric breakdown strength and average nearest cluster center distance was established and supported by numerical analysis. Further data is needed to confirm the relation between other properties such as glass transition temperature and elastic modulus.

Overall, our methodology provides an efficient approach to analyze nanocomposite materials and their properties, contributing to the advancement of this field.

5 Future work

While our current methodology has shown promising results in analyzing nanocomposite materials and their properties, there are several avenues for future exploration and improvement:

1. Algorithm Refinement: Further research can focus on fine-tuning the image binarization algorithms to improve their accuracy and decrease user error. Investigating advanced thresholding techniques and exploring machine learning-based approaches may lead to more robust and adaptive binarization methods.
2. Image normalization: Including image normalization as a preprocessing step before binarization can improve the binarization output. Additionally, we could explore the possibility of adding a histogram on top of the image transformation environment. This would allow the user to visualize the changes in the histogram as the binarization parameters are adjusted.

3. Extended Descriptor Analysis: Expanding the set of numerical descriptors can provide deeper insights into the nanocomposite materials. Incorporating additional descriptors that capture finer details of the microstructure, such as shape descriptors or spatial distribution metrics, could enhance the characterization capabilities.

4. Large-Scale Dataset Analysis: Expanding the dataset to a larger scale, encompassing diverse nanocomposite materials, can validate the generality and applicability of the proposed methodology across a wider range of materials and conditions.

5. Real-Time Analysis: Developing real-time image processing capabilities for on-the-fly analysis of microstructural changes could have significant applications in quality control and process optimization in materials manufacturing.

By addressing these future research directions, we can further enhance the capabilities and reliability of our methodology, ultimately advancing the understanding and design of nanocomposite materials and contributing to various fields of materials science and engineering.
1 Glass transition temperature figures

Figure 14: Scatter plot of delta glass transition temperature and volume fraction (Ash 2001 [10], Natajaran 2013-1 [50], Chuang [51], Natajaran 2013-2 [52], Bansal 2006 [57], Bansal 2005 [58], Ash 2004 [59], Tomer [60], Rungta [61]).
Figure 15: Scatter plot of delta glass transition temperature and number of clusters (Ash 2001 [10], Natajaran 2013-1 [50], Chuang [51], Natajaran 2013-2 [52], Bansal 2006 [57], Bansal 2005 [58], Ash 2004 [59], Tomer [60], Rungta [61]).

Figure 16: Scatter plot of delta glass transition temperature and ifiller (Ash 2001 [10], Natajaran 2013-1 [50], Chuang [51], Natajaran 2013-2 [52], Bansal 2006 [57], Bansal 2005 [58], Ash 2004 [59], Tomer [60], Rungta [61]).
Figure 17: Scatter plot of delta glass transition temperature and average cluster size (Ash 2001 [10], Natajaran 2013-1 [50], Chuang [51], Natajaran 2013-2 [52], Bansal 2006 [57], Bansal 2005 [58], Ash 2004 [59], Tomer [60], Rungta [61]).
2 Dielectric breakdown strength figures

Figure 18: Scatter plot of normalized dielectric breakdown strength and volume fraction (Bell [43], Prasad [44], Virtanen [45], Huang [62], Tuncer [63]).
Figure 19: Scatter plot of normalized dielectric breakdown strength and number of clusters (Bell [43], Prasad [44], Virtanen [45], Huang [62], Tuncer [63]).

Figure 20: Scatter plot of normalized dielectric breakdown strength and average cluster size (Bell [43], Prasad [44], Virtanen [45], Huang [62], Tuncer [63]).
Figure 21: Scatter plot of normalized dielectric breakdown strength and filler (Bell [43], Prasad [44], Virtanen [45], Huang [62], Tuncer [63]).
3 Elastic Modulus Figures

Figure 22: Scatter plot of normalized modulus and volume fraction (Chuang [51], Natarajan [52], Gao [53], Zhang [54], Chan [55]).
Figure 23: Scatter plot of normalized modulus and average cluster size (Chuang [51], Natara-ajan [52], Gao [53], Zhang [54], Chan [55]).

Figure 24: Scatter plot of normalized modulus and number of clusters (Chuang [51], Natara-ajan [52], Gao [53], Zhang [54], Chan [55]).
Figure 25: Scatter plot of normalized modulus and ifiller (Chuang [51], Natarajan [52], Gao [53], Zhang [54], Chan [55]).


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