MECHANICAL PROPERTY MODELING OF
GRAPHENE FILLED ELASTOMERIC COMPOSITES

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ABSTRACT

Accessing improved elastomeric composites filled with functionalized graphene sheets (FGSs) requires an understanding of how the FGSs aggregate and how the position of FGSs affects the mechanical properties of the final composite material. In this thesis, I study both effects by devising models for 2-D particles in the 10s of microns scale and comparing my results with experiments. These models enable an understanding of the effect of the particles in a level that is hard to be studied experimentally or by molecular models.

In the first part, I present a model for aggregation of 2-D particles and apply it to study the aggregation of FGS in water with varying concentrations of sodium dodecyl sulfate (SDS). The model produces clusters of similar sizes and structures as a function of SDS concentration in agreement with experiments and predicts the existence of a critical surfactant concentration beyond which thermodynamically stable FGS suspensions form. Around the critical surfactant concentration, particles form dense clusters and rapidly sediment. At surfactant concentrations lower than the critical concentration, a contiguous ramified network of FGS gel forms which also densifies, but at a lower rate, and sediments with time. This densification leads to graphite-like structures.

In the second part, I present a model for the prediction of the mechanical properties of elastomers filled with 2-D particles. I apply this model to the Poly-dimethylsiloxane (PDMS)-FGS system. For a perfect polymer matrix and when inter-particle forces are ignored the strength of the composite can be increased with the addition of particles but elongation at failure decreases relative to neat PDMS. Maximum load transfer to the particles is achieved when particles are covalently linked to span the whole polymer
matrix. Minimum drop in elongation at failure can be achieved by maximizing the distance between the covalently linked particles. When the assumption of a perfect polymer matrix is relaxed, it can be shown that there is a certain particle concentration range for which elongation at failure can be increased as the particles can protect the polymer by redistributing high stresses created by inherent polymer defects that would lead to early failure.
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2-D/3-D  2-dimensional/3-dimensional
DLA    Diffusion-Limited Aggregation
DLCA   Diffusion-Limited Cluster Aggregation
FEM    Finite Element Method
FGS    Functionalized Graphene Sheet
FGS$_2$ Functionalized Graphene Sheet with a carbon-oxygen ratio of 2
LSM    Lattice Spring Model
PDMS   Poly-dimethylsiloxane
RCA    Reversible Cluster Aggregation
RLCA   Reaction-Limited Cluster Aggregation
SAK    Shih-Aksay-Kikuchi (model)
SDS    Sodium Dodecyl Sulfate
SEM    Scanning Electron Microscopy
TEM    Transmission Electron Microscopy
vdW    Van der Waals (forces)
Chapter 1 Introduction

1a. Graphene-filled Conductive Elastomeric Composites

The addition of particles in polymeric matrices with the purpose of enhancing the mechanical properties of the material or lowering the final cost of the product is common in commercial applications since the early 20th century.\textsuperscript{1,2} More specifically, the addition of functionalized graphene particles in an elastomeric matrix results in a material that is elastic and also electrically conductive.\textsuperscript{3–6} Modeling the mechanical properties of these materials, in particular the entire stress-strain properties including the strength and strain at failure, is extremely difficult due to the large elongations involved and the large length-scales, the sheet-like shape and the large aspect ratio of graphene particles.

Conductive elastomeric composites are typically made using different types of carbonaceous fillers, such as carbon black or carbon nanotubes, or metallic fillers such as gold or silver.\textsuperscript{7} Even though the metallic fillers generally achieve higher electrical conductivities, they also yield composite materials of higher weight and higher cost and are not currently used for commercial applications.\textsuperscript{8} This makes carbonaceous fillers more appropriate for a large variety of applications. In this work, I will focus on graphene-filled elastomeric composites and more specifically a form of functionalized graphene that I will call Functionalized Graphene Sheet (FGS)\textsuperscript{9,10} dispersed in Polydimethylsiloxane (PDMS). The literature on FGS and graphene elastomeric composites is limited\textsuperscript{4–6,8,11,12} but there is a vast amount of work done with other carbonaceous fillers embedded in elastomers, particularly carbon blacks.
A great interest in non-insulating elastomers arose for antistatic purposes in the late 1930s when the surgical world became worried about the frequency of explosions in operating rooms due to static electricity. Another popular use for conductive elastomers was in the tires of automotive vehicles and aircrafts, again for anti-static purposes and in handling explosive or inflammable vapors, liquids and powders. Other more recent potential uses are as actuators, sensors and electrodes for potential artificial muscle and flexible electronics applications and as conductive coatings in composite airplanes.

Currently there is a very limited number of commercial products that use graphene as a filler. Some examples are automotive and bicycle tires (where graphene is added in addition to carbon black), skis, tennis rackets, bike helmets and other sporting products. Even though the commercial use is currently limited, there is a great promise for graphene to substitute carbon black in elastomeric composites as FGS has the property of achieving similar electrical conductivity values as carbon black when added in polymers but for lower filler content.

The addition of electrically conductive fillers in elastomers does not only affect the electrical properties of the resulting composite. The fillers enhance the mechanical properties of the elastomer as well, which makes them suitable for different applications. It has been observed, though, that there is a trade-off between the improvement of electrical conductivity and the enhancement of mechanical properties. More specifically, electrical conductivity seems to increase with filler loading due to the formation of more conductive pathways throughout the material, while elongation at failure decreases with filler loading.
However, elongation at failure increase has also been observed experimentally in polymers with the addition of particles. In the case of elastomeric matrices there seems to be a range of particle concentrations at which the elongation at failure increases before it starts to decrease. Understanding what causes this increase in elongation at failure could lead to an effective dissociation between the electrical conductivity and elongation at failure trade-off described above.

For this reason, I developed models that will allow a deeper understanding of these experimental results. A general categorization of the existing field of modeling of the mechanical properties of composites with specific emphasis on elastomeric composites is presented in Table 1.1. This table shows that one of the unique contributions of this thesis is the modeling of failure properties for non-spherical filler particles along with setting the groundwork for the modeling of aggregated filler structures.

More details about the models mentioned in Table 1.1 will be discussed later in this chapter. Accessing conductive elastomeric composites with improved mechanical properties without sacrificing electrical conductivity requires an understanding of how the filler particles and the elastomeric matrix interactions as well as their individual properties result in a composite material with specific mechanical properties. Assuming strong enough interactions between the filler and the elastomer, the interest lies on how these particles are dispersed, and how the intrinsic properties of the fillers and the matrix affect the properties of the final material. More specifically, FGS tends to form aggregates and the process of aggregate formation as well as the effect of these aggregates to the mechanical properties of the composites are not well-understood for non-spherical fillers. On top of that, the cured elastomer is an imperfect material and the
effect of these imperfections in the properties of elastomeric composites is an open research area. The main focus of this work is to understand: (1) the basic principles that drive aggregation of FGS, (2) the effect of structure of FGS on the failure of the filled elastomers and (3) the effect of pre-existing polymer defects on the failure of the filled elastomers.

Table 1.1. Models for the prediction of the mechanical properties of conductive elastomeric composites.

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1b. Goals of this Thesis

In this thesis, I have constructed two state-of-the-art models. A Reversible Cluster Aggregation (RCA) model that was used to simulate the aggregation process of graphene particles and a micromechanical Finite Element Method (FEM) model that was used to simulate the mechanical properties of graphene elastomeric composites with an emphasis on failure. Both models were created with the purpose of pushing the limits of the number of particles that can be simulated in order to explore the effect of particle dispersion. These two models were used in conjunction with experimental results in an effort to generate new insights and extent those results. Through my computational experiments, I will attempt to provide understanding in these areas:

1. The forces that contribute to the aggregation process of FGS and how they affect the resulting aggregate structures.
2. The effect of covalent linkage and position of filler particles in the mechanical failure of FGS elastomeric composites.
3. The effect of the intrinsic elastomer defects in the mechanical failure of FGS elastomeric composites.

These studies, described in the following chapters, complement experimental results by studying parameters that are hard to control experimentally and through them provide the needed understanding of the graphene aggregation process and the failure properties of graphene elastomeric composites. The remainder of this chapter will provide background on the mechanical properties of filled elastomers and a summary of what follows in the remaining chapters of this thesis.
**1c. Mechanical Properties of Elastomeric Composites**

Elastomers, particularly those that cannot undergo strain-induced crystallization, are generally compounded with a reinforcing filler.\(^{51}\) The advantages obtained include improved Young’s modulus, abrasion resistance, tear strength, tensile strength but they also result in an improvement of non-mechanical properties such as electrical conductivity, gas permeability, thermal stability etc. In this part, I start by providing information about the separate components that comprise my system: the elastomer and the FGS, I refer to previous measurements of the interfacial force strength between FGS and PDMS and then I discuss some complex phenomena of elastomeric composites.

**Rubberlike elasticity – defects**

Rubberlike elasticity is defined as the property of very high deformability and essentially complete recoverability.\(^{51}\) In order to achieve high deformability the material must be constituted of molecules that are long chains (i.e., polymers) and those chains must be flexible and mobile. Complete recoverability of the network structure is achieved from crosslinking of molecules.\(^{52,53}\)

The basic assumptions in the development of molecular theories of rubberlike elasticity are: 1) Intermolecular interactions are independent of orientation and therefore rubberlike elasticity is an intramolecular effect\(^{54}\) and 2) the Helmholtz free energy of the network is separable into (strain independent) liquid and elastic contributions.\(^{51}\) The affine theory additionally assumes that the chains move in proportion to the macroscopic dimensions of the elastomeric sample and, therefore, the junction points are embedded in
the network.\textsuperscript{54,55} The phantom theory, on the other hand, allows movement of the junction points with time.\textsuperscript{56,57}

A significant improvement relative to both popular theories (i.e., affine and phantom theories) was achieved when molecular defects were taken into account in the polymer network.\textsuperscript{58} There is significant experimental proof that inherent defects are always present in elastomers.\textsuperscript{59–61} These defects can be caused by pre-cracks,\textsuperscript{62} pre-existing small cavities that develop into cracks\textsuperscript{59} or even stress-raising features that exist in the polymer.\textsuperscript{60} Non-uniformities in the curing/crosslinking process in the elastomer are also prevalent and can be a source of defects.\textsuperscript{8} This thesis is the first to model the effect of these inherent defects of the elastomer in the ultimate properties of the composite material.

FGS

As the size of filler particles decreases, provided a certain degree of bonding between filler and polymer exists, the degree of reinforcement from the filler particles increases.\textsuperscript{63} This happens due to the increase of surface area interactions between the polymer and the filler phase and this is the reason that nanocomposites (i.e. composites that include fillers of nanometric size) have become such a popular research area.

Other than the size, the shape of the filler also plays an important role. For highly anisotropic particles, the orientation of the fillers can modify the mechanical response of the material.\textsuperscript{63} The particle aspect ratio, defined as the ratio of the largest over the smallest dimension, is one indication for the degree of anisotropy of the particle. High anisotropy generally provides more surface area for a given volume.
FGS, as a modified graphene product (a form of carbon with a thickness equal to one carbon molecule), has the property of nanometric size and a really high aspect ratio. Its theoretical surface area is 2,630 m$^2$/g.\textsuperscript{64} This allows significant load transfer from the polymer to the FGS even at low FGS concentrations.\textsuperscript{9,10,21}

Graphene is an atomically thin layer of sp\textsuperscript{2}-bonded carbon. Pure graphene is hard to produce in scale and that is why in this thesis I focused on FGS, a graphene-like material. FGS is produced with thermal exfoliation of graphite oxide (also referred here as FGS\textsubscript{2}, i.e. FGS with a carbon-to-oxygen ratio of 2).\textsuperscript{9,10} Exfoliation happens simultaneously with thermal reduction of the sheets. The final properties of FGS vary depending on the functionalities and defects that are created during the exfoliation/reduction process and the defects that are inherited from graphite oxide.\textsuperscript{65} An example of an FGS is shown in Figure 1.1(a) and an example of the lattice, including defects, is shown in Figure 1.1(b).

![Figure 1.1](image)

**Figure 1.1.** (a) Individual FGS produced from simultaneous exfoliation and thermal reduction of graphite oxide. This is a contact-mode AFM image. The scale shows the thickness measurement of the sheet and the inset shows an atomic-scale image of the HOPG lattice. (b) Example of defect structures within FGS. The two red spheres
correspond to oxygen atoms and the rest correspond to carbon atoms. Adapted from Schniepp et al.⁹

Graphene is known to have a Young’s modulus of 1 TPa and a tensile strength of 130 GPa.⁶⁶ The mechanical properties of FGS vary depending on the reduction process but an indicative value for Young’s modulus is about 200-750 GPa.⁶⁷ The dimensions of the sheets vary between 0.1 and 1 µm.⁹

**FGS-PDMS composites**

Pan studied experimentally the tensile behavior of the FGS-PDMS system and his results are summarized in Figure 1.2.¹¹,²⁴ From the stress-strain curves presented in Figure 1.2, it can be observed that with increased particle concentration Young’s modulus and strength are increased and elongation at failure is increased and then decreased.

**Other elastomeric composites systems**

Load transfer to a stiffer and stronger filler than the matrix and modification of the matrix structure caused by the filler addition are both reasons that are generally known to increase both Young’s modulus and strength, for polymeric and non-polymeric matrices.⁶⁸–⁷⁴ The effect of the fillers on elongation at failure, though, is not well understood.

The basic mechanism for load transfer is through strain amplification of the matrix around the filler particles.²⁷,³²,³³ At the same time, strain amplification leads to enhanced localized stresses at a given value of global strain. This can cause failure to occur at lower global elongation values of the filled system, as some regions are strained to failure.
earlier than others. Although this is a simplified version of the complex effects that happen during filler addition, the phenomenon of decreasing elongation at failure with increasing filler concentration is a typical behavior, with the exceptions of some studies (including the results in Figure 1.2) that showed a range of increasing elongation at failure before it starts decreasing. 

Figure 1.2. Stress-strain curves of FGS-PDMS composites as a function of FGS concentrations. Borrowed from Pan’s PhD thesis. 

Understanding the conditions that lead to an improvement in elongation at failure with particle addition will be key for the production of elastomeric composites with enhanced stretchability.
The addition of fillers in the elastomer can have a very complex effect on the mechanical properties of the resulting composite that are hard to predict based only on the properties of the individual components. Filler-polymer interfacial forces, filler dispersion and filler orientation are some of the parameters that will affect those properties. In addition, filler particles tend to aggregate and tend to affect inherent properties of the polymer, such as the crosslinking density and glass transition temperature.8.21

Some examples of the complex phenomena that appear in filled elastomers are the Payne and the Mullins effects. Both effects have been studied extensively for carbon black-filled elastomers and the nature of these effects are a source of a long debate in the literature.81 The Payne effect expresses the highly non-linear dependence of the complex (also known as dynamic) moduli to strain amplitude. During dynamic testing (i.e. testing under vibratory conditions) of carbon black-filled elastomers, the storage modulus decreases with strain amplitude and the loss modulus increases and then decreases with strain amplitude. This was first observed in the extensive work of Payne.82–84

This behavior was later confirmed in elastomers containing non-carbon black fillers.85–87 A key observation was that the Payne effect applied to low viscosity media as well.88–91 This emphasized the effect of the bonded filler network structure in Payne effect and reinforced the idea that the strong non-linearity in dynamic modulus is due to a cyclic breakdown and re-aggregation of filler-filler bonds.42–44,81,86

The Mullins effect refers to stress softening that happens in filled elastomers during dynamic loading. An example is shown in Figure 1.3, where the sample is subjected to
repeated stretching cycles of increasing maximum strain. In each cycle stress values are clearly reduced for strain values lower than the previous maximum.

Figure 1.3. Example of stress softening with successively increasing maximum strain for an E-SBR (Emulsion-Styrene Butadiene Rubber) sample filled with carbon black aggregates (N339). Borrowed from Klüppel. ⁸⁰

The micro-mechanical origin of the Mullins effect is not completely understood. ⁹²–⁹⁴ Some important effects that contribute to stress-softening are: breakdown or slippage⁹⁵,⁹⁶ and disentanglements of interfacial bonds,⁹⁷ strain-induced crystallization-decrystallization,⁹⁸,⁹⁹ rearrangement of network chain junctions,¹⁰⁰ breakdown of aggregates⁴² and hydrodynamic strain amplification from the fillers.⁹⁸–¹⁰⁰

The effect of the filler addition to the properties of the composite, therefore, can be very complex which has led to a great variety of modeling approaches developed in this field for the prediction and understanding of mechanical properties.
1d. Mechanical Properties Modeling of Elastomeric Composites

The prediction of the mechanical properties of composite materials was pioneered with the analytical methods developed by Voigt\textsuperscript{29} and by Reuss,\textsuperscript{30} which became known as rule of mixtures. For the case of the modulus, the rule of mixtures provides a lower and an upper bound based on the modulus of the individual components. Around the same period, Einstein worked on the prediction of the viscosity of a Newtonian fluid with a dilute suspension of stiff spherical particles.\textsuperscript{101,102} This problem was proved to be similar to modulus reinforcement inflicted by stiff spherical particles in an elastic matrix.\textsuperscript{27} Following this work, analytical solutions for the case of non-spherical fillers in elastomeric matrices were developed.\textsuperscript{31,33–35} Most notable examples are the Guth,\textsuperscript{32} Halpin-Tsai\textsuperscript{33} and the Mori-Tanaka\textsuperscript{34,35} models.

Particle fillers in polymers tend to form filler aggregates and filler aggregates tend to associate to form agglomerates.\textsuperscript{63} The importance of the effect of aggregation and agglomeration on mechanical properties was recognized very early for carbon black filled elastomers.\textsuperscript{103–105} Initially, simple analytical expressions, like the Guth-Gold equation,\textsuperscript{28} were used to calculate the change in modulus caused by the aggregates formed within the material.\textsuperscript{93}

Later, Witten et al. modeled the breakdown of clusters generated by the Diffusion Limited Cluster Aggregation model while ignoring effects coming from the elastomer matrix and the filler-matrix interactions and managed to predict a scaling law for the stress-strain behavior by using purely geometrical arguments on the aggregates.\textsuperscript{42} Even though this model could not explain stress softening effects related to hydrodynamic
strain amplification due to the presence of the filler, it is a result that showed a clear correlation between aggregate break-down and stress-strain values.

The effect of aggregate breakdown in the mechanical properties of elastomeric composites is impossible to ignore during the modeling of the Payne and Mullins effects. The only models that capture the micro-mechanical concepts of filler networking and non-linear viscoelasticity of reinforced elastomers are the Links-Nodes-Blobs model\textsuperscript{41} and the Cluster-Cluster Aggregation model,\textsuperscript{43,44} which is an extension of the model suggested by Witten et al.\textsuperscript{42} The basic difference between these two model is that the first one uses a simplified geometry for filler structures (blobs represent dense filler aggregates, links correspond to filler cluster that connect blobs and nodes correspond to connected links), while the Cluster-Cluster Aggregation model uses the Diffusion Limited Cluster Aggregation model\textsuperscript{106,107} to position each particle that is part of the aggregate.

Many phenomenological approaches have been utilized to capture the complex dynamic behaviors of elastomeric composites.\textsuperscript{81} Each of them seems to focus on a certain aspect of the dynamic mechanical behavior. For instance, the Payne effect was theorized to be caused by deformation, flow and alignment of the rubber molecules,\textsuperscript{108} or by bound rubber that surrounds the filler particles which causes a non-linearity due to desorption and reabsorption of this hard shell around carbon black particles.\textsuperscript{109,110} Many purely empirical mathematical models along with different combination of springs (including triboelastic solids) have been proposed for the same purpose.\textsuperscript{46-49}

Kraus was the first one to suggest a model based on breakage and reformation of carbon black aggregates and since then this idea has been used extensively.\textsuperscript{50,80,81} Some
of the most common phenomenological components of carbon black models are discussed below as utilized by Miehe and Keck:  

- **Elastic ground-stress response:** This phenomenon dominates the response of unfilled vulcanized rubbery polymers. The elasticity material behavior is characterized by two things: very high deformability and essentially complete recoverability.\(^5\)

- **Viscoelastic over-stress response:** This is a rate-dependent response observed in elastomers and elastomeric composites. This phenomenon appears in creep tests, relaxation tests and in cyclic loading processes. Micromechanically this can be explained by rearrangement of secondary weak bonds between polymer chains during deformation.

- **Plastoelastic over-stress response:** This is a rate-independent response observed in elastomeric composites. This phenomenon appears during cyclic deformation processes. Micromechanically it has been attributed to irreversible slip processes between the filler particles.

- **Rate-independent damage effect:** The stress softening that happens during the first loading cycles can be explained micromechanically by different mechanisms including destruction of bonds between the polymer chains and the filler particles. This is known as Mullins effect and it can be interpreted as a damage effect in which the evolution of the damage depends critically on the maximum stretch reached in the deformation history.
Overall, even though the existing literature for the modeling of the mechanical properties of elastomeric composites is vast, the majority of that literature is focused on modeling of complex phenomena. There are only a few studies for the modeling of failure in polymer composites (including simulations of tearing and tear deflection caused by fillers) using lattice models.\textsuperscript{112-117} None of these models was used for elastomeric composites, though, and none was focused on understanding the increase in elongation at failure that happens on certain ranges of filler concentration. The only exception is Sanborn’s model for FGS-PDMS composites.\textsuperscript{38}

1e. Contributions and Organization of this Thesis

In my research work presented in this thesis, I studied the aggregation of FGSs and the effect of their position in the mechanical properties of FGS-PDMS composites. This was done through the development of two models that can handle aggregation and mechanical property calculation, respectively, in a scale that includes hundred or thousand of 2D particles.

First, in Chapter 2, I present a model based on a diffusion limited aggregation approach that encompasses attractive and repulsive forces between 2D particles. This model allows restructuring of the aggregates by allowing aggregation as well as deaggregation of particles and it is used to study the aggregation process of FGS particles in water in the presence of sodium dodecyl sulfate (SDS) surfactant. The results from the model follow the same pattern as a function of SDS concentration as the corresponding experimental results. There is a critical surfactant concentration above which thermodynamically stable dispersions are obtained. For SDS concentrations way below the critical concentration, FGSs tend to form a gel and then slowly densify with time and
For SDS concentrations close to the critical, FGSs form dense aggregates that sediment fast.

In Chapter 3, I present a finite element method (FEM) model for 2D particles embedded in an elastomer, with springs modeling the interfacial forces between the two material elements. The main purpose of this model is to study failure of the composite material. For this, a Von Mises failure criterion has been implemented in an element-by-element basis. Boundary effects that can cause early failure at high particle concentrations were tackled by defining regions of the polymer matrix near the boundaries that cannot fail and by straining the material from points closer to the center. Inherent material defects were modeled by defining regions of the material with a lower Von Mises strength than the remaining polymer matrix.

Next, in Chapter 4, the above FEM model is used to model the mechanical properties of FGS-PDMS composites with the assumption of a perfect polymer matrix and no interparticle forces between the FGSs. The model showed that, under these assumptions, increase in strength can be achieved with the addition of particles but elongation at failure is not increased relative to the neat elastomer. Maximum load transfer can be when particles are covalently linked to effectively increase their aspect ratio. The reduction in elongation at failure is minimized when the covalently linked structures are well-dispersed, i.e. their inter-particle distances are high.

Finally, in Chapter 5, the same FEM model is used but with the assumption of a perfect polymer matrix relaxed. It is assumed that the material contains weak regions that fail earlier than the remaining material. In this case, addition of particles can lead to increase and then decrease of elongation at failure and to an increase in strength. The
increase in elongation at failure is attributed to a redistribution of the high stresses around
the regions of the material that fail early. The subsequent decrease of elongation at failure
at higher particle concentrations is attributed to stress concentration zones created by the
added particles.

Chapter 6 contains my full conclusions and thoughts for potential other usages of
these models and areas that can be improved as well as suggestions to experimentalists
for production of materials with enhanced mechanical properties.
Chapter 2 Reversible cluster aggregation and growth model for graphene suspensions*

2a. Introduction

Graphene,118 graphene oxide,119,120 and reduced graphene oxides9 as atomically-thin macromolecular sheets are used in an increasing number of practical applications such as liquid fuels,121 polymer composites,21,122,123 energy storage and energy conversion devices (e.g., batteries, supercapacitors, solar cells),124–133 and inks (for printed electronics and sensors).134–136 In most of these applications, the molecular sheets have to be first dispersed in a liquid medium in order to break up powder aggregates and achieve the advantages of individual sheets. To do so, two prevalent colloidal dispersion methods are used: (i) decrease the magnitude of the van der Waals (vdW) attractive forces to the $k_B T$ range (where $k_B$ is the Boltzmann constant and $T$ temperature) by lowering the Hamaker constant through index matching (which is also used as a method for graphite exfoliation),137 or (ii) counteract the vdW forces by inducing repulsion between the sheets through electrostatic, steric, or electrosteric interactions.138,139 Ultimately, during the production of a device, the dispersed suspensions are converted to an aggregated state either through the stacking of graphene particles with themselves or with the colloidal particles of other phases. In such aggregated structures, a deterministic control of the topological features is of paramount importance to define properties by controlling parameters such as accessible area for chemical reactions, load transfer for mechanical

* This is a modified version of an article published by the AIChE journal under the same name.219
properties, electron and heat transfer for electronic and thermal properties. To this end, research efforts have been exclusively experimental to observe the effects of dispersion quality on the final properties of the products.\textsuperscript{122,139–144}

However, while these experimental studies have been invaluable in many aspects, an accurate connection between the filler’s network structure and the properties of the final materials has not been established. In theoretical modeling studies of the dependence of properties to particle dispersion, a well-defined topological state, spanning from the length scale of the atomically-thin sheets, needs to be defined as input to a given model. If we could predict the relative position of the graphene particles, we could then aim at predicting the properties of the materials and yield a deeper understanding of the underlying mechanisms. This information is difficult to obtain by experimental methods. Even though individual graphene particles and aggregates of particles can be imaged through Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) techniques, the interpretation of those results can be difficult because of the low atomic number contrast between graphene and carbon-based polymers, the small thickness and wrinkled morphology of graphene sheets\textsuperscript{123} and because of inherent difficulties in plate-like particle imaging (such as telling the difference between stacked and individual sheets, the natural variations in particle lengths, the anisotropy of their shapes etc.).\textsuperscript{145}

In this chapter, I am focusing on a modeling approach to establish the dispersion state of the filler particles. This will potentially provide a way of producing input for modeling studies of graphene-filled materials and a theoretical base to understand the important factors that affect the dispersion state of these particles. In addition, allowing
for easy incorporation of flow in the suggested aggregation model can provide a tool that will allow better process control and design of processes that include atomically-thin macromolecules. Similar to what has been done before for spherical and non-spherical particles.\textsuperscript{146–148}

To that end, I present a reversible cluster aggregation and growth model for atomically-thin macromolecules that predicts qualitatively the experimentally observed macroscopic colloidal aggregated structures.

As a case study, I focus on the prediction of aggregated structures experimentally observed with graphene-like materials although our model is not limited to graphene but is generic for any atomically-thin molecular sheet. Based on the experiments\textsuperscript{139} that I model, the length-scale of interest for this type of problem is in the order of nm in thickness and \(\mu\)m or tens of \(\mu\)m in the planar orientation of the molecular sheets. The time scales can vary from minutes to hours or even months.\textsuperscript{139} These are significantly larger than the typical scales handled by molecular dynamics or even coarse-grained molecular dynamics,\textsuperscript{149} Brownian dynamics,\textsuperscript{150} and dissipative particle dynamics\textsuperscript{151} simulations. A Stokesian dynamics simulation\textsuperscript{152} would seem more appropriate in terms of length-scale but there are no reported efforts to model the dispersion behavior of a large number of graphene-like particles. Two possible reasons for this lack of literature on Stokesian dynamics are the difficulties of representing the accurate shape of graphene and of approximating the long-range inter-particle forces. These problems are innate to modeling graphene particles at these length-scales.\textsuperscript{153} My approach is to simplify the geometry of the particles to rigid linear segments and to use a diffusion limited aggregation (DLA)-type of approach to simplify the force field and deal with the long
time scales of this problem. As I show in the Results and Discussion section, these assumptions hinder the ability to obtain analytically quantitative results; but, they are sufficient for qualitative purposes.

The DLA model was introduced in 1981 by Witten and Sander and it immediately spurred an immense interest in the field of colloidal-particle dispersion and aggregation. DLA is a lattice model that starts with a seed particle at the origin and new particles are added, one at a time, which perform random walks until they collide with the seed (i.e., the growing cluster) and become a part of it, or until they touch a boundary, in which case they are removed and a new particle is added. This leads to the formation of a cluster with a correlation exponent that can be related to experimental results for metal-particle aggregates. This work gave rise to many similar models that tried to capture the physical reality of the aggregation process of different colloidal-particle systems, including the diffusion limited cluster aggregation (DLCA) model, where particles as well as clusters of particles are allowed to diffuse in space; models with finite aggregation probability, where collisions do not always lead to aggregation and can reach the reaction limited cluster aggregation (RLCA) limit as this probability tends to zero; and, the restructuring aggregation models, where clusters are allowed to reorganize with time either by the deaggregation of particles from the formed clusters (reversible aggregation) or by reorganization of particles within the formed clusters. The word “cluster” in this thesis (and consistent with the above literature) indicates the product of a successful collision between (i) two particles, (ii) a cluster and a particle or (iii) two clusters. The word “aggregation” is used to describe any event that leads to increase in cluster size.
Aggregate restructuring is a phenomenon that has been proven experimentally and I consider it an important aspect of our approach, especially to model the recent experimental results of Hsieh et al. on the aggregation of graphene in aqueous surfactant solutions. These results showed that there is restructuring of graphene aggregates leading to time dependent densification towards more compact structures over the time period of one year. The Shih-Aksay-Kikuchi (SAK) model was the first reversible aggregation model to incorporate interaction potential in the calculation of the deaggregation probability of particles. The SAK is essentially a DLCA model that allows deaggregation of particles based on a deaggregation probability that is a function of the number of neighbors: fewer neighbors lead to higher probability of deaggregation. In this model, the particles are spherical and thus contact each other only at a point.

This approach is very attractive for this case because the aim is to create a general Reversible Cluster Aggregation (RCA) growth model that can be used for systems with different interaction potentials (the difference in interaction potential caused by different surfactant concentrations as is expressed mathematically in the next part). But, since I aim to model atomically-thin macromolecules that contact with each other at different points with variable contact angles and areas, in our case, the interaction potential will also depend on the contact area (comprised of contact angle and contact point) between the sheets. In order to allow rotation, I follow a non-lattice approach as opposed to the lattice approach of the SAK model and I also add an aggregation probability calculation, in addition to the deaggregation probability that is found in the SAK model, to make it more amenable to generalization. To the best of my knowledge, there is no work that
deals with reversible aggregation of atomically-thin macromolecules or sheets even though there are DLA-type models that deal with non-spherical particle shapes.\textsuperscript{173,183–185}

The RCA model developed in this study is detailed in the following section. I test its validity by utilizing Hsieh et al.’s recent experimental results\textsuperscript{139} on the aggregation of reduced graphene oxide sheets which I will refer to as functionalized graphene sheet (FGS) from here on. In the aforementioned work, FGSs were first dispersed in an aqueous sodium dodecyl sulfate (SDS) solution by ultrasonication at different adsorption levels of SDS.\textsuperscript{139} Above a threshold SDS concentration of 10 µM ($C_\text{crit}$, where $C$ is the SDS concentration) at 0.1 mg/mL FGS, suspensions stayed dispersed; while below that threshold concentration, aggregation and sedimentation were observed. Variations in the dispersion state were attributed to the adsorption of anionic dodecyl sulfate (DS\textsuperscript{−}) molecules onto FGSs that imparted varying levels of electrostatic repulsion between the sheets at different SDS concentrations. When dealing with the fully dispersible FGS, five basic types of structures were observed under optical microscopic characterization with varying SDS concentration as summarized in Figure 2.1 (adapted from\textsuperscript{139}): (i) a highly ramified network of aggregates (Figure 2.1(a)) that spans through the entire system (i.e., a gel-like state) when no SDS was added; (ii) less-ramified aggregates (Figure 2.1(b)) at around $C = 5$ µM; (iii) large compact aggregates (Figure 2.1(c)) of $\sim 10$ µm in size along with some micrometer size particles at around $C = 10$ µM; (iv) dispersed single- or few-layer sheets (Figure 2.1(d)) at $C > 10$ µM, threshold concentration; and (v) hard aggregates of a few µm in size (Figure 2.1(d)) corresponding to partially oxidized graphite particles that do not fully disperse to single graphene oxide sheets. These
observations display the effect of variable interaction potential between the FGSs as SDS adsorption on FGS changes.

![Figure 2.1](image)

**Figure 2.1.** Representative optical microscope images of FGSs dispersed at a concentration of 0.1 mg/mL in aqueous SDS solutions after sonication. SDS concentration in each suspension was: (a) 0 µM (DI water), (b) 5 µM, (c) 10 µM, (d) 20 µM. The scale bar is the same for all images. Adapted from Ref. 139.

However, the optical microscopic images of Figure 2.1 only display the state of the suspensions right after the dispersion of the suspensions by ultrasonication. When these suspensions are allowed to age up to one year, ultraviolet-visible (UV-Vis) light absorption of the supernatant indicates a significant amount of sedimentation below the threshold SDS concentration of 10 µM as shown in Figure 2.2 (adapted from 139). While the blue curve corresponds to images presented in Figure 2.1, the supernatants of the suspensions below 10 µM threshold concentration become highly transparent as aggregates settle out with aging time. This indicates that the aggregates of Figures 2.1(a), 2.1(b), and 2.1(c) densify further with time. While these experiments do not provide a clear mechanism for the densification process, the RCA growth model I present in the following section suggests that at $C < C_{\text{crit}}$ the restructuring of the graphene aggregates is the cause of densification with time but there are kinetic reasons that limit the
restructuring rate of the aggregates. The model also predicts a threshold surfactant concentration ($C_{\text{crit}}$) above which thermodynamically stable dispersed single or few-particle aggregates are observed as outlined with light gray shaded region in Figure 2.2.

**Figure 2.2.** UV-Vis absorbance of suspensions with FGSs dispersed at a concentration of 0.1mg/mL, in SDS solutions with various SDS concentrations, a few minutes after sonication (blue line) as well as after the first centrifugation (1 h later, green line), and after centrifugation 4 days (red line) and 1 year (purple line) later; All samples were diluted 1:9 prior to absorbance measurements. The dark gray region marks the surfactant concentration values for which an aggregated state is formed. The light gray region shows the surfactant concentrations for which the particles remain dispersed. The x-axis is logarithmic but the value of 0 was added on the left to help in a comparison with Figure 2.1. Adapted from Ref. 139.
2b. Model and Application

The suggested RCA model is in principle a reversible aggregation model that explores the spectrum between DLCA and RLCA. The particles are represented in two-dimensions (2-D) by line segments of unit length that are moving freely (off-lattice simulation) in a square matrix with periodic boundary conditions by performing translational and rotational steps. Imminent collisions between particles/clusters happen with a certain probability (which I will call aggregation probability) and produce clusters. Particles can detach themselves from the clusters that they are part of with a certain probability that I will call deaggregation probability.

The algorithm initially places the particles at random positions and random orientations in a square matrix, making sure that they do not overlap with each other, do not form clusters and do not touch the boundaries. At each time step, one of the existing particles/clusters is picked. Depending on the step, this particle/cluster is destined to perform either a rotation or a translation (this option interchanges step by step). The direction of movement is decided; and, based on an aggregation probability calculation, two particles/clusters that are sufficiently close to each other and are meant to collide will either collide and aggregate or will not move at all. At the end of each step, a particle is picked at random and if it belongs to a cluster then it is decided whether it will deaggregate from all its neighbors or not based on a deaggregation probability calculation. A more detailed algorithm is provided in APPENDIX 2.A.

The above description is based on the assumption that line segments in a 2-D matrix represent plate-like particles in 3-D. Imagine that there is a third dimension perpendicular to the simulation space and the line segments extend in that space; then these particles
can be seen as 2-D plates that are all parallel to the axis that defines the third dimension and are restricted within the same boundaries with respect to that dimension (i.e., concentric). This is the basic assumption that have to be taken to reduce this model to 2-D. No movement in the third dimension is assumed; but, the third dimension cannot be ignored it entirely since our particles need to have a non-zero volume in order to use the electrostatic equations that are presented below. Assuming that the particles are concentric is a reasonable assumption that ensures that all particles will interact with each other when they collide in 2-D and simplifies the calculation of the total interaction energy for colliding particles that are presenting below.

The actual thickness of the graphene-like particles I model is less than 1 nm, and the aspect ratio of graphene sheets is very high, typically on the order of $10^3$. Since there is such a large difference in length scales, I ignore the effect of thickness in physical interactions between the particles. Even though the thickness is ignored in physical interactions between different particles, it cannot be ignored for the vdW force calculations as this would mean that the particles are massless and thus exert no force. In the energetic calculations that are presented below, the particles are treated as $1 \, \mu m \times 1 \, \mu m$ plates with a thickness of 1 nm.

The above RCA growth model was used to simulate the experimental results reported in Ref. as summarized in the introduction. The only adjustment I had to do to the model described above to tackle this problem was to calculate the aggregation and deaggregation probability parameters for this particular case. Below, I present the Arrhenius-type relations that were used followed by an explanation of how the aggregation and deaggregation barriers are calculated through the calculation of the
energy potential and how I calculate the distance between linear segments by relating it to the coordinates of the particles. The aggregation and deaggregation probabilities are given by Eqs. (2.1) and (2.2), respectively:

\[
P_{\text{agg}} = f_1 \exp \left( -\frac{E_{\text{agg}}}{k_B T} \cdot \frac{1}{f_0} \right) \tag{2.1}
\]

\[
P_{\text{deagg}} = f_2 \exp \left( -\frac{E_{\text{deagg}}}{k_B T} \cdot \frac{1}{f_0} \right) \tag{2.2}
\]

where \( f_0, f_1, \) and \( f_2 \) are constants, and \( E_{\text{agg}} \) and \( E_{\text{deagg}} \) are the energy barriers for aggregation and deaggregation, respectively. \( f_1 \) and \( f_2 \) express the aggregation and deaggregation frequency and \( f_0 \) is a scaling factor for the aggregation and deaggregation energy barriers which is used to reduce the total time scale of the aggregation and deaggregation events in order to make the simulations computationally feasible. More details on the physical and numerical parameters used in our model and the values used for the simulations presented here can be found in APPENDIX 2.B.

The two energetic barriers are calculated from data of the interaction energy as a function of distance among the colliding particles and then they are simplified to the equivalent step potential barriers as shown in Figure 2.3. The aggregation energy barrier is equal to the maximum of the interaction energy of a pair of sheets as a function of distance, while the deaggregation barrier is equal to the difference between that maximum and the value of the interaction energy at the distance of 1.5 nm,\(^{139}\) to account for a steric layer from an adsorbed SDS monolayer (i.e., the distance that is about equal to twice the width of a hydrocarbon chain). Assuming that the only effective forces are
the vdW attractive forces and the electrostatic repulsive forces, I used the equations calculated for parallel plates of infinite length\textsuperscript{186,187} similar to the procedure followed in \textsuperscript{139}:

\begin{align*}
\varphi_{\text{elec}} &= 64k_B T n_b \kappa^{-1} \tanh^2 \left( \frac{1}{4} \psi_s \right) \exp(-\kappa h) \quad (2.3) \\
\varphi_{\text{vdW}} &= -\frac{A}{12\pi} \left[ \frac{1}{h^2} + \frac{1}{(h + 2d)^2} - \frac{2}{(h + d)^2} \right] \quad (2.4) \\
\Phi_{\text{total}} &= \int \varphi_{\text{vdW}}(h(l)) dl + \int \varphi_{\text{elec}}(h(l)) dl \quad (2.5)
\end{align*}

where $\varphi_{\text{elec}}$, $\varphi_{\text{vdW}}$ are the electrostatic and the vdW potentials per area of the colliding particle, $\Phi_{\text{total}}$ is the total potential of the colliding particles, $n_b$ is the ion number density, $\kappa^{-1}$ is the Debye length, $\psi_s$ is the FGS potential which was calculated from the Poisson-Boltzmann equation using measurements of the charge induced on FGS through the adsorption of SDS surfactants,\textsuperscript{139} $h$ is the distance between the sheets, $A$ is the Hamaker constant,\textsuperscript{188} and $d$ is the thickness of the sheets.
Figure 2.3. Total energy of interaction of two parallel sheets during collision (blue solid line) and calculation of the respective aggregation ($E_{agg}$) and deaggregation ($E_{deagg}$) energies. The dashed red line shows the extracted deaggregation step-potential used by the model while the dashed and dotted black line shows the extracted aggregation step-potential. Both potentials have the same maximum equal to the maximum of the total energy of interaction. The gray dotted vertical line indicates the assumed steric layer at 1.5 nm. This calculation is repeated for every imminent collision as the relative positions (angle and point of contact) of the particles is different in each case.

However, in this case, we deviate from the model of parallel plates of infinite length by considering non-parallel sheets as discussed below. Here, $h$ in Eqs. (2.3) and (2.4) is now given as $h_1$ or $h_2$, depending on whether the distance is calculated from the edge or from the main body of the collided particle (as shown in Figure 2.4), and they are both expressed in terms of the x-coordinate of the particles. This way, the integration can be done along the length of the colliding particle as expressed in Eq. (2.5).
Figure 2.4. Two line segments are represented with black. The distance as a function of the x-coordinate is represented by the length of the blue arrows for $h_1$ and by the length of the red arrows for $h_2$ (in this case, it is the distance from the point $(x_4,y_4)$). The purple arrow is taken at the point where $h_1(x_p) = h_2(x_p)$. The $h_1$ equation is used when $x_p < x < x_1$ while the $h_2$ equation is used when $x_2 < x < x_p$. In the x-coordinate scale at the bottom the $x_0$ domain is shown between the brackets (in this case it is $[x_2,x_1]$).
\[ h_1 = \frac{[(a_2 - a_1)x_0 + (b_2 - b_1)]}{\sqrt{1 + a_1^2}} \]  

\[ h_2 = \min \left( \sqrt{(a_1 x_0 + b_1 - y_3)^2 + (x_0 - x_3)^2}, \right. \]  

\[ \left. \sqrt{(a_1 x_0 + b_4 - y_4)^2 + (x_0 - x_4)^2} \right) \]

for the cases of body-body and edge-body distance calculations, respectively. \( \min(a,b) \) is a function that outputs \( a \) if \( a \leq b \) or \( b \) if \( b < a \). Each line segment is expressed by an equation of the form:

\[ y = a_i x + b_i \]  

with \( i = 1 \) for the moving particle (with coordinates of the two edges \((x_1,y_1)\) and \((x_2,y_2)\)) and \( i = 2 \) (with coordinates \((x_3,y_3)\) and \((x_4,y_4)\)) for the collided particle. \( x_0 \) is the \( x \) coordinate of the moving particle \((i = 1)\) and varies between \( x_1 \) and \( x_2 \).

Since Eqs. (2.3) and (2.4) express the per area interaction energy of a plate that is parallel to an infinite plate, I decreased the values of these equations by a factor of \( 10^2 \) (which is factored in \( f_0 \) – for details see APPENDIX 2.B) to approximate the per area interaction energy of an infinitesimal plate interacting with a finite plate and then the infinitesimal plate interaction is integrated along the length of the colliding particle \((x_0)\) to take the angle difference into account. This procedure is equivalent to considering each particle as a sum of infinitesimal parts that are all parallel to their interacting particle.

When a collision of two sheets (either single sheets or sheets that are part of a cluster) is imminent, the above energetic calculation is performed in order to calculate the interaction energy for different distances between the sheets. From these data the
aggregation and deaggregation energies between the two particles are calculated as shown in Figure 2.3. These values are substituted into Eqs. (2.1) and (2.2) to calculate the probability for aggregation and deaggregation, respectively. The aggregation probability value defines whether these particles/clusters will collide, in which case they aggregate and merge in one cluster, or they will not collide at all. The deaggregation probability value, in case of a successful collision, defines the probability that the aggregated particles may deaggregate in future steps.

For computational simplicity, I assume that deaggregation of a particle signals deaggregation from all its neighbors simultaneously, following the SAK model. The overall deaggregation barrier \( (E_{\text{deagg}}) \) is assumed to be equal to the sum of the deaggregation barriers that were calculated during the collision of each pair of particles that is part of the deaggregation process. In order for deaggregation to occur in this way, it was necessary to assume that the deaggregation barrier calculation is independent to the direction of the deaggregating step. This is not very far from the truth as the maximum of the energy barrier is always very close to the point of collision, which means that the relative positions between the deaggregating sheets are close to the relative positions of the aggregating sheets. Thus, the parameters that matter the most in the calculation of the aggregation and the deaggregation barriers are the point of collision and the angle created by the two particles at that point and not the angle of the relative movement between them.

The transformation of the continuous potential to a step potential barrier for aggregation and a step potential barrier for deaggregation, as seen in Figure 2.3, reduces the computational load and even though I expect it to affect the dispersion of the particles.
around clusters I do not expect it to affect their size and structure. The main effect of this assumption is that during the collision of clusters the only energetic calculation that is performed is between the collided particles.

In summary, the assumptions of this model and the assumptions introduced to tackle this particular problem are:

1) The system is simplified to 2-D and the graphene particles, that are normally non-flat sheets, are represented by straight and rigid line segments. These represent plate-like particles that are concentric and parallel with respect to the dimension perpendicular to the plane and their thickness is ignored during physical interactions.

2) The only acting forces are vdW and electrostatic.

3) The equations of interaction forces for plates of infinite length are assumed to be valid for particles of finite length and for edge-body interactions after a reduction by a factor.

4) Forces are only effective during collision and deaggregation attempts. During a collision, the only energetic calculation is between the two colliding particles, which have to overcome the aggregation barrier in order to form a new cluster.

5) There is a steric barrier of 1.5 nm between the particles due to adsorbed SDS.

6) During deaggregation, it is assumed that the energy for deaggregation is the sum of the calculated deaggregation energies between the particle that tries to deaggregate and all its direct neighbors (the particles it was in direct contact with at that point). For each case, the deaggregation energy is assumed to be independent of the angle of the relative movement between the deaggregating particles.
7) The diffusion coefficient does not depend on the direction that the particles move and there are no effects from the liquid medium.

8) Sedimentation only happens during centrifugation and thus gravitational forces are ignored in our simulation, although gravitational effects are considered later in the Results and Discussion section once the resulting structures are determined.

2c. Results and Discussion

I first present the results of the simulations from the implementation of the above RCA model by comparing the cluster structures to the optical microscopy images of Figure 2.1 and presenting how the cluster size changes with surfactant concentration and time. Then, I show the change in gravimetric Peclet number, $Pe_{gs}$, of the clusters with surfactant concentration and time and explain why at $C_{crit}$ a high percentage of the particles is expected to sediment early as shown in Figure 2.2 and for lower surfactant concentration I show a densification of the clusters with time that can lead to sedimentation of the formed gel later in time. Finally, I discuss the behavior of the presented model in terms of aggregation and deaggregation rates and explain that even though equilibrium has not reached the clusters formed at high $C$ are not expected to grow further due to their dynamic nature.

Cluster Size and Critical Concentration

In Figure 2.1, I presented the different structures that are observed under optical microscope for different surfactant concentrations right after sonication of the samples. These structures varied from highly ramified aggregates at low surfactant concentrations, to dense aggregates around $C_{crit}$, and to well-dispersed suspensions for even higher...
surfactant concentrations. Figure 2.5 shows equivalent structures of clusters produced by our model. The different surfactant concentrations correspond to different inter-particle forces and all results are captured at the $6 \times 10^6$ simulation step which corresponds to about half minute of experimental time (see APPENDIX 2.C for calculation of diffusion time scale). In this case, two main types of structures are identified: ramified clusters (Figures 2.5(a), 2.5(b)) of average size that decreases with surfactant concentration and dispersed single or few-layer particles (Figure 2.5(d)).

![Images from simulations for different surfactant concentrations with constant concentration of particles (~0.49 particles/µm$^2$, 1,000 particles in a 45 x 45 µm matrix at the step $6 \times 10^6$). Particles that are parts of the neighboring simulation domains (the boundary conditions are periodic) appear in green. Particles that belong to clusters that have crossed the boundaries and reappear on the other side appear also in green and their unconnected parts have been moved back to show the complete shape of each cluster and appear in black. All other particles that are part of the main simulation domain appear in black.](image)

**Figure 2.5.** Images from simulations for different surfactant concentrations with constant concentration of particles (~0.49 particles/µm$^2$, 1,000 particles in a 45 x 45 µm matrix at the step $6 \times 10^6$). Particles that are parts of the neighboring simulation domains (the boundary conditions are periodic) appear in green. Particles that belong to clusters that have crossed the boundaries and reappear on the other side appear also in green and their unconnected parts have been moved back to show the complete shape of each cluster and appear in black. All other particles that are part of the main simulation domain appear in black.

To determine the growth rate of the clusters for different surfactant concentrations, the average number of particles per cluster ($\bar{s}$) as a function of time was determined as shown in Figure 2.6. At short times, the lower the surfactant concentration, the higher the
net aggregation rate (i.e., the rate of change in average cluster size) is. For surfactant concentrations of $10^{-5}$ and $0.1 \, \mu M$, the average cluster size follows a similar pattern, with the low concentration having clearly higher net aggregation rate initially. At longer times, however, both systems reach the same limit as growth eventually stops near the limit of total number of particles in the system (with the system $C = 10^{-5} \, \mu M$ reaching that limit earlier due to higher aggregation rate). Growth rate generally slows with time in each case, independent of concentration. This reduction in growth rate was expected due to a decrease in the number of single particles in the system. The clusters that are formed have higher inter-cluster distances and diffuse slower relative to the single particles that existed initially.

**Figure 2.6.** Results from simulations for different surfactant concentrations with constant concentration of particles (~0.49 particles/$\mu m^2$, 1,000 particles in a $45 \times 45 \, \mu m$ matrix). The vertical axis depicts the average number of particles per cluster while the horizontal
axis represents the simulation time. The dotted black horizontal line indicates the maximum cluster size, equal to the total number of particles (1,000). This data represents the 5-point moving average of the average values from 3 simulations with the standard deviation of the 3 values drawn as a faded region around each corresponding line. The dark gray region indicates the aggregated state and the light gray region marks the dispersed state.

Above a surfactant concentration of 0.1 µM, there is a sudden drop in the cluster growth rates with surfactant concentration. At the 10 and 100 µM concentrations, cluster growth is nearly zero for high simulation times, corresponding to the dispersed states observed in Figure 2.5(c). Once a thermodynamically stable dispersed state is achieved, the clusters are expected to stop growing and remain embryonic. The results in Figure 2.6 suggest that this equilibrium state has not yet being reached in our simulations; this claim is discussed further in the last subsection of Results and Discussion by looking at the average cluster lifetime.

The transition from fast growth (at short times) to slow or no cluster growth regime helps to identify a region of sudden change in the net aggregation rate pattern between the SDS concentrations of 0.1 and 10 µM. A transition from fast cluster growth regime to almost zero growth takes place in this region. At this intermediate concentration \((C = 1 \text{ µM})\), there also appears to be a significant number of small clusters of size 10 µm and smaller just like in case (iii) (Figure 2.1(c)). Thus, there are two indications (a transition zone in growth rate and 10 µm-sized clusters) that \(C = 1 \text{ µM}\) is the critical concentration as predicted from this model. One more characteristic of the critical concentration is that it tends to produce denser aggregates (as seen in Figure 2.1) that lead
to more particles sedimenting and thus lower UV-Vis absorbance (as seen in Figure 2.2). I quantify this claim in the following subsection by calculating the $Pe_g$ of clusters and noting its shift with SDS concentration.

**Cluster Sedimentation**

Traditionally, $Pe_g$ has been used as the sedimentation metric in colloidal science. $Pe_g$ expresses the balance between Brownian motion and buoyancy versus gravity. A $Pe_g$ value of 1 or lower is indicative of non-sedimenting individual particles while a value a lot higher than 1 indicates strong gravitational forces and therefore fast sedimentation. Here, I define the $Pe_g$ of an individual particle as defined in [186]:

$$Pe_g = \frac{4\pi \Delta \rho \alpha^3 g l_c}{3 k_B T}$$

(2.9)

where $\Delta \rho$ is the difference in density between the particle and the solution, $\alpha$ is the hydrodynamic radius of the particle, $g$ is the gravitational acceleration and $l_c$ is a characteristic sedimentation distance, which is taken to be equal to 1 mm, which is an order of magnitude higher than the length of our simulation domain.

To evaluate whether the clusters generated by our model sediment or not I generalized Eq. (2.9) to calculate $Pe_g$ for clusters. For this, I substituted $\alpha$ with radius of gyration, $R_g$, of the cluster instead of its hydrodynamic radius since these numbers are close to each other and the former is easier to calculate. The density of the clusters was calculated as the ratio of total mass of graphene particles and water occupying the volume not-occupied by the particles over the total volume. The volume of the clusters is assumed to be equal to the volume of a disk with a radius of $R_g$ and thickness equal to the
length of one graphene particle ($l$). This is consistent with the existing assumption of treating each individual particle as $1 \, \mu m \times 1 \, \mu m$ plates with a fixed $1 \, \mu m$ depth in the direction perpendicular to the 2-D plane:

$$R_g^2 = \frac{1}{N} \sum_{i=1}^{N} R_i^2 \quad (2.10)$$

$$\rho = \frac{Nm_{fgs} + (\pi R_g^2 l - NV_{fgs})\rho_w}{\pi R_g^2 l} \quad (2.11)$$

where $N$ is the total number of particles of the cluster, $R_i$ is the distance between the center of each particle and the center of mass of the cluster, $m_{fgs}$, the mass of one FGS, $l$ is the length of the graphene sheets in the dimension perpendicular to the 2-D plane (i.e., $1 \, \mu m$), $V_{fgs}$ is the volume of one FGS, and $\rho_w$ is the density of water.

$m_{fgs}$ was taken equal to $8.178 \times 10^{-16} \, g$ for a $1 \, \mu m^2$ FGS area, assuming an area of a carbon hexagon of $5.239 \times 10^{-8} \, \mu m^2$ and a C/O ratio of 18. $V_{fgs}$ is $7 \times 10^{-4} \, \mu m^3$ assuming an area of $1 \, \mu m^2$ and a thickness of $0.7 \, nm$. Even though it is hard to calculate the exact thickness of FGS, XRD data show that the interlayer spacing of graphite oxide increases to $0.7 \, nm$ during the oxidation of graphite.$^{10}$

It is noted that my goal is not to model the simultaneous aggregation and sedimentation processes. There are modeling and experimental efforts that have focused on this challenging problem.$^{190,191}$ My approach is to ignore sedimentation first during the aggregation process and to simply evaluate a sedimentation metric that would tell how prone to sedimentation clusters and particles are.

The cluster-$Pe_g$ metric helped me correlate the simulation data to the UV-Vis absorbance data of Figure 2.2 where it is seen that the supernatant becomes highly
transparent around $C_{\text{crit}}$. Below that concentration, the supernatant becomes transparent at a slower rate and above $C_{\text{crit}}$ the absorbance does not decrease significantly throughout a year. Experimentally, persisting high UV-Vis absorbance values of the supernatant indicate very slow sedimentation or no sedimentation with time. This can happen (i) when a contiguous connected particle network e.g., a gel structure or (ii) dispersed particles or dispersed ramified particle clusters with a low enough Peclet number form. In the first case, while strong gels can resist sedimentation, they can densify with time, shrink, and sediment. In the second case, dispersed ramified clusters may also restructure with time, densify, and sediment at a faster rate as their Peclet number increases and single particles may form dense clusters later on. Thus, while high UV-Vis absorbance corresponds to systems that resist sedimentation either due to the formation of a contiguous network structure or dispersed low $Pe_g$ particles/clusters, low UV-Vis absorbance values relate to dense aggregate systems.

A metric that is useful for a comparison of the simulation results with the absorbance data of Figure 2.2 is the percentage of particles that belong to clusters with a $Pe_g$ number higher than 1. Those are the clusters that would tend to sediment because of the relative high gravimetric forces that they experience. In Figure 2.7, I present how this metric varies with simulation time and surfactant concentration. The higher the percentage of particles that belong to high $Pe_g$ clusters, the higher the percentage of particles that might sediment, as long as a strong gel that resists sedimentation is not formed.
**Figure 2.7.** Results from simulations for different surfactant concentrations with constant concentration of particles (~0.49 particles/µm², 1,000 particles in a 45x45 µm matrix). This data represents the 5-point moving average of the average values from 3 simulations with the standard deviation of the 3 values drawn as a faded region around each corresponding line. The vertical axis presents the percentage of sheets that belong to clusters with $Pe_g$ that exceeds the value of 1 (i.e. gravimetric force is more important than Brownian motion) as a function of time.

As shown in Figure 2.7, the percentage of particles associated with clusters of high $Pe_g$ decreases with increasing SDS concentration. At $C = 10$ and 100 µM, $Pe_g << 1$ and thus sedimentation is not expected in agreement with experimental data in Figure 2.2. Similarly, Figure 2.6 shows that at $10^{-5}$ and 0.1 µM particles tend to organize in large
clusters. This is an indication for the formation of a gel network, given a large enough particle concentration, which also prevents sedimentation of those particles.

However, at the SDS concentration of 1 µM, there is a significant percentage of particles with $P_{eg} > 1$ that can sediment as they do not form large clusters as in lower surfactant concentrations. The average size of clusters formed for the time scale of the simulations remains below 10 particles per cluster. This means that, for SDS concentrations around 1 µM a gel is not formed for the time scale of the simulations and the number of clusters with high $P_{eg}$ that are formed will be free to sediment. This observation also agrees with the data from Figure 2.2 that shows a decrease in UV-Vis absorbance around the critical surfactant concentration.

For $C = 1$ µM, it can also be seen that the rate of formation of clusters that can sediment is much lower than for lower surfactant concentrations but it is non-zero. The entire length of the simulations (15 million steps) corresponds to about 1.5 minutes (according to the approximate calculation shown in APPENDIX 2.C) and an average of 30% of particles belongs to clusters that can sediment. Comparing that with Figure 2.2 the green line shows that a significant percentage of particles will sediment in 1 h at $C_{\text{crit}}$ (about 10 µM for experimental case). My simulations might have overestimated the rate of creation of dense clusters at $C_{\text{crit}}$ (about 1 µM for our simulation), since 1 h of real time corresponds to 631 million simulation steps; But, I cannot be entirely sure since no results were collected for smaller times (except right after dispersion).

A more appropriate metric for gelation would be the gravimetric Peclet number as defined by Poon and Haw$^{192}$, if the right critical value were known for this system. A critical gravimetric Peclet value below which gelation occurs was calculated by Kim et
al. for the case of adhesive spheres but not for the case of linear particles that experience attractive and repulsive forces.

Combining the cluster size information of Figure 2.6 and a sedimentation analysis of the percentage of particles based on $Pe_g$, I have addressed the low absorbance values for $C_{\text{crit}}$ in Figure 2.2 at a given time; but, I have not yet addressed the drop in absorbance with time for $C < C_{\text{crit}}$. In order to address this slow sedimentation behavior that occurs at lower surfactant concentrations, I will now consider a local densification through restructuring in the next subsection.

**Densification through Restructuring**

In order to investigate the local density of the particle clusters with time, a new metric is introduced: the average angle formed between neighboring particles. This presents the mean of the angle formed between each pair of directly neighboring particles within each cluster (i.e., particles that are in contact with each other). An angle difference of 90° indicates vertically oriented neighboring particles, while an angle difference of 0° indicates parallel neighboring particles. Clusters with lower average angle difference consist of particles that are on average closer to each other tending towards a layered and thus denser structure. This gives a better idea of the local density of the clusters as it indicates how close neighboring particles are to each other.

Figure 2.8 shows how the average angle varies with time for different surfactant concentrations. First important observation is that the average angle of the neighboring particles increases with surfactant concentration. This is a result of the non-linear relation between $E_{\text{agg}}$ and $P_{\text{agg}}$ as expressed in Eq. (2.1). Generally, $E_{\text{agg}}$ increases with increasing
surfactant concentration because of the $\psi_s$ term that appears in Eq. (2.3). This translates to different $P_{agg}$ distributions as a function of average angle of neighboring particles for each surfactant concentration. The result is a lower probability for neighboring particles to form small angles as the surfactant concentration (and therefore the intensity of repulsive forces) increases. This behavior is observed even for really low times as I start with a well-dispersed system and there are no pre-existing clusters that would affect the results.

**Figure 2.8.** Results from simulations for different surfactant concentrations with constant concentration of particles (~0.49 particles/µm$^2$, 1,000 particles in a 45x45 µm matrix). The vertical axis presents the average angle difference between neighboring aggregated particles as a function of time. The dark gray region indicates the aggregated state and the light gray region marks the dispersed state.
Another observation from Figure 2.8 is that for surfactant concentrations below 1 µM, there is a clear continuous drop of average angle difference with time indicating densification through restacking, while there is no clear indication of reduction of this metric with time for surfactant concentrations above 1 µM. This drop can be attributed to a sampling of more states between clustered particles. When a particle deaggregates from the interior of a large cluster there is a larger chance that this particle will collide again with the same cluster and reaggregate with it in a different angle. Overall, smaller angles have higher $\Phi_{total}$ due to larger area interactions and, as can be seen from Figure 2.3, this leads to higher $E_{agg}$ and to lower deaggregation probabilities (as seen from Eq. (2.2)), and, therefore, bonds of smaller angles tend to survive longer.

This densification behavior can be correlated to the real system. As in Figure 2.2, there is a clear reduction in absorbance and thus sedimentation with time for samples of surfactant concentration lower than the critical surfactant concentration. Combining the results from the current and the previous subsection, the experimental results of Figure 2.2 become more clear: At the critical concentration, a large number of high $Pe_g$ clusters is formed and those clusters sediment. Below that SDS concentration, a gel is formed given a high enough concentration of particles. With time, these gels densify and tend to form more graphite-like structures that will eventually sediment. According to Figure 2.2, sedimentation of particles for low surfactant concentrations happens with a slower rate. The reason for the difference in sedimentation rates can be attributed to the time scale difference of the two mechanisms that produce those sedimenting clusters.
Aggregation and Deaggregation Rates

The aggregation and deaggregation probabilities as defined in Eqs. (2.1) and (2.2) are basically the probabilities of an aggregation or deaggregation event occurring given that a collision or a deaggregation attempt has occurred, respectively. In order to calculate the net aggregation rate \( r_{\text{agg}} \) I first calculated the aggregation rate \( r_{\text{agg}} \) by multiplying the aggregation probability with the rate of collisions and the deaggregation rate \( r_{\text{deagg}} \) by multiplying the deaggregation probability with the rate of deaggregation attempts. \( r_{\text{agg}} \) is the difference between \( r_{\text{agg}} \) and \( r_{\text{deagg}} \):

\[
r_{\text{agg}} = r_{\text{agg}} - r_{\text{deagg}} = \]

\[
= P_{\text{agg}} r_{\text{collision}} - P_{\text{deagg}} r_{\text{deagg,att}}
\]

where \( P_{\text{agg}} \) and \( P_{\text{deagg}} \) are the average values of the probabilities defined in Eqs. (2.1) and (2.2). \( r_{\text{collision}} \) is the rate of imminent collisions (this includes potential collisions that did not happen because the aggregation barrier was not crossed), and \( r_{\text{deagg,att}} \) the rate of deaggregation attempts, i.e., the rate at which a particle will be tested for deaggregation with its neighbors (equivalent to rate of collisions for aggregation). As mentioned in the Model and Application section, in each step, a particle at random is picked for deaggregation and if this particle is part of a cluster it is attempted to be deaggregated from its neighbors. Therefore, the rate of deaggregation attempts, \( r_{\text{deagg,att}} \) is equal to the percentage of particles that belong to clusters (i.e., particles that are not single).

In Figure 2.9, I present how the average aggregation and deaggregation rates change with time and surfactant concentration. Figure 2.9(a) shows the values of \( r_{\text{agg}} \). As expected from Figure 2.6, the higher the value of surfactant concentration the lower the
value of $r_{agg}$. For low surfactant concentrations, a decrease of $r_{agg}$ with time is observed, while for high surfactant concentrations, $r_{agg}$ remains almost constant. The decrease for low $C$ can be attributed to the fact that fewer free particles remain in the matrix with higher relative distances from each other, which causes a decrease in collision rate. This makes aggregation events more rare with time. This phenomenon is not observed for high $C$ as the size of the clusters does not change significantly with time. The initial jump observed in $r_{agg}$ for all surfactant concentrations can be attributed to an averaging starting with values of zero at zero time step. In the cases of $C = 10^{-5}$ and 0.1 µM the initial increase is accompanied by a fast decrease for times below the millionth time step. This is again due to the increase in cluster size which happens at a high rate at these concentrations and times.

Figure 2.9. (a) Rate of aggregation calculated using the variables shown in Eq. (12). (b): Rate of deaggregation as calculated by the variables in Eq. (12). This data represents the 5-point moving average of the average values from 3 simulations.

Figure 2.9(b) shows $r_{deagg}$, which follows a similar trend to $r_{agg}$. For low $C$, a decrease of $r_{deagg}$ can be seen with time, while for high $C$, $r_{deagg}$ remains relatively
constant with time. This decrease in the rate of deaggregation events can be attributed to a decrease in the deaggregation probability. The larger the clusters the larger the percentage of particles that are in the interior of those clusters. Particles that are in the interior of the clusters have a larger number of neighbors and thus a lower probability to deaggregate. The initial increase in \( r_{\text{deagg}} \) that is observed for all surfactant concentrations is real (as opposed to the one observed in Figure 2.9(a)) and is caused by the fact that the simulations start with a dispersed system and the existence of clusters is a prerequisite for deaggregation to occur.

An aggregation event is not necessarily equivalent to a deaggregation event. An aggregation event is the result of the collision of two particles (that might be single particles or part of a cluster) that merge into one cluster. A deaggregation event is a result of a successful deaggregation attempt between a particle that belongs to a cluster and all its direct neighbors. This means that a deaggregation event results in the separation of a cluster in two or more clusters, while an aggregation event always merges two clusters/particles into one. Therefore, \( r_{\text{agg}} \) is expected to maintain higher values than \( r_{\text{deagg}} \) even during equilibrium.

Further, even though \( r_{\text{deagg}} \) has higher values for lower \( C \), this does not mean that the large clusters formed at these surfactant concentrations are more dynamic than the ones for high \( C \). One metric that can help quantify the dynamic nature of the clusters formed in our model is the average cluster lifetime (\( \tau_c \)):

\[
\tau_c = \frac{\xi}{r_{\text{deagg}}} \quad (2.13)
\]
where $\bar{s}$ is the average cluster size. This value approximates the time for an average cluster (in each surfactant concentration and time) to deaggregate completely.

Figure 2.10 shows how the average cluster lifetime changes with time and surfactant concentration. For low $C$, the lifetime of the clusters is high and is getting larger as their size grows. For high surfactant concentration, their size remains low with time. This indicates that the small clusters formed at these surfactant concentrations are very dynamic relative to the large clusters formed at lower $C$. The initial drop in the value of lifetime is caused by the initial increase in deaggregation rates observed in Figure 2.9.

![Figure 2.10](image)

**Figure 2.10.** Change of the average cluster lifetime as calculated by Eq. (13). This data represents the 5-point moving average of the average values from 3 simulations with the standard deviation of the 3 values drawn as a faded region around each corresponding line.
At $C = 1 \, \mu M$, Figure 2.10 reveals an interesting behavior: At initial times, as the clusters remain small they are more dynamic than the clusters formed at high $C$. As the cluster size grows their lifetime exceeds the lifetime of clusters formed at higher $C$. The fact that clusters appear more dynamic at $C = 1 \, \mu M$ than at higher $C$ is not necessarily representative of the physical reality but is indicative of how our model works, i.e., allowing restructuring of the clusters through continuous deaggregations and reaggregations. In real systems, a lot of this restructuring happens by bending	extsuperscript{194} of graphene particles and their relative movement to each other without deaggregation really occurring.

Overall, none of the simulations has reached equilibrium. For low surfactant concentrations $r_{\text{agg}}$ and $r_{\text{deagg}}$ are decreasing continuously (Figure 2.9) and the relative angles of neighboring particles are also decreasing (Figure 2.8). For lower surfactant concentrations, the size of the clusters is increasing (Figure 2.6), although slowly. Nevertheless, from Figure 2.10 it is concluded that the small clusters that are created at high surfactant concentrations have a very short life time, are very dynamic, and they do not grow further as they never go beyond an embryonic cluster stage. Embryo clusters are expected to form even in thermodynamically stable dispersed colloidal suspensions due to random fluctuations in our system that can be explained by statistical mechanics.

Finally, I expect the initial concentration of particles to have an effect on the aggregation and the deaggregation rates. More specifically, a lower initial particle concentration would lead to lower aggregation rates due to the larger initial distances between the particles. This lower aggregation rate also leads to lower deaggregation rates because the rate of deaggregation attempts is proportional to the number of aggregated
particles, as mentioned earlier. Overall, I do not expect the initial particle concentration to have an effect on the behavior of the system, other than reducing the overall size of the clusters (due to the reduced number of available particles) and reducing both the aggregation and deaggregation rates.

2d. Conclusions

This is the first reversible aggregation model for non-linear particles and it can help in building intuition on problems about graphene-like or other atomically-thin particle aggregation or needle(rod)-like particles aggregation that move on the same 2-D plane (e.g., an interface).

Both the experiments and the simulations give similar trends related to the particle cluster size, an indication for the existence of a critical concentration of surfactant at which many dense clusters are formed, an indication for the formation of a gel below that concentration which tends towards a graphite-like structure with time and mostly dispersed single particles above the critical surfactant concentration.

One point of disagreement between experiments and simulations is the actual value of the critical surfactant concentration: the experiments indicate that this value is about 10 µM of SDS while the simulations point towards a value in the order of 1 µM. A quantitative disagreement is something that was expected based on the number and weight of my assumptions and especially since the simulations are performed in 2-D. At $C > C_{\text{crit}}$ our model captures the state of a thermodynamically stable colloidal dispersion well with the formation of embryonic clusters with very short life times that never reach the stable cluster (nucleus) size.
The assumption that probably had the largest effect on the results is the rigid nature of graphene. In reality it is known that graphene particles that come in touch with each other find a favorable position really fast as the particles are able to fold and bend to get to more energetically favorable positions. What is done in these simulations instead is to sample different energetic states by allowing deaggregation and reaggregation of the particles. This is something that is expected to have a significant effect on the time scales of the results generated by the RCA model.

My approach ignored the effect of flow since it was not relevant to the modeled experiments; but, flow effects can be incorporated in this algorithm by altering the diffusion step size and probability of moving in different directions for each step.

**Appendix 2.A**

The algorithm used in our simulations is shown in the flow chart of Figure 2.11 and is also described below in a high-level pseudocode form:

Repeat for each particle

Repeat until the current line segment is placed in a way that does not overlap with the previously placed segments.

Pick a random position for each linear segment (x and y coordinates) and make sure that its distance from each boundary is at least equal to the length of the segments.

Pick a random orientation (tangent) for this line segment.

If there is an overlap of this line segment with the ones previously placed then start all over.
End

Organize the segments in cells according to their position.

Calculate the center of mass of each line segment.

End

Time stepping

Pick a cluster or single particle randomly.

If the step number is an even number perform a translation step of the whole cluster.

Pick a random direction for the cluster to move.

The step size is calculated as the minimum of a fixed step size (that is inversely proportional to the square root of the size of the cluster) and the minimum step at which there is a collision between any line segment that belongs to this cluster with another line segment that does not belong to the same cluster.

Else if the step number is an odd number perform a rotation step of the whole cluster.

Pick a random rotation direction for the cluster (clockwise or counter-clockwise).

The rotational step size is calculated as the minimum of a fixed step size (that is inversely proportional to the square root of the size of the cluster) and the minimum rotation step at which there is a collision between any
line segment that belongs to this cluster with another line segment that
does not belong to the same cluster.

End

If there is a potential collision between line segments of different clusters then
calculate the energetic barriers for aggregation and deaggregation and the
resulting probabilities (according to the equations presented in the main text).

If the line segments stick to each other (aggregate) then they form one cluster,
else they remain in their original position before the occurrence of this step.

Keep track of the parts of the cluster that have crossed the boundaries (this
information is important for the rotation of each cluster).

Pick one line segment at random and calculate the probability of its deaggregation
from its surrounding segments. The deaggregation probability is calculated from
the combined deaggregation barriers that were calculated during the aggregation
of this segment with all the segments it is aggregated with.

If deaggregation occurs organize the line segments in smaller clusters and update
information about the parts of these new clusters that have crossed the boundaries.

Calculate the center of mass of each cluster.

Organize the segments in cells according to their position.

End
**Figure 2.11.** Flow chart of the algorithm used on the simulations. In (a) I show the flow chart of the creation of a particle dispersion and in (b) I show the time stepping algorithm that allows 1) the movement of clusters and individual particles (which can result to aggregation) and 2) deaggregation of existing clusters.

Note: All the random number generators that were used are uniformly distributed random number or uniformly distributed pseudorandom integers.

**Appendix 2.B**

The first parameter that has to be chosen is the concentration of the particles in the matrix. As the starting point is a random dispersion of particles, I had to make sure that the concentration is low enough to create a dispersion that is truly random. When this is not the case the line segments tend to have similar orientation in order to fit between other line segments without colliding with them. One more thing that we need to be careful with when picking this parameter is to make sure that no cluster that will potentially form will span the matrix from one end to the other as this could lead to collision of a cluster with itself and thus essentially an infinite cluster of particles (gel) that would be impossible to rotate. The theoretically maximum length of a cluster is the sum of the lengths of the line segments that it is composed by but in practice we discovered that a typical cluster size of 1,000 particles for the DLA limit of our model is 40. For this purpose we decided to choose a 45x45 matrix, where the unit length is the length of our particles. The above values also ensure a random initial dispersion.

I assume that the particles in the bulk (i.e., when a step does not lead into a collision) move due to thermal fluctuations, which lead to stochastic motion. At each time step one particle/cluster performs one translational or rotational step. Since the diffusion rate of a
sphere is inversely proportional to its radius, I indirectly set the **maximum step size** inversely proportional to its hydrodynamic radius. To reduce computational load I replaced the hydrodynamic radius with the square root of the number of particles of the cluster as the two metrics are proportional. For the case of a single particle, the translational step size is set equal to a fraction of the total length of the line segment (typically 5%), while the **maximum rotation step size** (i.e., the angle of rotation of the cluster around its center of mass) is defined in a way that the theoretically maximum displacement of any point of the rotating particle/cluster is the same as the already defined translational maximum step size for that cluster size.

**Energy of aggregation and energy of deaggregation scaling factor** ($f_0$). The energy barriers calculated by the above equations are very high and thus the probability for aggregation or deaggregation is practically zero. One reason for that is that I used energetic interactions for a finite sheet interacting with an infinite one. Another reason is that FGSs are wrinkled sheets; this wrinkliness could potentially prevent the sheets from coming as close enough to each other as I hypothesized in the simulation and only a proportion of their surface really comes in contact. This difficulty is overcome by rescaling the energy barriers using $f_0$. After experimenting with different values of $f_0$ I decided to use the value of 1,000 as it leads to aggregate generation in reasonable time-scales.

**Pre-exponential factors for aggregation** ($f_1$) and **deaggregation** ($f_2$). Both parameters should have values between zero and one. I set $f_1$ equal to one; this way the aggregation
probability is equal to one when the aggregation barrier is equal to zero. In order to decide the pre-exponential factor for deaggregation the fundamental difference between aggregation and deaggregation has to be explained. The random motion of particles creates random collisions, which can lead to aggregation. Thus, there is a natural factor reducing aggregation frequency, which is the frequency at which collisions happen. This is something that is not inherent to deaggregation since I only artificially check for deaggregation with arbitrary frequency. The deaggregation probability that I have calculated strongly depends on the number of times it is checked whether a particle should deaggregate or not. Since deaggregation is checked at each time-step (by picking one particle) that effectively increases the deaggregation probability. I correct that increase caused by frequent deaggregation check by multiplying the deaggregation probability with $f_2$, which is less than one. After trying different values for $f_2$ I decided to use the value of 0.002.

The concentration of surfactant ($c$) is essentially an independent variable for this study. I have correlated that number to the surface charge ($\sigma_0$) using conductometric titration measurements$^{195}$ and used the surface charge value to calculate the ion number density ($n_b$), the FGS surface potential ($\psi_s$) and the Debye length ($\kappa^{-1}$).

\begin{align*}
    n_b &= I \cdot N_A \\
    \psi_s &= sinh^{-1}\left(\frac{\sigma_0}{\sqrt{8\epsilon_0\epsilon_r k_B T n_b}}\right)
\end{align*}  

(B1)  

(B2)
\[ \kappa^{-1} = \frac{\varepsilon_0 \varepsilon_r k_B T}{\sqrt{2 N_A e^2 I}} \]  
\hspace{2cm} (B3)

\[ I = c - \frac{\sigma_0 S}{N_A} \]  
\hspace{2cm} (B4)

where \( I \) is the ionic strength of the electrolyte, \( N_A \) the Avogadro constant, \( \varepsilon_0 \) the permittivity of free space, \( \varepsilon_r \) the dielectric constant, \( k_B \) is the Boltzman constant, \( T \) is the temperature, \( e \) is the elementary charge and \( S \) is the graphene surface area.

**The length of the particles** is equal to one and is basically used as a length unit. For the energetic calculations this length is assumed to be 1 \( \mu \text{m} \).\(^{10}\)

There is a series of parameters that are only used for numerical purposes and their value should not affect the result for the simulations. They play an important role, though, because if they are not adjusted properly they can lead to errors. These parameters are:

- **touch_dist**: The particles are not allowed to actually touch each other because that could create problems (such as overlapping of the particles) due to truncation errors. That is why I choose leaving a finite but really small distance between them.

- **min_step**: This is the distance below which the particles are assumed to be touching. This is again introduced in order to avoid particle overlapping.

- **search_steps**: This parameter is related to the numerical method that calculates collision of the rotating particles with the neighboring particles. The algorithm first looks at the solution domain to identify any change in sign.\(^{196}\) The frequency
of points that is checked is determined by this parameter, thus the greater it is, the more accurate the method. If a change in sign is identified, a bisection algorithm is used to identify the root with greater accuracy.

- **Cell_size**: The domain is divided into cells in order to group them in a way that will make it easier to identify their neighbors.\textsuperscript{197–199} If the size of these cells is too small the algorithm might fail to identify some neighbors, while if it is too large the simulation becomes computationally expensive.

**Appendix 2.C**

Lotya et al.\textsuperscript{200} constructed a semi-empirical relation between the lateral size of different nanosheets measured by statistical TEM and their size measured by Dynamic Light Scattering (DLS). I used the DLS size of the particles to calculate their diffusion coefficient in water and from that I found an approximate time-scale for the step size performed by the particles in the simulations.

Using the relation from \textsuperscript{200} I found that the sheets (that have lateral size of about 1 \( \mu \text{m} \)) have a size of 560 nm calculated by DLS. This number ends up being proportional to the hydrodynamic radius of graphene particles\textsuperscript{200} and even though these particles are not spherical I used this number to derive an approximate diffusion coefficient using the Stokes-Einstein equation:

\[
D = \frac{k_B T}{6 \pi \eta_w \alpha}
\]

where \( T \) is the temperature assumed to be 300 K, \( \eta_w \) is the viscosity of water at 300 K, assumed to be \( 8.9 \times 10^{-4} \) Pa s and \( \alpha \) is the hydrodynamic radius of the particle substituted by the size calculated by DLS.
From Eq. (C1) I calculated the diffusion coefficient of our particles in water to be around $4.4 \times 10^{-13} \text{ m}^2/\text{s}$. This coefficient was used to derive a time scale for the simulations. The step size ($s$) that each particle can perform in one time step is equal to 50 nm. I define the diffusion time scale in terms of this step size, $\tau_D = s^2/D \approx 0.0057 \text{ s}$.

Since at each time step I pick one of our particles to perform a step, it takes about 1,000 steps for each of the particles to move once. Thus, a million time steps correspond to about 5.7 seconds.
Chapter 3 Micromechanical model for graphene-filled composites

3a. Introduction

The majority of the elastomeric composite models that exist in the current literature are meant to predict the zero-strain elastic modulus\textsuperscript{27,29–31,33–35} or are phenomenological and try to explain complex dynamic effects.\textsuperscript{41–50} The basic problems with predicting failure in elastomeric composites are the high-strains required, which are computationally demanding and the fact that fundamentally there are no analytical conditions for elastomeric fracture\textsuperscript{†} that can consistently predict elongation at failure.

Griffith’s fracture criterion for elastic materials states that no tearing will take place unless sufficient energy is released to meet the requirements for fracture (known as threshold fracture energy).\textsuperscript{201} This statement is the basis for the existing statistical thermodynamic fracture models.\textsuperscript{59,60,202–204} The most popular model for prediction of strength of elastic materials is the one suggested by Lake and Thomas, which provides a way to calculate this fracture energy through calculating the energy of the chains across the path of the crack.\textsuperscript{202} There is a surprisingly large effect to these values, though, from crosslinking density and the distribution of molecular weights of the polymer molecules.\textsuperscript{203} The addition of silica particles was shown to affect the crosslinking density and fracture toughness of epoxy resin polymer networks.\textsuperscript{205}

\textsuperscript{†} The terms fracture, tearing and cracking are used interchangeably here as they come from the respective literature. Usually tearing refers to soft matter while fracture and cracking refer to hard matter.
In order to investigate the effect of the fillers on the strength and elongation at failure of elastomeric composites, micromechanical methods are the ones that allow the design of the necessary computational experiments to tackle length-scales that involve multiple filler-particles. The two main methods used in the literature are the Finite Element Method (FEM) and the Lattice Spring Model (LSM). In terms of failure modeling, the LSM method is more straightforward since it allows failure of individual springs and the failure can propagate through the lattice. FEM, on the other hand, is a general technique that solves boundary value problems. This allows more degrees of freedom for failure modeling. Evaluating failure criteria for FEM models of fiber-reinforced polymer composites was the focus of a multi-year effort named the World-Wide Failure Exercise (WWFE). The result was many different realistic models with the models of Zinoviev et al. and Puck and Schurmann standing out as able to resemble the curve of an ideal plasticity.

Pan studied experimentally the mechanical behavior of the PDMS system embedded with FGSs and his results are summarized in Figure 3.1. From the stress-strain curves presented in Figure 3.1, we observe that with increased particle concentration the modulus is increased, the strength is increased and elongation at failure is increased and then decreased.
As discussed earlier, the effect of FGS concentration on the zero-strain modulus is not a surprise and it can be predicted with various analytical or computational models. Sanborn used an LSM method to investigate the elongation at failure and strength values of FGS-PDMS composites. He discovered that, in agreement with Pan’s experiments, an increased concentration of fillers always increases the strength of the material and the elongation at failure increases and then decreases. This was attributed to a continuous increase in the number of tears with filler concentration. While the number of tears continuously increases, the size of each tear decreases with increased filler concentration.

Although Sanborn’s model was a very good effort in explaining the failure mechanisms of the FGS-PDMS system, it lacked in some fundamental ways. Namely, Sanborn’s model could not reach high elongations (only up to about 1% strain) and the behavior for low elongations was scaled to match the elongations of the experimental system, the interface between FGS and PDMS was perfect (i.e., no slippage between the
FGS and the corresponding PDMS node was allowed; This is the reason his model could not reach higher elongations), the dispersion could not be truly random since only three FGS orientations were allowed due to mesh limitations. Consequently, this model was lacking in terms of not incorporating the high-strain behavior of the material and due to the limited available FGS orientation options, it was not appropriate for electrical conductivity predictions, either.

The most important limitation in Sanborn’s model was the latter, the lack of random dispersions. The lack of possible positions to place the FGS forced him to allow overlap of the FGS particles and this way the FGSs could span the entire material in the tensile loading direction for high particle concentrations. Since the tears cannot penetrate the FGS in his model and there is also no way around the FGS, this arrangement creates more and more tear arresting regions with higher particle concentrations.

My FEM approach, presented above, overcomes the above limitations in particle dispersion. The FEM allows capturing of the discontinuities created by the addition of filler particles, through the generation of the appropriate mesh and thus allows us to test truly random dispersions as opposed to Sanborn’s model. The main drawback of FEM is that the number of particles that can be simulated is limited\textsuperscript{113} and the modeling of failure is less straightforward relative to the LSM methods that involve the break of springs.

In terms of the first drawback, I managed to push the current limits of FEM and simulate FGS-PDMS composites with close to 200 embedded FGSs. I achieved that through employing an FEM model with trusses as FGSs that are connected to a hyperelastic material with the use of springs and we calculated stress as a function of strain using the computationally efficient Dynamic Relaxation method. In terms of the
second drawback, I defined failure of individual elements by reducing the modulus of those elements by several orders of magnitude when a certain value of shear stress is reached. More details on the model are given below.

Regardless the limitations in Sanborn’s work, his idea of simulating FGS as linear particles in a 2-D domain and his experimentation with different particle distributions gave inspiration for an important part of the work presented in this thesis.

3b. General Model – Large Polymer Domain

In order to understand the effect of the filler dispersion on mechanical properties while addressing the above limitations from Sanborn’s model, I constructed a micromechanical 2-D model that is representative of the graphene-elastomer system (the work for this model was based on unpublished work by Belotserkovets and Sallah). The basic material elements that constitute my model are: 1) the elastomer, which is modeled as a hyperelastic material and forms a continuous phase, 2) the 2-D macromolecular particles/sheets, which are modeled as trusses dispersed in the elastomeric continuous phase, and 3) the interfacial forces between particles and elastomer, which are modeled as linear springs.

The reason for the use of a 2-D model, instead of a 3-D model, is to reduce computational complexity and manage to deal with a large number of particles. This allows me to create an FEM that can study the effect of 2-D fillers in the composite properties on an aggregate level. Even though I expect this to have an effect on the accuracy of the particle concentration relation with the composite properties, it is useful for the discovery of general trends.
The use of springs for modeling of interfacial forces gives us additional degrees of freedom to achieve the desired composite properties. This was a lesson learned from the efforts of Belotserkovets and Sakellaris who used a perfect interface to model the particles that used in unrealistically large elongation of the filler particles. The extreme value of zero for the spring constants would correspond to no particles being present in the matrix while a value of infinity for the spring constants would correspond to a perfect interface. A perfect interface in my model leads to numerical failure of the model because of the large discrepancy in modulus between the particles and the elastomer. The addition of springs made our model more realistic from a physical sense and feasible from a computational sense. Springs are used frequently in a variety of simulations techniques like Molecular Dynamics and LSM to approximate forces. This is equivalent to assuming a linear function for the interface forces between the elastomer and the filler particles.

The total problem of calculating the stresses of an elongated material is addressed by solving Newton’s second law equation:

$$\nabla \cdot \sigma + \rho g = \rho \ddot{u}$$  \hspace{1cm} (3.1)

where $\sigma$ is the stress vector, $g$ is the matrix of gravitational forces, $\ddot{u}$ is the acceleration matrix and $\rho$ is density. The stress and displacement for Eq. (3.1) are calculated through the equations for the Hyperelastic model for the PDMS, along with the added contribution of the trusses for particles as transferred through the linear springs that model the interfacial forces. All these separate material constituents of our model are described below.

The above equation is integrated using dynamic relaxation, which helps to find the form of the material that satisfies it along with the corresponding reaction forces for each
value of elongation of the lower and upper boundaries. All my computations were implemented using Dynaflow, a nonlinear transient finite element analysis program.\textsuperscript{214}

**Hyperelastic model for PDMS**

The Hyperelastic stored energy function used was:

\[
\psi = \frac{1}{2} G (l_b - 3) + U(J) \tag{3.2}
\]

where:

\[
U(J) = B (J \ln (J) - J + 1) \tag{3.3}
\]

\[
J = \det F \tag{3.4}
\]

\[
l_b = J^{-2/3} \underline{b} : \underline{\delta} = J^{-2/3} \text{tr}(\underline{b} \cdot \underline{\delta}) \tag{3.5}
\]

\[
\underline{b} = F F^T = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & 1 \end{bmatrix}^T = \begin{bmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{3.6}
\]

where \(G\) is the shear modulus, \(B\) is the bulk modulus, \(F\) is the deformation gradient \(\frac{\partial x}{\partial \underline{X}}\), \(x(X, t)\) is the motion vector with initial condition: \(x(X, t = 0) = X\), \(\lambda_1\) and \(\lambda_2\) is the stretch in each dimension (\(x = \lambda_1 X\) and \(y = \lambda_2 Y\)) and \(\underline{\delta}\) is the Kronecker delta. The operator \(\text{tr}\) indicates trace of a matrix and \(\det\) indicates the determinant.
The Kirchhoff stress is calculated as:

\[ \tau = J \, p \, \delta + G J^{-2/3} \text{dev}(b) \]  

(3.7)

with:

\[ p = dU/dJ = B \ln (f) \]  

(3.8)

and:

\[
\text{dev}(b) = \begin{bmatrix}
\lambda_1^2 - \frac{1}{3} \text{tr}(b) & 0 & 0 \\
0 & \lambda_2^2 - \frac{1}{3} \text{tr}(b) & 0 \\
0 & 0 & 1 - \frac{1}{3} \text{tr}(b)
\end{bmatrix}
\]  

(3.9)

The Cauchy stress is calculated as:

\[ \sigma = \tau/J \]  

(3.10)

As mentioned in the beginning of this section there are three basic elements that comprise our model: hyperelastic material (elastomer), trusses (filler particles) and springs (interface). The hyperelastic material forms a continuous phase, the trusses are dispersed in an equivalent mesh (mesh that contain nodes that coincide on their coordinates with some nodes of the polymer mesh) and the two materials are connected with springs. This is shown in Figure 3.2. The particle (blue line) is placed in the polymer matrix (continuous phase) that has been meshed (black lines). On the right side of Figure 3.2 a black node for the polymer and a blue node for the filler particle are shown. These nodes are overlapping at time zero and move further apart as the polymer is stretched. The two nodes are connected with springs (in blue, the coefficients of the longitudinal and perpendicular direction are defined separately). As the two nodes
(polymer/black dot and filler particle/blue dot) move further apart from each other, the elongation of the spring is increased and the force exerted through the springs also increases.

**Figure 3.2.** On the left, a part of the mesh of the polymer matrix is shown (black lines) with a straight vertically oriented filler particle (blue line). On the right, a pair of nodes of the particle and polymer is shown that are connected with a spring (each pair of nodes completely overlap at time zero when the elongation is zero). In reality, we have two different springs because the longitudinal (relative to the direction of the truss) and perpendicular spring constants are defined separately.

**Trusses for filler particles**

The sheet-like filler particles are modeled using linear trusses. A truss is an element that connects two points in space and only transmits axial forces. For our case, there are two (translational) degrees of freedom for each truss, as they cannot bend.

Each particle is comprised of a series of linear trusses between each pair of consecutive nodes. More specifically, each particle is comprised of 6 nodes and contains
5 trusses that connect each pair of those 6 consecutive nodes. The number of trusses equals the number of nodes minus 1.

Even though a single truss does not bend, a sheet-like particle is free to bend overall because each of the nodes of each truss is free to perform translational movement and each truss shares only one node with its neighboring trusses.

For our simulations, meshing of our continuous phase (i.e. the elastomer) was done using gmsh.\textsuperscript{215} I made sure to include 6 equally spaced nodes for every particle (i.e. 5 truss segments). Those nodes were added twice to the mesh, once for each of the two separate materials (polymer and truss), and were connected to each other using springs.

**Springs for interfacial forces**

The initially overlapping nodes of the trusses and the polymer are connected using springs. Each pair of nodes is connected using a pair of springs defined separately in the longitudinal and perpendicular direction of the truss. These springs are defined as linear and their coefficients are defined to be equal in both the longitudinal and the perpendicular directions. The filler-matrix interface is assumed to not fail as observed experimentally by Sallah.\textsuperscript{8}

**Tearing**

Tearing is a problem that does not have a straightforward solution in FEM models (as opposed to LSMs). I implemented tearing of the continuous elastomeric phase by reducing the Bulk and Shear moduli of the elements of the elastomer that reach shear stress values above a certain limit by 3 orders of magnitude. When the von Mises stress
reaches the selected limit, then the element acts as a really soft region emulating a torn region. The result is that the element will have a higher elongation and lower stress than its surrounding elements, which now have to withstand higher stresses due to the failure of the original elements and this increased stress leads to tear propagation.

Note that the terms shear and von Mises stress are used interchangeably in this work. They are a stress invariant of the Cauchy stress tensor equal to:

\[
\tau = \sqrt{J_2} = \frac{1}{2} \left\{ \frac{1}{3} [(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2] + 2(\tau_{12}^2 + \tau_{23}^2 + \tau_{31}^2) \right\} \tag{3.11}
\]

where \( \sigma_{ij} \) and \( \tau_{ij} \) are elements of the Cauchy stress tensor.

The terms shear and gamma strain are also used interchangeably in this work. They are defined as:

\[
\gamma = \frac{2}{\sqrt{3}} \left\{ [(\varepsilon_{11} - \varepsilon_{22})^2 + (\varepsilon_{22} - \varepsilon_{33})^2 + (\varepsilon_{33} - \varepsilon_{11})^2] + (\gamma_{12}^2 + \gamma_{23}^2 + \gamma_{31}^2) \right\} \tag{3.12}
\]

where \( \varepsilon_{ij} \) and \( \gamma_{ij} \) are elements of the Cauchy strain tensor.

**Weak regions**

Weak elements are introduced in the polymer by defining specific elements of low shear strength (two orders of magnitude lower than the rest of the polymer). In the simulations presented below, for imperfect polymer meshes (i.e. polymer meshes that include weak regions), I added 5 weak regions in each. Four of these regions are centered near the corners of the materials (2 \( \mu \)m away from each boundary) and one in the center.
of the material. Each of these regions includes all the elements that are comprised of at least one node that is within 0.25 \( \mu \text{m} \) from the corresponding center of that weak region.

An example is shown in Figure 3.3(a). The boundaries of the polymer are shown in magenta, the nodes are shown in light blue and these nodes are connected with light gray lines to form the elements. The elements filled in red color are the weak elements that have a lower von Mises strength than the rest of the matrix. The five regions formed are not completely circular in this figure but I ran multiple examples for each particle concentration to ensure that this randomness will not introduce a bias in the results. The corresponding error bars that are shown in the elongation at failure and strength figures for imperfect polymer meshes in the Results and Discussion section are a representation of the variation introduced by the particle dispersion and the corresponding small changes in the mesh and weak regions.

**Random dispersions**

Random dispersions were generated by placing one edge of each particle randomly in the matrix using a uniform distribution for each of the \( x \) and \( y \) coordinates and then choosing the orientation of the particle again from a uniform distribution, given a particle length of 1 \( \mu \text{m} \). If the line segment that represents the particle touches the walls or overlaps with other particles then this particle is rejected and is not placed in the matrix. A representative example is shown in Figure 3.3(b) for a case of 97 particles.
Figure 3.3. An example of a mesh for a 9x9 µm polymer matrix with 97 particles. The polymer boundaries are shown in magenta, the nodes of the polymer are shown with the light blue “T” symbols and they are connected together with light gray lines that form the elements. (a) The red elements are the weak regions that have a lower shear strength value than the rest of the matrix. (b) The particles are shown in blue. Each particle is 1 µm long and is divided in 5 equal truss segments by its underlying nodes.

Meshing in all my simulation results was done given a certain particle dispersion in a way that ensured that each filler particle was divided in 5 equal truss segments from its underlying nodes, and the density of elements on the material boundaries is 5 elements per micron. The elements are mostly quadrangles but there are some triangles present as well in some of the simulations. The number of triangles is always lower than 10 while the total number of elements is usually in the order of 1,000 or 10,000.

The number of truss segments per truss was increased to 10 for the case of small polymer domains.
3c. Small Polymer Domain

For the simulations of Chapter 4 I used 2x2 µm polymer matrices, as I chose to focus on the effect of certain small parts of the particle structure, and reach higher particle concentrations. This focus gave rise to boundary effects that were not present in the 9x9 µm polymer matrix studies.

Elimination of boundary effects for upper and lower boundaries

During simulations with small 2x2 µm polymer matrices and high particle concentrations the samples were observed to fail frequently in the upper and lower boundaries. It was concluded that this was due to boundary effects introduced by the particles. In the case of random dispersions, these boundary effects by the particles are created from a bias in the way the particles are dispersed. Figure 3.4 shows an example where the high stress regions (shown in red and yellow) are close to the upper and lower boundaries.

As I described in the previous section, randomly dispersed particles that touch or cross the boundaries are rejected. This means that close to the boundaries the effective particle concentration is lower than in the center of the material and there is a lack of particle centers since a particle cannot cross a boundary. Particle edges, as will be shown in Chapter 4, are high-stress regions and particle centers are low-stress regions. This means that the boundaries have a bias against low-stress regions.
Figure 3.4. Von Mises stress distribution for a random dispersion of 10 particles under strain; the high stress region is located on the lower boundary and other high stress regions are located close to the upper boundary.

My approach to avoid the lack of particles and low concentration of low-stress regions near the boundaries was to stretch the material from points closer to the center. As shown in Figure 3.5(a), the 2x2 µm matrix was stretched at the nodes located at \( y = 1.5 \) µm and \( y = 0.5 \) µm positions (as indicated by the dashed lines). The boundaries are also stretched at the same rate as the nodes at \( y = 1.5 \) µm and \( y = 0.5 \) µm and the result is shown in Figure 3.5(b).
Figure 3.5. (a) The 2x2 µm polymer matrix mesh used in the simulations with vertical particles. The elements filled with gray color are non-failing and the elements filled with white colors can fail. The magenta lines indicate the boundaries. The nodes placed at $y = 1.5 \, \mu m$ and $y = 0.5 \, \mu m$ are stretched upwards and downwards, respectively, at the same rate. The upper and lower boundaries are also strained at the same rate as the nodes at $y = 1.5 \, \mu m$ and $y = 0.5 \, \mu m$, respectively. (b) The stretched version of the neat mesh from figure (a). The magenta lines show the initial position of the boundaries before the material is stretched. (c) The 2x2 µm polymer matrix mesh with an example of vertically oriented covalently linked particles. The particles are shown in blue and the green dots correspond to pairs of truss and polymer nodes that are connected with springs. The particle dispersion is comprised by one long horizontal particle to which all vertical particles are covalently linked. The green dots at these particle junctions correspond to springs that connect the truss to the matrix. The trusses share the same nodes at the junction and therefore their interparticle forces are the same as the intra-particle forces.

Figure 3.5(b) illustrates the elongated version of the matrix from Figure 3.5(a). The main elongation happens in the center region of the matrix. The region above the upper dashed line and below the lower dashed line are not strained in the y-direction and the strain on their x-direction is an effect from the stresses that propagated from the center of
the matrix. The resulting shape of the matrix ends up looking similar to a dogbone. This happens to be the shape of samples during experimental tensile testing\textsuperscript{216,217}. The dogbone samples experimentally are designed to avoid boundary effects on the grips during the stress-strain measurement\textsuperscript{217} and this concept was the inspiration for the described approach.

This bias did not present a problem with large polymer domains because of the relatively low particle concentrations used. Low particle concentrations result in higher relative distances between particles that do not allow the cancellation of high stress regions (particle edges) by low stress regions (particle centers). Figure 3.4 shows an example where high stress regions are protected by low stress regions and therefore the high stress regions are concentrated near the boundaries. In small polymer matrices, these boundary effects can dominate and can affect the start of failure. Therefore, I designed this simulation technique to facilitate the study of smaller polymer composite matrices with high particle concentrations. This technique (described in this part) enables the study of smaller domains that are more computationally feasible and therefore it could also be useful for other potential studies.

**Elimination of boundary effects for left and right boundaries**

The second problem faced was boundary effects from the left and right boundaries. As shown in Figure 3.5(b) the polymer matrix gets compressed near those boundaries at high global strains between the two dashed horizontal lines. The stress distribution under strain is shown in Figure 3.6 for a structured dispersion. These compressed regions (shown in red color) can be the starting points for failure that propagates through the
material. My solution to this problem was to define the material as two separate regions: A non-failing region (shown in gray in Figures 3.5) and a failing region (shown in white).

**Figure 3.6.** Von Mises stress distribution for a structured dispersion of particles under strain; the polymer in this case is pulled from nodes closer to the center. High stress regions appeared on the right and left boundaries (red color).

In the simulations presented in the following chapters, I ensured that, with the technique described above, failure starts from particle edges and not from the boundaries.

**Vertically oriented and covalently linked particles**

In these simulations the particles are placed in a way that span the material throughout the y-axis and they are covalently linked. The covalent inter-truss links have
the same properties as the intra-truss links. The different particles are sharing the same nodes in the connecting points and, therefore, they cannot be separated from each other.

An example of this type of dispersion is shown in Figure 3.5(c). In this figure the filler particles (modeled as trusses) are shown in blue and the green dots show the positions at which the truss nodes are connected to their underlying polymer nodes using springs. The general design followed in these simulations is that a long horizontal particle is placed in the center, as shown in Figure 3.5(c), and vertical particles are connected to either side of that horizontal particle.

The vertical particles are connected to the horizontal particle at the junctions by sharing the same truss nodes. This means that these particles remain connected throughout the simulations.

In order to eliminate the effect of every non-relevant parameter that could possibly affect the stress-strain curve, the same mesh was used for all vertically oriented particle simulations and the position of the horizontal particle remained the same.

Looking at the dispersions it is important to be reminded that the direction of loading is parallel to the y-axis and all vertically oriented particles are oriented the same way, as shown by the arrows in Figure 3.5(a).

**Vertically oriented non-linked particles**

In these simulations the same dispersions as for the previous category are used with the sole exception that there is no horizontal particle to which the vertically oriented particles can be attached. The meshing and particle positions for the remaining particles are the same as in the covalently linked particles case.
3d. Choice of parameter values for FGS/PDMS composite

The basic physical material and computational parameters that were chosen for our simulations are described below.

**Polymer modulus:** The modulus of the polymer was adjusted according to experimental stress-strain curves produced by Sallah for PDMS.\(^8\) The shear modulus was set equal to 0.3491 MPa and the bulk modulus was set equal to 20 times the shear modulus.

**Truss modulus:** The FGS modulus is about 1,000 times higher than the PDMS modulus and for this I set it equal to 1,000 the Young’s modulus of PDMS.

**Truss dimensions:** Each FGS is comprised of 5 truss segments of equal length to allow rotational degrees of freedom on the nodes and therefore allowing the FGS to bend. Here, I treat FGS as 1 \(\mu\)m \(\times\) 1 \(\mu\)m plates with a fixed 1 \(\mu\)m depth in the direction perpendicular to the 2-D plane. This translates to an FGS length of 1 \(\mu\)m (0.2 \(\mu\)m per truss segment) and a truss cross-sectional area of \(10^{-15}\) m\(^2\). For the case of small polymer domains (2x2 \(\mu\)m), the truss is divided into 10 truss segments and the total truss length remains the same (1 \(\mu\)m).

**Number of springs:** Each truss segment is contained within a pair of nodes and each of these two nodes is connected to the underlying polymer mesh with a pair of springs. One spring is defined in a direction perpendicular to the truss plane and the other is defined in a direction parallel to the truss plane. These springs represent the interfacial forces between FGS and polymer. The more of these springs are present (i.e. the greater the number of the truss segments per FGS), the greater the effect of the FGS on the matrix. Therefore, the spring coefficients have to be adjusted accordingly based on the
number of truss segments per FGS. In total, there are 12 springs per FGS connecting it to the polymer matrix in the simulations of large polymer matrices. Each truss is divided to 5 equal truss segments that have 6 nodes in total; each node is connected to the polymer matrix through 2 springs. For small polymer domains there are 22 springs per FGS. In this case, each truss is divided to 10 equal truss segments that have 11 nodes in total; each node is connected to the polymer matrix through 2 springs. One example is the green dots in Figure 3.5(c).

**Spring coefficients:** The spring coefficients were selected to be equal to 0.1 N/m in order to produce the desired effects of increase in elongation at failure. A lower coefficient does not produce a significant effect on modulus with the addition of particles. A higher coefficient causes early failure as trusses act as significant defects on the matrix.

**Weak region size:** Since I did not want to account for aggregate effects on this model, the weak region radius was set equal to 0.25 µm to allow the FGS particles to completely cover the weak region if the FGS allows it. This choice may have allowed to see the elongation at failure effect at lower particle concentrations.

**Weak region strength:** The local shear strength of the weak regions was defined to be equal to 0.1 MPa. This value was chosen to ensure that the weak regions fail much earlier than the rest of the polymer matrix.

**Polymer strength** (with and without weak regions): For the cases of a perfect polymer (i.e. when weak regions are not present) matrix, the local shear strength was defined as 0.5 MPa to match the PDMS global strength measured by Sallah. For the case of an imperfect polymer matrix the shear strength was set equal to 1.5 MPa. In the latter case the polymer needed to be stronger locally to reach the same global strength as the
first case. The reason for this is that the weak regions that are introduced in the imperfect polymer matrix act as defects.

**Rate and direction of tensile loading:** Both the upper and lower boundaries are stretched in opposite directions during the simulation of the tensile test. Both boundaries move with constant velocities equal in magnitude to half length of the domain over time $t_f$, which is equal to 1,000.

**Dynamic relaxation parameters:** The Cundal damping coefficient was set equal to 0.5. The time step was set equal to 0.81 times the critical time step for the simulations of the imperfect polymer matrix. The critical time step is defined as the minimum element length (dependent on mesh size) over the speed of sound in the material.
Chapter 4 Particle concentration, particle position, and covalent linkage effects on mechanical properties of FGS-PDMS composites

4a. Introduction

Control of the nanoparticle dispersion within a polymeric matrix is hard to be achieved and that is one of the greatest stumbling blocks to the large-scale production and commercialization of nanocomposites. A common approach in the literature is to model the particle dispersions as random, but in reality the nanoparticles tend to aggregate within the polymer.

Controlling the structure of the filler particles is hard to achieve experimentally due to the inter-particle forces and other external forces that act on the particles during preparation of the composite. There are, though, promising techniques for better control of dispersion, such as the use of magnetic or electric fields, that are gradually giving more control to the experimentalists over the particle dispersions. Understanding the fundamental rules for designing the particle dispersion in a composite material could aid the experimentalist to design better materials.

For the case of nanosheet-filled composites, Sallah did a great effort in controlling the dispersion by experimenting with different surface chemistries of the nanoparticles (graphene oxide and FGS), which have a different type of aggregation in the matrix. Perhaps the greatest leap in Sallah’s and McDonald’s work, though, is the use of a filler particle that is the product of broken down parts of a graphene aerogel. This filler
possibly contains parts of covalently-linked graphene particles, which is very promising since this linkage effectively increases the aspect ratio of FGS particles.

An increased aspect ratio leads to greater increases in Young’s modulus due to the increased surface area available for load transfer.\textsuperscript{33} Here, I orient the particles in the tensile loading direction and maximize their aspect ratio in the same direction by covalently linking them. I expect this type of dispersions to lead to increased load transfer. At the same time I test what type of particle positions will minimize the observed decrease in elongation at failure and discuss the conditions that could lead to an increase in elongation at failure.

Griffith in his seminal paper raised the issue of stress concentrators.\textsuperscript{201} The reason that brittle materials fail earlier than predicted theoretically is the existence of defects or high-stress regions from which failure can propagate to the rest of the material. Even though in this chapter I assume a perfect matrix for the neat material, the concept of stress concentrators and alleviating those high-stress regions is key in understanding what causes failure in a material and translates from brittle materials to polymers as well.

4b. Model

The simulations performed here are for vertically oriented covalently-linked and non-linked particles and the polymer matrix is assumed to be perfect. The details of the model are described in Chapter 3. Here, I list some of the assumptions, as they will become important later in my analysis:

- The system is simplified to 2-D and the sheet-like particles are assumed to be line segments with a fixed surface area (i.e. the thickness on the dimension perpendicular the plane is also assumed to be 1 \( \mu m \)).
• No movement is allowed on the dimension perpendicular to the plane.
• Neat elastomer behaves hyperelastically (there is visco-elastic or plasto-elastic component).
• Neat elastomer is perfect (i.e. uniform strength distribution among all elements).
• Failure for any element of the polymer occurs when its Von Mises stress reaches a certain value.
• Particle-polymer interface does not fail.
• Covalent links do not fail.
• There are no inter-particle forces other than the case of covalent linkages.
• Particles are oriented.

4c. Results and Discussion

In this part, I explore the effect of particle concentration, particle position and covalent linkage on mechanical properties for oriented particles. Overall, individual particles act as defects but addition of oriented and covalently linked particles can increase the strength of a perfect polymer matrix. No increase in elongation at failure was observed relative to the neat polymer due to the model assumptions. Smallest drop in elongation at failure was observed for particle pairs that are close enough to act synergistically, but are far from other pairs. Finally, some conditions that can lead to elongation at failure increase are suggested.
**Single particle**

Here, a perfect polymer matrix is defined as a matrix that has no defects and, therefore, fails when a material reaches its intrinsic bond strength. There are no special regions within the matrix that can fail earlier than that. Even though perfect materials might be impossible to make, this experiment helps to illustrate that filler particles can act as defects.

In my simulations, the addition of a single particle, in any position of the elastomeric matrix, led to a reduction in global strength and elongation at failure. Figure 4.1 shows an indicative case where the particle was added in the middle of the matrix. In Figure 4.1(a) the reduction in strength caused by the addition of the particle is apparent (the same exact meshing and polymer parameters were used for the neat and the composite material containing the single particle). Figure 4.1(b) shows the von Mises stress distribution in the matrix in the presence of the particle. The existence of a single particle creates a non-uniform tensile stress distribution around the particle. The stress is maximum at the edges of the particle and becomes minimum towards the center of the particle.
Figure 4.1. (a) The stress strain curve for the case of 1 particle placed in the middle of the polymer matrix (orange) and for the equivalent polymer mesh without the particle (blue). (b) Mises stress distribution in the matrix for the case of one particle placed in the middle (shown in black). High stresses are developed in the edges of the particle. (c) Gamma strain distribution in the matrix at the point of tear initiation. The tear initiates at the lower edge of the particle. (d) Gamma strain distribution in the state where the material is completely torn. The failure was caused by the propagation of the tear that initiated in the lower edge of the particle seen in Figure (c).

Overall, single particles act as defects because of the high tensile stresses developed due to strain amplification. In this case, linear particles seem to develop high stress regions around their edges during tensile loading. In Figure 4.1(c), it is shown that a tear
initiates from one of the edges of the particle (in this case the lower edge), which is consistent between all simulations that I ran with particles dispersed in a perfect polymer. As I mentioned in the previous chapter, I modeled tears by lowering the modulus of the torn region. This leads to high local strains and visually it can be seen by the high values of gamma strain. The red region at the lower edge of the particle has a gamma value that is about one order of magnitude higher than the rest of the material. Figure 4.1(d) shows the failed material when the initial tear has propagated throughout the continuous polymeric matrix.

**Vertically oriented and covalently linked particles**

Different simple dispersions of vertically oriented covalently linked particles that span the matrix from its lower to the upper boundary were designed to generate understanding of the effect of covalent linkage of particles in a perfect polymer matrix. The first experiment is designed to show the protective effect that neighboring particles can have in lowering stress concentration in the matrix and increasing the elongation at failure.

Figures 4.2(a-d) show the four dispersions tested, Figure 4.2(e) shows the stress-strain curves for all of these dispersions and Figures 4.2(f) and 4.2(g) show the nodal Mises stress distribution. A first observation from Figure 4.2(e) is that strength can be increased with the addition of particles relative to the neat. This agrees with most experimental observations for elastomeric composites since the particles tend to carry additional load.\(^8\) As long as the increase in Young’s modulus is significant to
counteract the general decrease in elongation at failure that happens with the addition of particles, strength is increased.

All vertically oriented particles, in Figures 4.2(a) to (d), are covalently linked to the long horizontal particle that spans the matrix from left to right. Figure 4.2(b) contains the same four vertical particles as Figure 4.2(a) plus four more that are each placed at a 0.1 µm distance from the previously existing particles, either right above or right below them. The result of this addition, as can be seen in Figure 4.2(e), is a significant increase in Young’s modulus, strength and elongation at failure. The reason for the large increase in Young’s modulus and strength is the fact that the number of particles was almost doubled between the two dispersions and these additional particles carry additional load. The reason for the increase in elongation at failure is the fact that the new particles added at a 0.1 µm distance above or below the existing particles helped to better redistribute the stress created by the already existing particles. This mechanism becomes more apparent when only one additional particle is added.

Figure 4.2(c) contains one additional particle relative to Figure 4.2(b), drawn in red. The addition of this particle leads to significant decrease in elongation at failure and to almost no change in Young’s modulus. As can be seen in Figure 4.2(f), there is a high-stress region appearing right above this new particle.
Figure 4.2. (a-d) The four dispersions tested. Each dispersion contains the same particles as the one on its left plus some addition particles. (e) Stress-strain curves for the neat polymer and for the dispersions shown in (a-d). (f) Nodal Mises stress distribution for dispersion (c) for 45% global strain. (g) Nodal Mises stress distribution for dispersion (d) for 45% global strain.

When another particle is added at a 0.1 µm distance, right above the particle drawn in red (as shown in Figure 4.2(d)), the elongation at failure increases, again, significantly (Figure 4.2(e)). It can be confirmed, from Figure 4.2(g), that the high stress region that appeared right above the new particle in Figure 4.2(f) has now disappeared. Neighboring particles, therefore, can help increase the elongation at failure through lowering the local stresses. The importance of stress concentrators in the failure of the material was first proven by Griffith for brittle materials.201

This work shows that this concept can be expanded to elastomeric composites and alleviating high stress regions is the key to increasing elongation at failure. When positioned properly, addition of particles can help in better redistribution of stress in the
matrix and to a consequent increase in elongation at failure. Nevertheless, elongation at failure for the composite material never exceeded the values for the neat polymer in any of my simulations under the assumptions listed in the previous part.

Two more things worth noting from Figures 4.2 are that the stress near the boundaries can still be high, as can be seen from Figures 4.2(f-g), but it does not cause material failure because it is limited in the non-failing area shown in gray in Figure 3.5. This means that the boundary effects are effectively eliminated. Case (c) of Figure 4.2(e) shows a sudden drop in global stress at about 45% global strain that corresponds to material failure and then a secondary increase in stress for higher global strain. This secondary increase is a result of pulling of the springs of the covalently linked particle structure and of pulling the remaining section of the polymer (shown in gray in Figure 3.5) that does not fail.

The second series of experiments with vertically oriented covalently linked particles is designed to show the effect of increased particle concentration. As shown in Figures 4.3(a-c), all particles have a corresponding neighboring particle at a 0.1 µm distance right above or right below them. The only thing that changes between Figures 4.3(a-c) is that the concentration of particles is increased by adding pairs of particles at 0.1 µm to each other and on the opposite sides of the horizontal particle.
Figure 4.3. (a-c) The three dispersions tested. Each dispersion contains the same particles as the one on its left plus some addition particle pairs (particle pairs are particles on both sides of the horizontal particle are in a 0.1 µm distance from each other). (d) Stress-strain curves for the neat polymer and for the dispersions shown in (a-c). (e) Nodal Mises stress distribution for dispersion (b) for 45% global strain. The red ellipses indicate the tear initiation regions. (f) Nodal Mises stress distribution for dispersion (c) for 45% global strain. The red ellipse indicates the tear initiation regions.

Figure 4.3(d) shows the stress-strain curve of the three tested dispersions. The addition of particle pairs results in a significant increase in Young’s modulus which leads to an increase in strength, as well, and this is consistent to what is shown above. The addition of the particle pairs, though, has an effect of decreasing elongation at failure. This is due to increased particle concentration resulting in more high-stress regions. Figure 4.3(e) shows the Mises stress concentration for dispersion (b). The red ellipses show the areas of tear initiation. Figure 4.3(f) shows the equivalent graph for dispersion
(c). The point of tear initiation, in this case, is in the region of the highest particle concentration (among two particles on the lower side of the matrix that are only 0.2 µm away from each other) and happens at lower global strain than dispersion (b).

Looking at the strained mesh can provide more insights about the interaction between matrix and particles. Figure 4.4(a) shows the mesh for the dispersion of Figure 4.3(b) at 45% global strain and Figure 4.4(b) shows the mesh for the dispersion of Figure 4.3(c) at the same global strain.

**Figure 4.4.** Stretched versions of two of the loaded meshes shown in Figure 4.3. The magenta lines show the initial position of the boundaries before the material was stretched. The particles are shown in blue and the green lines correspond to the springs that connect pairs of trusses and their underlying polymer nodes. The particle dispersion is comprised by one long, initially horizontal, particle to which all vertical particles are covalently linked. (a) The mesh for the dispersion of Figure 4.3(b) at 45% global strain. The red ellipse shows an area where an initially horizontal particle segment reorients vertically and acts as a connecting segment for vertical particles. (b) The mesh for the dispersion of Figure 4.3(c) at 45% global strain. The red ellipse shows an area where the
initially horizontal particle acts as a connecting segment of vertical particles but with less sharp angles relative to the segment in Figure (a).

Figure 4.4(a) reveals the mechanism of reinforcement that contributes to the higher stress and elongation values observed for covalently linked particle pairs (e.g. Figure 4.2(d) relative to Figure 4.2(c)). The red ellipse, in Figure 4.4(a), highlights an area where the 0.1 µm segment of horizontal particle that connects the two neighboring vertical particles acts as an extension of the two vertical particles and make it appear as one continuous particle spans the material. So the upper particle of 1 µm length, together with the lower particle of 1 µm and the 0.1 µm segment that connects them effectively act together as a vertically oriented particle of 2.1 µm length.

In Figure 4.4(b), at the same global strain as Figure 4.4(a), but with a denser particle concentration, the particles are closer to each other and there is an antagonistic effect with regards to the use of the horizontal particle. In other words, the initially horizontal particle segments that connect the vertically oriented particles, do not contribute in the effective elongation of the particles (i.e. through re-orientation of the initially horizontal covalently linked particle) as much as they did in Figure 4.4(a). Focusing on the red ellipse of Figure 4.4(b), the initially horizontal particle segment is not vertically oriented anymore, as it appeared to be in Figure 4.4(a). The upper particle in Figure 4.4(b) seems to use the initially horizontal segments to pull the lower two particles like a slingshot. The two vertical particles below the ellipse are pushed closer to each other by the vertical particle right above the red ellipse, creating a high stress region between them, as seen in Figure 4.3(f), where tearing initiates.
To summarize, addition of particles can lead to an increase or decrease in elongation at failure based on whether the newly added particles act synergistically or antagonistically. If the newly added particles protect some high stress regions by redistributing stresses then elongation at failure can be increased but if these particles are not protected by other particles (e.g. red particle in Figure 4.2(c)) or if the concentration of particles increases significantly in certain regions with the addition of those particles (i.e. if those particles act antagonistically) then elongation at failure can be decreased.

**Vertically oriented non-linked particles**

For the case of vertically oriented and covalently linked particles it was shown that the increase in concentration can lead to large increases in Young’s modulus and to strength values that exceed the strength of the neat polymer. In an effort to separate the effect of covalent linkage to the orientation effect I show here what happens when the horizontal particle is removed from the previous simulations.

The result of the removal of the horizontal particle (to which all vertical particles are connected) is that the particles are not covalently linked any more. All the dispersions tested are equivalent to the dispersions in the previous paragraph and are shown in Figures 4.5.
Figure 4.5. (a-e) The five non-linked dispersions tested. Each dispersion corresponds to one of the dispersions shown above, with the horizontal particle is removed. (f) Stress-strain curves for the neat polymer and for the dispersion shown in (a-e).

The dispersion of Figure 4.5(a) corresponds to the one in Figure 4.2(a), Figure 4.5(b) corresponds to Figure 4.2(b) (and to Figure 4.3(a)), Figure 4.5(c) corresponds to Figure 4.2(c), Figure 4.5(d) corresponds to Figure 4.2(d) (and to Figure 4.3(b)) and Figure 4.5(e) corresponds to Figure 4.3(c).

When the horizontal particle is removed from the original dispersions we see 1) a less significant increase in Young’s modulus with the addition of particles that leads to 2) smaller increases in strength that did not exceed the strength of the neat polymer and 3) less significant variations in elongation at failure as a function of particle concentration.
The less significant increase in Young’s modulus relative to the covalently linked particles should be expected based on the observations from the previous part. As shown in Figure 4.4(a), covalent linkages can effectively elongate the particles. Longer vertically oriented particles can carry additional load. The smaller increases in strength are a consequence of the reduced increase in Young’s modulus.

The reduced variations in elongation at failure should not be considered a general trend as these simulations were designed to be compared with the covalently linked case instead of inducing the general trends of oriented particles. A more comprehensive study would include larger variation of the particle positions on the y-scale. Those variations would allow for more degrees of freedom in terms of stress redistribution, which would lead to greater variation in the elongation at failure. Using the elongation at failure variations of the covalently linked particles are expected to be even higher if particle positions were varied in the y-axis.

The stress-strain curves of Figure 4.5(f) show a continuous decrease (although not as significant as in the covalent case) in elongation at failure with concentration. The dispersion (b) curve cannot be seen in the plot because it is right below the stress-strain curve of dispersion (c). These results do not prove that any addition of non-covalently linked particles will lead to a decrease in elongation at failure but the observation of decreasing elongation at failure with filler concentration agrees with the general trend observed in the literature. The key is to understand the conditions that lead to an increase in elongation at failure at certain filler concentration ranges. In this particular case, the neighboring particles have edge-to-edge proximity and therefore the low-stress particle center cannot protect a high-stress particle edge (see Figure 4.1(b)).
Putting everything together in an effort to give a general direction to experimentalists for dispersion control, the drop in elongation at break can be minimized by creating structures that span the whole material in the direction of loading and therefore can redistribute stress over large areas. Increasing the distance between those structures is of utter importance to avoid the creation of stress concentration sites.

**Elongation at failure enhancement**

So far, my model has shown that even though elongation at failure can sometimes increase with the addition of particles, it does not exceed the elongation at failure value of the neat polymer when the polymer is assumed to be perfect. This is true for different types of dispersions that were tested in a perfect polymer matrix including random, structured and covalently linked dispersions.

It ends up that under the assumptions of the model this is an expected behavior and not just an artifact caused by limited statistics or a general lack of imagination on the tested dispersions. An informal proof would go as follows: The addition of particles causes local stress inhomogeneities in the matrix (including lower and higher stresses relative to the neat). The high stress regions in the composite cause earlier start of failure relative to the neat. When the polymer matrix starts failing, the remaining non-failed part of the matrix has to carry additional load in order to complement for the load that was carried from the now failed polymer region. Therefore, this additional load causes other regions of the material to also reach a Von Mises stress value equal to the material strength and the tear propagates faster for the composite relative to the neat material.
The assumptions of the model can act as a guide to achieve the increase in elongation at failure that is observed experimentally since at least one of them needs to be violated for elongation at failure increase to occur. More specifically, addition of inter-particle forces can lead to stress redistribution over larger areas, which could enable distributed tearing. Failure of inter-particle or interfacial forces can lead to a stress release at certain regions and delaying the start and propagation of tears. Strain-induced crystallization could also lead to slowing of the tear propagation process and distributed elongation. An imperfect polymer matrix due to inherent polymer defects, cross-linking inhomogeneities etc. could generate high stress regions that the particles could alleviate.

One practical example from the literature that could lead to elongation at failure increase (again due to violation of the model assumptions) is the creation of kirigami-like structures. Given that graphene has achieved a lot higher strains than theoretically believed with the employment of the kirigami technique, a similar trick could be employed for the elastomeric composite system. The basic principle behind kirigami structures is cutting a 2-D structure in strategic positions in order to allow out-of-plane bending that makes the structure stretchable. The Föppl-von Kármán number (ratio of in-plane and out-of-plane stiffness) is the crucial parameter to evaluate the potential of a substance to become stretchable by the employment of the kirigami technique. Modeling of the mechanical properties of a material containing such kirigami structures would require generalization of the model to 3 dimensions.

Another example from the literature is the employment of knowledge acquired from materials found in nature. Nacre possesses mechanisms that permit the material to redistribute stresses through inelastic deformation. More specifically, nacre is
comprised of layers of adjacent polygonal tablets. During tension or shear, those tablets separate as slippage between the layers is enabled. In order for slippage to happen, the layers have to overcome the resistance introduced by their contacting nano-asperities.\textsuperscript{226,227} A similar situation could be created in my studied system if the particles are placed parallel to each other in small distance with polymer in between. The inter-particle forces between the filler particles can act in similar ways as the nano-asperities, introducing steady shear resistance, with some inter-particle bonds destroyed during particle movement and new bonds created. Modeling of the properties of such composite would require incorporation of those inter-particle forces in the model.

4d. Conclusions

The introduced model shows that individual particles act as defects but covalently linking them and orienting them can significantly improve the composite properties. The model showed that increase in strength can be achieved with the addition of particles, in agreement with experiments. Distributing pairs of particles that span the matrix in the tensile direction in the furthest possible distances minimizes the decrease in elongation at failure that happens with the addition of those particles.

Elongation at failure was not improved relative to the neat and this was attributed to the model assumptions. Two of these assumptions will be relaxed on the next chapter.
Chapter 5 Effect of inherent polymer defects on mechanical properties of FGS-PDMS composites

5a. Introduction

Inherent material defects, like pre-cracks, have been proven to affect the fracture properties of composites as well. For elastomers, in particular, there is a considerable body of evidence that there are pre-existing small cavities that develop into tears and stress-raising features are also present at a typical spacing of 10 to 100 µm. The number and distribution of those cavities is shown to be affected by the type of cross-linker.

According to Griffith, the reason of the discrepancy between theoretical predictions of strength and experimental measurements is the existence of microscopic flaws. Even though the effect of pre-existing defects is known to be large, there was no effort to incorporate them in an elasticity theory until recently that the Real Elastic Network Theory (RENT) was developed. RENT is a good effort in taking molecular defects into account in an elastic network but there is still a long way ahead from being used for failure prediction in composites due to the large length scales and large strains required.

My micromechanical model, on the other hand, was easily generalized to include regions of the elastomer that are weaker than the rest of the material. At the same time I was able to simulate large areas of the matrix with up to 250 particles and reach high strains.
5b. Model

The simulations performed here are for randomly oriented non-linked particles for the perfect and imperfect polymer matrices. The details of the model are described in Chapter 3. Some of the assumptions behind these simulations are listed here:

• The system is simplified to 2-D and the sheet-like particles are assumed to be line segments with a fixed surface area (i.e. the thickness on the dimension perpendicular the plane is also assumed to be 1 μm).

• No movement is allowed on the dimension perpendicular to the plane.

• Neat elastomer behaves hyperelastically (there is visco-elastic or plasto-elastic component).

• Failure for any element of the polymer occurs when its Von Mises stress reaches a certain value.

• Particle-polymer interface does not fail.

• Covalent links do not fail.

• There are no inter-particle forces other than the case of covalent linkages.

The basic difference between this chapter and Chapter 4 are that the particles here are not assumed to be oriented and that weak regions are introduced in the polymer matrix to simulate inherent elastomer defects.

5c. Results and Discussion

I have used the above model to study the effect of random dispersions of up to 250 particles. In this part I will show that in a material without defects, addition of randomly dispersed particles reduces the elongation at failure and strength of the material. In a
more realistic scenario, where the material has internal defects, I observed an increase and then decrease in elongation at failure and strength. The increase was attributed to better redistribution of local stresses in the polymer matrix through the particles. As the concentration of particles increases, they start acting as defects that are more important than the pre-existing polymer defects.

**Random dispersion, perfect polymer**

Further addition of particles decreases the elongation at failure further, because of the higher local stresses that develop in the polymer matrix. The higher local stresses lead to earlier failure of the material as it reaches the local failure strength at lower global strains.

The above phenomenon of the reduction of strain at failure with the addition of particles in a perfect polymer matrix was observed for different ranges of our parameter values. In Figure 5.1, I am showing the stress-strain curves for random dispersions with different particle concentrations. The random dispersions in each case are produced by using the same particles as for the directly lower particle concentration, plus some additional particles placed randomly in the remaining space. In other words, the case of 20 particles has the same 10 particles as in the 10-particle case plus 10 more, the case of 40 particles has the same particles as the 20-particle case plus 20 more, etc. This strategy eliminates the effect of randomness as the difference between each concentration and the next can be attributed to the addition of particles instead of the relocation of existing particles.
As is evident from Figure 5.1, the addition of particles in a perfect polymer matrix reduces the elongation at failure in each case.

**Figure 5.1.** Stress-strain curves for a range of particle concentrations of randomly dispersed particles and a perfect polymer matrix. Each concentration has the same particle positions as the concentration right below it for the existing particles and the rest particles are dispersed randomly. For example, the 250-particle dispersion has the first 160 particles dispersed the same way as the 160-particle concentration and the remaining 90 particles are dispersed randomly.

In a perfect polymer matrix, the effect of stress redistribution that the FGS particles offer is not advantageous. A neat polymer matrix has a uniform stress distribution among its elements. The more particles are added, the less uniform this stress-distribution becomes and the more high-stress regions are introduced in the matrix. These high-stress
regions are potential areas for tear initiation and thus can lead to failure at lower global strain values.

This elongation at failure decrease with particle concentration can lead to a decrease in strength when the particles do not carry sufficient load, as happens in this case. In the case of covalently linked particles (chapter 4), the decreasing elongation at failure did not lead to decrease in strength because the particles were carrying more load (as can be concluded by the large increase in Young’s modulus).

This general reduction in stress agrees with experiments. A good example is Sallah’s work on FGS composites. To capture potential increases in elongation at failure that happen in a certain range of particle concentration the intrinsic polymer defects need to be taken into account. In the next section, I will show that the stress-strain behavior with particle concentration changes when weak regions are introduced in the polymer matrix.

**Random dispersion, imperfect polymer**

When the existence of weaker regions is accounted for in the polymer, the existence of filler-particles can in some cases increase the strength and the elongation at failure of the composite material. Those weaker regions in the polymer can be caused by powerful stress raisers like dust or dirt particles, by accidental nicks in molded or cut surfaces or by crosslinking inhomogeneities.

Those weak regions are modeled by including all the elements that contain at least one node within a 0.25 µm radius from 5 centers, one near each corner and one in the middle of the material, as shown in Figure 3.3(a). The particles are dispersed randomly in
different concentrations and a characteristic stress-strain curve for each particle concentration is shown in Figure 5.2.

![Stress-strain curves for a range of particle concentrations of randomly dispersed particles and an imperfect polymer matrix. The legend shows the w/w percentage of FGS in the polymer matrix.](image)

**Figure 5.2.** Stress-strain curves for a range of particle concentrations of randomly dispersed particles and an imperfect polymer matrix. The legend shows the w/w percentage of FGS in the polymer matrix.

The particle concentrations in weight percentages were calculated using the assumption that each FGS particle weighs $8.178 \times 10^{-16}$ g and the polymer matrix has dimensions of $9 \times 9 \times 1 \mu m$ and a density of $965 \text{ kg/m}^3$. The 0.005, 0.01, 0.02, 0.05, 0.07, 0.1 and 0.2 % w/w values correspond to 5, 10, 19, 48, 67, 97 and 195 particles, respectively.
As can be seen in Figure 5.2, the elongation at failure for the 0.005 and 0.01 % w/w particle concentrations has a value of about 60 %, about the same as the neat polymer, then for particle concentrations between 0.02 and 0.1 % w/w this value increases to a range between 65 and 70% and then it drops again below the value of 60% for a particle concentration of 0.2% w/w (these findings will be analyzed statistically in the next section). Figure 5.3 provides an explanation on why that happens based on the distribution of Von Mises stress in the matrix. Given that failure is caused when shear stress reaches critical value of local strength, the key to understand failure is the stress distribution within the material.

Figures 5.3(a-c) present the Von Mises stress distribution for 10 % global strain and Figures 5.3(d-f) present the Von Mises stress distribution for 56 % global strain. The particle concentrations are 0.005 % w/w for (a) and (d), 0.05 % w/w for (b) and (e) and 0.2 % w/w for (c) and (f). Each sub-figure contains a legend on the upper left corner that contains the maximum and minimum values for Von Mises stress as computed in the matrix.

In Figure 5.3(a) a mostly uniform stress distribution is observed except on the upper left corner where a single particle, almost parallel to the y-axis, disturbs the stress uniformity. In Figure 5.3(b), there are more particles that are almost parallel to the y-axis and therefore more stress non-uniformities are present in the matrix. Both Figures 5.3(a) and 5.3(b) have similar values of minimum and maximum Von Mises stress present in the matrix. In Figure 5.3(c), where the particle concentration is even higher and the relative distances among the particles becomes small, a significant increase in the maximum Von Mises stress and a decrease in the minimum Von Mises stress are
observed. More particles create more extreme stress non-uniformities in the polymer matrix when no weak regions have started failing.

While Figures 5.3(a-c) are captured in low enough strain so that no weak regions have failed, Figures 5.3(d-f) are captured closer to failure and in all cases all 5 weak regions have failed. These 5 regions are the low stress regions that appear in blue in the 4 corners and center of the material in each of the Figures 5.3 (d), (e) and (f). As can be seen in Figure 5.3 (d), where very few particles are present, those failed weak areas are a major source of stress concentration in the material, as each weak region is surrounded on its right and left side by high-stress regions. The left side of the weak region in the center of the material is the area that reaches the highest stress value and that same region is the one that failure propagates from at about 60 % strain.

For Figure 5.3(e), even though the global strain is the same as in Figures 5.3(d) and (f), the Von Mises stress values developed are lower than in the other two cases (can be seen by looking at the maximum Von Mises stress values in the corresponding legends). Thus, the 0.05 % w/w FGS concentration leads to more stress non-uniformities when no weak regions have failed (i.e. 5.3(b) versus 5.3(a)), and to fewer stress non-uniformities when failed regions are present.
**Figure 5.3.** Von Mises stress distribution at 10% global strain and (a) 0.005% FGS, (b) 0.05% FGS, (c) 0.2% FGS and 56% global strain and (d) 0.005% FGS, (e) 0.05% FGS, (f) 0.2% FGS. The 5 weak regions appear as low-stress regions (blue) in figures (d), (e) and (f), since they have failed. The maximum value indicated is the value of the point with the maximum von Mises stress in Pa divided by 10$^{12}$.

Figure 5.3(f) appears even more deformed relative to Figure 5.3(d). Most weak regions are surrounded by particles, which reduces their Von Mises stress. Overall, the maximum Von Mises stress value exceeds the corresponding values for Figures 5.3(d) and (e) as there is an area on the right side of the lower left weak region where the high stress spot created by the weak area coincides with a particle edge (as I showed in Figure 4.1(b), particle edges are high-stress regions).

Even though the dispersions used in the above examples are random, the resulting behaviors are consistent between different samples and lead to an increase in elongation at failure at intermediate concentrations.

**Strain at failure as a function of FGS concentration, imperfect polymer**

The results for strain at failure, coming from four simulations for each particle concentration, are shown in Figure 5.4. Each data point represents the mean between four simulations and the error bars show the standard deviation values. The basic trend unveiled in this figure is that strain at failure increases and then decreases with FGS concentration, as expected by Pan’s experiments.$^{11}$

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Figure 5.4. Strain at failure values for different FGS concentrations and random dispersions. Each data point represents the mean between four different simulations at each concentration and the standard deviation is shown with the error bars.

As shown in Figure 5.4, there is a clear increase in elongation at failure at 0.02% w/w particle concentration relative to the lower particle concentrations (0.005 and 0.01% w/w) and the highest concentrations (0.1 and 0.2% w/w). The 0.05 and 0.07% w/w particle concentrations seem to be achieving around the same elongation at failure values as the 0.02% w/w concentration but with an increased error.

The increase and then decrease of elongation at failure with particle concentration that was described in the previous section appears to be a general phenomenon. The particles allow a better redistribution of the stresses in the matrix up to a certain concentration before starting to act as defects that are comparable in importance to the existing defects of the material (i.e. failed weak regions).
This redistribution of stress that happens at particle concentrations between 0.02 and 0.07% w/w allows the material to reach higher elongations by enabling the transfer of load from weak to stronger regions and therefore allowing more regions of the material to reach high elongations.

Essentially what happens is that the particles allow a better redistribution of the stress, relative to the neat imperfect polymer. This allows total strength of the composite to get closer to the strength of the equivalent polymer that would not include any inherent defects. Therefore, all the particles do is allowing the material to reach its existing potential that was prevented in the case of neat polymer by the existing polymer imperfections.

The lower FGS concentration for elongation at failure reversal relative to the experiments might be caused by the different percolation thresholds for 2-D versus 3-D systems and by the fact that our particles were placed straight, while FGSs are usually wrinkled.⁹

**Strength as a function of FGS concentration, imperfect polymer**

As shown in Figure 5.5, this model predicts that strength also increases and then, possibly decreases with FGS concentration. This result might contradict Pan’s experimental results that show a continuous increase in strength but it agrees with Sallah’s results of FGS in thermoplastic polyurethane (TPU).⁸
Figure 5.5. Strength values for different FGS concentrations and random dispersions. Each data point represents the mean between four different simulations at each concentration.

The increase in strength with particle concentration that starts at 0.02 % w/w FGS was expected as particles carry additional load and cause an increase in Young’s modulus. The increase in Young’s modulus in combination with an increase in elongation at failure causes the increase in strength that was observe up to 0.07 % w/w FGS concentration.

For 0.1 and 0.2% w/w FGS concentration the strength seems to not only stop decreasing but to also possibly decrease, relative to the 0.07% w/w FGS concentration.

I believe that the main reason for this behavior is the design of weak regions in my simulations. I know from the literature that there should be weak spots in larger length-scales as well. With larger defect regions present, more particles will be needed to achieve the optimal stress redistribution in the matrix. In those cases, aggregates and an
increased number of individual particles would contribute to further reinforcement of the material.

The interfacial forces, defined by the springs, were fitted based on global parameter values (strength and strain) and not based on analytical calculations. Those forces are also concentrated in a limited number of regions (6 nodes that are the edges of the 5 truss-segments). This force concentration affects the load transfer between particles and matrix. At high concentrations this stress concentration effect can become more prevalent due to the high proximity of the particles.

Another reason for this behavior of strength with particle concentration is the lack of inter-particle forces from our model. Inter-particle forces should become important on higher particle concentrations, since there are more particles that are close enough to each other in the matrix to interact with each other at those concentrations. These forces would allow carriage of load between particles and therefore they would allow redistribution of stress on larger length scales.

Comparing my results to Pan’s experimental results from Figure 3.1, we see that the elongation at failure reversal happens at a much lower particle concentration in my simulations relative to the experiments and this also had an effect on the strength. The main reason I identified for this difference is 1) the fact that our model is 2-D and not 3-D, 2) the fact that filler particles are assumed to be straight instead of wrinkled, and 3) the size and number of weak regions. The concentration of those weak regions in the matrix should have a significant effect on failure and this remained a fixed parameter in the presented results.
5d. Conclusions

For a perfect polymer, and random particle dispersion, elongation at failure was shown to decrease continuously with concentration. When the polymer is assumed to be imperfect (i.e. weak regions are introduced that fail earlier than the rest of the matrix), then addition of particles was shown to cause an increase in elongation at failure for a certain particle concentration range (0.02-0.07 % w/w FGS). The reason for the increase is the effective redistribution of stresses by the particles from the edge of the failed regions to parts of the matrix with lower stresses. The subsequent decrease in elongation at failure with higher particle concentrations is caused by stress concentration due to the high proximity of particle edges.

At the same time, the model showed that strength increases and then, possibly, decreases for imperfect polymers. This decrease could be an artifact of the model due to the design of weak regions and interfacial forces or lack of inter-particle forces.
Chapter 6 Conclusions and Final Remarks

This thesis provided the background and presented advanced tools for the prediction of the mechanical properties of elastomeric composites with non-spherical fillers. But, the model is generic in nature and thus the conclusions should be applicable to all fillers in general. In this chapter, I reiterate some of the conclusions drawn in this work, I provide suggestions to experimentalists and a direction for improved mechanical property modeling in elastomeric composites.

My first contribution was the creation of the first model for aggregation of 2-D particles that allows restructuring of the aggregates. The Reversible Cluster Aggregation model, described in Chapter 2, is a lattice-free model that allows rotation and translation of particles as well as aggregation of the particles to form clusters and deaggregation of the particles from those clusters. This was used to simulate a system of FGS particles in an aqueous SDS solution but it can be generalized to any type of 2-D or rod-like particles.

The results from these simulations agree with the experimental observations for FGSs dispersed in aqueous SDS in varying surfactant concentrations. There was an indication for the existence of a critical surfactant concentration around which dense clusters are formed that sediment quickly. Below that surfactant concentration, the particles form a gel that densifies with time and tends towards a graphite-like structure. Above that critical surfactant concentration, mostly single particles or small embryonic clusters are obtained and those small clusters have very short lifetimes and never reach the stable cluster nucleus size.
Experimentally, these results give a clear direction of how surfactants can be used for dispersion control of FGS. At low surfactant concentrations, i.e. when inter-particle forces are dominated by vdW interactions, a particle gel can be created inside that material that might yield improved electrical properties. Even though the experiments simulated took place in water, the viscous effects of dispersing particles in an elastomer could be overcome by the addition of a solvent. Regardless of the solvent addition, the applicability of DLA-type models in particle dispersions in rubber is acceptable for particle concentrations above the gel point.\textsuperscript{80} This is because even though particle diffusion is strongly suppressed in highly viscous media, highly entangled rubbers give rise to fluctuations of colloidal particles around their mean position. The fluctuation length is comparable to the entanglement length of the rubber.\textsuperscript{43,44,229} For high filler concentrations, the mean trajectory length of aggregating particles or clusters can become smaller than the fluctuation length of the particles generated by the entanglement of the rubber. This condition is fulfilled for particle concentrations above the gel point.\textsuperscript{230}

This RCA model is, therefore, a promising tool to study the aggregation process of 2-D particles in water and in more viscous media given high particle concentrations. From a computational perspective, therefore, the interest lies in applying this model for predictive purposes and in improving it. In terms of applications the potential of the model for prediction of the filler structure in elastomeric composites was discussed already. In terms of improvement, the main drawback of the model that I identified in my simulations was that the critical surfactant concentration value predicted was an order of magnitude lower than what was found in experiments. The area for improvement that is expected to contribute the most in terms of the model’s predictive ability is to account for
the foldable nature of graphene. In the RCA the particles are rigid and have to deaggregate and reaggregate many times until they find an energetically favorable position. In reality, graphene can bend and fold and this facilitates the search for an energetically favorable position. Therefore, overcoming the assumption of particle rigidity could lead to shorter time scales for aggregation. Another way to increase prediction accuracy is to expand the model to 3-D.

A third way to improve this model is through incorporation of flow effects for the dispersion medium. This improvement could happen through adjustment of the diffusion step size and the probability of movement in each direction. Incorporation of flow would not only improve the accuracy of the model but it would also allow usage of this model to study lower particle concentrations (below the gel point) in elastomers.

My second large contribution was the creation of a model for mechanical property prediction of elastomers with non-spherical fillers that can handle simulations on a level that includes hundreds of particles. This is an FEM model of a hyperelastic matrix (representing the polymer) with trusses (representing the 2-D particles) dispersed within the polymer boundaries with the two materials being connected with linear springs (representing the interfacial forces between the two materials). This model was applied to study the dispersion effects of FGS dispersed in PDMS as well as the effect of inherent polymer defects in mechanical properties.

It was found that covalently linking the particles to span the entire material in the direction of tensile loading increases load transfer due to the increased aspect ratio of the particles. To minimize the decrease in elongation at failure the covalently-linked structures need to be well-dispersed in order to avoid the creation of high-stress regions at
points of high particle concentration. No increase in elongation at failure was observed, though, relative to the neat polymer when the polymer is assumed to be perfect and no inter-particle forces are taken into account. When the assumption of a perfect polymer was relaxed, and was assumed, instead, that weak regions are present in the polymer that fail earlier than the remaining material, the elongation at failure was increased for a certain range of particle concentration.

I see two important consequences from these results that could guide experimental efforts towards the manufacturing of improved elastomeric composites. First, the creation of well-dispersed covalently linked structures should lead to improved mechanical properties. Covalently linked structures could potentially be created through the method of broken graphene aerogel particles described in Sallah’s thesis.\textsuperscript{8} Dispersion control could be achieved through the usage of electric or magnetic fields.\textsuperscript{220–222} Second, the result of inherent polymer defects leading to increase in elongation at failure can be tested experimentally. If confirmed, a potential next step would be the design of defect sites in ways that would lead to increased elongation at failure with particle addition.

From a computational perspective, I see a great potential of the model to be used under different contexts to aid material design. First, more complex particle dispersion scenarios can be tested if inter-particle forces are incorporated into this model. Inter-particle forces could also be modeled with the use of springs with negative spring coefficients (i.e. decreasing force with increased inter-particle distance). These forces would allow stress redistribution over larger areas of the material and would therefore enable protective mechanisms between particles that are not currently present (e.g. distributed deformation). Each assumption of the model can be tested separately to
discover the conditions under which elongation at failure increase can be achieved. For instance, on top of the incorporation of inter-particle forces the effect of strain-induced crystallization can be tested through defining changing material properties with strain and decreasing interfacial forces (between particles and polymer) could also be tested by tweaking the properties of the springs.

A second idea for expanded usage of this model is to test the effect of aggregate structures. This would require the incorporation of inter-particles forces and knowledge of particle positions within aggregate structure. As mentioned earlier, the RCA model should be applicable for the study of dispersions of 2-D particles in rubber in high particle concentrations and could be expanded to lower particle concentrations with the incorporation of flow. The bottleneck in using the RCA model to create input aggregate structures for the FEM model is the resulting mesh size. A small mesh leads to a large need for computational resources due to the increased number of nodes and due to the need for a smaller time step required by the dynamic relaxation algorithm. The RCA model leads to really small inter-particle distances for aggregated particle pairs (in the order of nanometers), which creates the need for a small mesh. Solving this problem would enable usage of the FEM model to study the effect of aggregate structures in mechanical properties.

A third idea for usage of the FEM model is the prediction of electrical conductivity within the composite. This requires knowledge of the contact resistance values of the particles within that medium and the position of the particles within the medium. The FEM model provides information about particle position for different strain values and this could allow prediction of electrical conductivity as a function of global strain.
Assuming electron transfer between particles through a tunneling mechanism, the whole problem of electrical conductivity calculation is equivalent to calculating the total resistance of a network of resistors, where each particle pair forms a resistor with a resistance value that depends on the inter-particle distance.

To summarize, this thesis provides tools for understanding the effect of the addition of 2-D particles in elastomeric composites but also talks about general concepts applicable to all types of particles. These tools provide understanding of the effect of particle position in ultimate mechanical properties, along with how particles assume those positions (i.e. the aggregation process). This opens new routes for engineers to manufacture these improved composite materials and to further study some important effects that affect the mechanical properties of these materials.
Cited Literature


17. Flexible liquid crystal display with integrated driver circuit and display electrodes formed on opposite sides of folded substrate. September 1993.


36. Sheng N, Boyce MC, Parks DM, Rutledge GC, Abes JI, Cohen RE. Multiscale micromechanical modeling of polymer/clay nanocomposites and the effective clay


46. Dean GD, Duncan JC, Johnson AF. Determination of non-linear dynamic


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Kaunisto E, Rasmuson A, Bergenholtz J, Remmelgas J, Lindfors L, Folestad S. A


160. Meakin P. The effects of random bond breaking on diffusion limited cluster–


170. Díez Orrite S, Stoll S, Schurtenberger P. Off-lattice Monte Carlo simulations of


182. Liu J, Shih WY, Sarikaya M, Aksay IA. Fractal colloidal aggregates with finite 

183. Parkinson J, Kadler KE, Brass A. Self-assembly of rodlike particles in two 
dimensions: A simple model for collagen fibrillogenesis. *Phys Rev E.* 

184. Parkinson J, Kadler KE, Brass A. Simple physical model of collagen 
fibrillogenesis based on diffusion limited aggregation. *J Mol Biol.* 


186. Russel WB, Saville DA, Schowalter WR. *Colloidal Dispersions.* Cambridge: 

1976.

188. Hamaker HC. The London—van der Waals attraction between spherical particles. 

1277.


200. Lotya M, Rakovich A, Donegan JF, Coleman JN. Measuring the lateral size of


