

**VAN DER WAALS INTERACTIONS BASED RHEOLOGICAL ANALYSIS FOR
ELECTROSTERICALLY STABILIZED NANO-SIZED ALPHA SILICON
CARBIDE-LACTOBACILLUS GG DISPERSIONS**

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Virginia Polytechnic Institute and State University
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ABSTRACT

Although enormous potential benefits are envisioned with the application of nanotechnology in conjunction with biological systems, interactions of nano particulate materials with biological materials is not well understood. The focus of this dissertation is to determine the mathematical relationships of the forces between nanoparticles and biological agents. The systems under investigation are the α -SiC/H₂O/LGG polar based systems. The mathematical analysis for the surface forces, based on the attractive van der Waals forces for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar solvent based systems are presented and discussed. The rheological parameters including pH, zeta potential, shear rate, shear stress and viscosity that alter the dispersion mechanisms are also presented and discussed. The concurrence of the experimental analysis with the mathematical modeling is also presented. The rheological analysis in these systems for determining of the optimum amounts of dispersant, binder, plasticizer and solids loading using the Krieger-Dougherty fit and Liu's model are presented and discussed. α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar solvent based samples were also fabricated to test for an application area of nano-bio technology: A novel nano and micro porous materials fabrication process. Porous materials are used for a variety of applications including insulation, filtration, catalytic substrates, textiles and consumer goods and

accounts for billions of dollars in sales annually. Results from the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar solvent based slip and freeze cast samples and their characterization using digital and electron microscopy are presented and discussed. Finally, the green and sintered density, porosity and strength of the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar solvent based dispersion samples are determined and discussed.

DEDICATION

This document is dedicated to my father, mother, brother, and sister in-law for
providing me the strength, guidance, support and encouragement
to accomplish this academic career goal.

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CHAPTER 1

INTRODUCTION

1.1 Nano-Bio Technology

Nanotechnology is an emerging field with potential applications in almost every aspect of human life. It is also an area which is very diverse with respect to the applications as related to electronics, optics, medicine and micro-fluidics. One of the interesting interdisciplinary areas that is growing at a tremendous pace is the overlap with nanotechnology and biotechnology, often termed as nano-bio technology. [1]

The interface between biological agents and inanimate materials forms a broad interdisciplinary research area which plays a significant role in medical implants for the human body, biosensors and biochips for diagnostics, biomimetic materials, bioelectronics and tissue engineering. [2] A fundamental understanding of the surface forces that play a significant role at this interface between the ‘nano’ and ‘bio’ may allow advances in the many areas of nano-bio technology. Analysis using colloidal processing and rheological techniques are necessary to understand the interfacial properties as required for the desired application. This fundamental and practical understanding can potentially help determine the biocompatibility, potential utilities and applications of new nano tools for various bio based applications. [3]

1.2 Colloidal Processing

As the size of particles decreases, the surface forces between the particles increase which leads to particle agglomeration. Therefore, while using micron or nanoparticles it is difficult to prevent agglomeration between the particles due to the strong attractive van der Waals forces between them. In order to prevent the nanoparticles from agglomerating it is essential to disperse them in a liquid (polar or non polar) using a suitable dispersant. [1]

Colloidal processing thus becomes essential for nano-particulate based dispersions. Understanding and controlling the rheological properties including their solids loading and viscosity are critical for colloidal processing. For fabricating parts from micron or nano sized particles it is important to understand the maximum solids loading of the system to be fabricated so as to minimize the shrinkage. [4]

Significant research on micron sized particles has been done with various ceramic particles including silicon carbide, silicon nitride, silicon dioxide, zirconia and alumina. [5-12] However, research aimed at understanding the surface forces and rheology of nano-sized particles is fairly recent and the processing techniques are still being developed. [13, 14] The use of nanoparticles for colloidal processing can have several potential benefits as discussed in the later sections of this dissertation.

1.3 Why are Nanoparticles Necessary?

Nanoparticles are particles in the size range of 10^{-9} m with critical dimensions that do not exceed 100 nm in length in any given direction. [15] Their small size and large surface area make them useful for a variety of applications. Many different types of nanoparticles have been used for various applications including ceramics, gold, silver and carbon nanotubes. [4, 13, 16-20]

Nanoceramics are critical as some of these materials can withstand high temperatures. The commonly used nanoceramics are silicon carbide, silicon nitride, silicon dioxide, alumina, titania, zirconia, carbon nanotubes and barium titanate. They have unique properties which can be used for a variety of applications.

1.4 Application of Nano-Bio Technology: Micro and Nano Porous Materials Fabrication

The porous materials industry accounts for billions of dollars annually. Several methods including sol gel, using a fugitive phase and spinoidal decomposition are used to fabricate porous materials. However due to various reasons including increasing costs, disposal of the exhaust gases and cost and space needed for storage of the fugitive material there is an opportunity to develop new techniques that can potentially be used to address some of these issues. [21] The use of nanoparticles and biological agents can potentially minimize the abovementioned issues as will be explained in detail in the later sections of this dissertation.

1.5 Research Objectives

The driving force for this research is to:

1. Calculate the surface forces particularly the attractive van der Waals forces in α -SiC/H₂O/ α -SiC (nano-nano) and in α -SiC/H₂O/LGG (nano-bio) polar solvent based systems in order to determine the molecular weight and choice of dispersant necessary to create the electro-steric hindrance for achieving stabilized dispersions when using biological agents.
2. Determine the rheological parameters including the suspension solids loading, pH, zeta potential, viscosity, shear stress and shear rate affecting the dispersion in α -SiC/H₂O/ α -SiC (nano-nano) and in α -SiC/H₂O/LGG (nano-bio) polar solvent based systems in order to achieve stabilized dispersions.
3. Fabricate and characterize the stabilized α -SiC/H₂O/ α -SiC (nano-nano) and α -SiC/H₂O/LGG (nano-bio) polar solvent based systems to experimentally verify the calculations and predictions from #1 and #2 above.
4. Determine the mechanical properties including the green and sintered density, porosity and strength of the stabilized α -SiC/H₂O/ α -SiC (nano-nano) and α -SiC/H₂O/LGG (nano-bio) polar solvent based slip and freeze cast systems to demonstrate fabrication of porous materials.

1.6 Chapter Overviews

Chapter 2 is a literature review section wherein a basic understanding of the research areas mentioned in the dissertation, the current research in the related areas and the terminology used are discussed.

In chapter 3, the raw materials, the characterization techniques and the experimental procedure used are discussed.

In chapter 4, the results from the mathematical analysis, rheological analysis, experimentation, characterization and mechanical testing are presented and discussed in detail.

The conclusions drawn from the research presented in this dissertation are discussed in chapter 5.

In chapter 6, future work that may be investigated is presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Mathematical Parameters Controlling Dispersions

The dispersion of nanoparticles is an area of considerable interest for various applications. Though a lot of work has been done with dispersing micron sized particles in a polar medium, dispersing micron sized particles in a non polar systems and nano sized particles in polar and non polar solvents has not been sufficiently explored. [4, 22, 23] The dispersing of nanoparticles with biological agents such as bacteria, fungi and viruses in a non polar and polar solvent is an interesting area which has not been explored yet. Development of a well dispersed nanoparticle-biological agent system may lead to a new method for fabricating micro and nano porous materials. Also, a thorough understanding of the forces involved at the nano-bio interface can also help address issues with drug delivery, gene delivery and biosensor technologies. [1]

For dispersions of nanoparticles the appropriate control and balance of the attractive and the repulsive barrier is essential. At the nano size range, the attractive van der Waals forces between particles become very significant and are responsible for the strong forces of attraction between particles leading to particle agglomeration. [24, 25]

2.1.1 Surface Forces

Phenomenon such as dispersion, wetting, adhesion, coatings, agglomeration, polishing, and friction (which are important materials processing techniques) are controlled by the

surface forces between the particles involved. [26-28] There are several kinds of surface forces (both attractive and repulsive) that act between particles in a solvent (polar or non polar) based system. A few of the important ones are listed below [24, 26, 29]:

1. van der Waals forces
2. Electrostatic and ion correlation forces
3. Solvation and structural forces
4. Hydration and hydrophobic forces
5. Polymer-mediated forces
6. Thermal fluctuation forces

However, at the nano-scale level it is the van der Waals forces that are the strongest and hence we will look at these forces in more detail. [24, 30, 31]

2.1.2 van der Waals Forces

In order to understand the van der Waals forces let us first look into its derivation from the Ideal Gas Law by Emil Clapeyron. [32, 33]

Considering a static sample of gas, we can write the relations for pressure (P), temperature (T), volume (V) and number of moles (n) as,

$$PV = k_1 \tag{1}$$

$$\frac{V}{T} = k_2 \tag{2}$$

$$\frac{P}{T} = k_3 \quad (3)$$

$$\frac{V}{n} = k_4 \quad (4)$$

$$\frac{1}{nT} = \frac{1}{k_6} \quad (5)$$

$$\frac{P}{n} = k_5 \quad (6)$$

where, ' k_1 ', ' k_2 ', ' k_3 ', ' k_4 ', ' k_5 ' and ' k_6 ' are different constants.

On multiplying equations (1), (2), (3), (4), (5) and (6) equation (7) is obtained.

$$\frac{P^3 V^3}{n^3 T^3} = \frac{k_1 k_2 k_3 k_4 k_5}{k_6} \quad (7)$$

In equation (7) the right hand side (RHS) is made equal to a constant ' R ', cube.

$$\frac{k_1 k_2 k_3 k_4 k_5}{k_6} = R^3 \quad (8)$$

Taking cube root of equation (8) leads us to the value for ' R ', which is also known as the gas constant or the universal gas constant. [32]

Substituting equation (8) in equation (7) and solving we have equation (9).

$$\frac{PV}{nT} = R \quad (9)$$

On rearranging the terms, we have it in the expression as seen in equation (10).

$$PV = nRT \quad (10)$$

The ideal gas is expected to differ from the real gas in at least two aspects [33]:

1. In the ideal gas, the molecules were treated to have a pure spherical shape.
However in the real gas, this might not be the case.
2. In the ideal gas, the forces of cohesion were considered negligible (and hence not considered during the derivations). However in the case for a real gas this cannot be completely neglected.

Looking into these discrepancies while studying the deviations of the real gas from the ideal gas, the Dutch physicist van der Waals proposed that there were non-covalent and non-electrostatic interactions between neutral atoms and molecules. [34-36]

The best known correction for the system is given by van der Waals in his essay on ‘On The Continuity of the Liquid and Gaseous States’. [33] According to van der Waals, there are two corrections that need to be made to equation (10). The first being a correction to the volume term, considering the molecules to be of a finite size, and the second being a correction on the pressure term, considering the influence of pressure of the forces on the cohesion on the gas. [33]

Utilizing these correction parameters, equation (11) is obtained.

$$(P + \frac{a}{V^2})(V - b) = nRT \quad (11)$$

Equation (11) is also called as the van der Waals equation that is used to give the relation between temperature, pressure and volume changes.

It is to be noted that the ‘ a ’ and ‘ b ’ are constants for the same mass of gas and also depend on the amount and the nature of the gas used. The value of ‘ b ’ is proportional to the amount of the gas and the value of ‘ a ’ is proportional to the square of the amount of gas. Considering these factors, we have the modified gas laws as seen in equation (12).

[37]

$$(P + \frac{n^2 a}{V})(V - nb) = nRT \quad (12)$$

where, it is understood that the molecules of finite volume are taken into account by the constant ‘ b ’ and the attractive forces between the molecules are taken into account by ‘ a ’.

With equation (12) the gas laws were now valid over a much larger pressure range. [33, 37]

The attractive forces acting between the molecules are referred to as the van der Waals forces.

This concept of the attractive force is also used to describe the properties of condensed matter physics. Mie's version of describing the complex intermolecular interactions is given by the 'Pair Potential' concept in equation (13). [37]

$$W(r) = -\frac{A}{r^n} + \frac{B}{r^m} \quad (13)$$

where, ' A ' and ' B ' are constants. The first term is the attractive term and the second term is the repulsive term. The left hand side of the equation is the potential energy in the system.

A more commonly seen form for equation (13) is the Lennard- Jones Potential which is seen in equation (14).

$$W(at/at) = -\frac{A}{r^6} + \frac{B}{r^{12}} \quad (14)$$

where, the net interaction potential energy, ' $W_{at/at}$ ', between atoms separated by a distance ' r ', can be characterized by the balance between the attractive London dispersion force taken into account by the constant ' A ' and the Born repulsion term, which is formed due to the overlap of the electron clouds, which is taken into account by the constant ' B '.

The value of ' A ', maybe related to the ' a ' and ' b ' in the van der Waals equation (12) as seen in equation (15).

$$A = \frac{9ab}{4\pi^2Na^3} \quad (15)$$

Thus, the molecular forces between non-polar molecules may be referred to as the van der Waals forces or the London dispersion forces or the dispersion forces.

The van der Waals forces can be classified into three categories as mentioned in the following sections [34, 38, 39]:

1. Dipole-Dipole Forces (Keesom, 1912):

Keesom in 1912 showed that for a covalent molecule (such as a HCl molecule) if the molecule has a permanent dipole moment, then due to the positive and the negative charge rearrangement, the positively charged end of the permanent dipole will attract the negatively charged end of the permanent dipole leading to the arrangement of molecules in a specific orientation with respect to each other. However, the contribution by these forces to the overall van der Waals force total is not significant.

For example: Interactions between two hydrochloric acid molecules. $\text{HCl (g)} \leftrightarrow \text{HCl (g)}$

2. Dipole-Induced Dipole Forces (Debye, 1920):

Debye in 1920 showed that a molecule with a permanent dipole can induce a dipole in another molecule leading to an attractive force playing between the

molecules. These attractive forces are termed as Debye forces. These too do not contribute significantly to the overall van der Waals forces acting in the system. For example: Interactions between a hydrochloric acid molecule and a nitrogen molecule. $\text{HCl (g)} \leftrightarrow \text{N}_2 \text{ (g)}$

3. Dispersion Forces (London, 1930):

London in 1930 showed that there are other attractive forces that come into effect between non polar atoms or molecules. The origin of these forces is explained to be caused by the motion of the electron cloud which might be displaced relative to the positive nucleus of the atom at any given instant. The atoms involved thus acquire an instantaneously induced dipole moment and can induce another atom in the near vicinity leading to a net attractive force between the atoms. This is the main contributing force towards the van der Waals force calculation. These forces act for a short period of time and also act along a short distance and hence are referred to as short-range forces. [40, 41]

For example: Interactions between two nitrogen molecules. $\text{N}_2 \text{ (g)} \leftrightarrow \text{N}_2 \text{ (g)}$

As from equation (12), the Keesom, Debye and Dispersion forces also follow the same ratios (they decay rapidly to the sixth power of the inter-atomic or the molecular distance) in slightly different forms.

In order to calculate the dispersion forces between atoms let us consider an atom to have an instantaneous dipole moment (μ) at a given instant of time. With this the electric field (E) that will be acting along the axis of the dipole (x) can be given by equation (16). [38]

$$E = \frac{1}{4\pi\epsilon_0} \left(\frac{2\mu}{x^3} \right) \quad (16)$$

where, ' ϵ_0 ' is the permittivity of free space.

The presence of another atom in the vicinity makes the atom get polarized (depending on the polarizability of the atom, ' α ') and if we consider its acquired dipole moment to be ' μ' ', it will be given by equation (17).

$$\mu' = \alpha E \quad (17)$$

The potential energy of this system (V) will be given by equation (18).

$$V = -\mu' E \quad (18)$$

Substituting equation (17) and equation (16) in equation (18) we have equation (19).

$$V = - \left(\frac{1}{4\pi\epsilon_0} \right)^2 \left(\frac{4\alpha\mu^2}{x^6} \right) \quad (19)$$

London in 1930 used quantum mechanics calculations and arrived at the equation (20).

$$V = - \frac{3}{4} \left(\frac{1}{4\pi\epsilon_0} \right)^2 \left(\frac{\alpha^2 h \nu}{x^6} \right) \quad (20)$$

where, ' ν ' is the frequency of the polarized orbital and ' h ' is the Planck's constant.

The force that is acting between atoms can also be calculated as seen in equation (21).

$$F = \frac{\partial V}{\partial x} = \frac{A}{x^7} \quad (21)$$

where, 'A' is a constant.

Equation (20) can also be modified to the commonly seen version for the London Dispersion force given by equation (22).

$$-V = \frac{3}{2} \frac{\alpha_1 \alpha_2}{(4\pi\epsilon_0)^2} \frac{1}{r^6} \frac{I_1 I_2}{I_1 + I_2} \quad (22)$$

where, 'I' is the ionization energy, with $I = h\nu$, and 'ν' is the electron absorption frequency.

With the polarizability volume $\alpha' = \alpha/4\pi\epsilon_0$, equation (22) becomes equation (23).

$$-V = \frac{3}{2} \frac{\alpha'_1 \alpha'_2}{r^6} \frac{I_1 I_2}{I_1 + I_2} \quad (23)$$

Along similar lines, the Debye energy is given by equation (24).

$$V = -\frac{\mu^2 \alpha'}{4\pi\epsilon_0} \frac{1}{r^6} \quad (24)$$

where, the polarizability volume, 'α' is given by equation (25).

$$\alpha' = \frac{\alpha}{4\pi\epsilon_0} \quad (25)$$

Similarly, the Keesom energy is given by equation (26).

$$V = -\frac{2}{3kT} \left(\frac{\mu_1\mu_2}{4\pi\epsilon_0} \right)^2 \frac{1}{r^6} \quad (26)$$

The Debye and Keesom forces require permanent dipole moments and hence are not present in all materials. However, London dispersion forces exist in all materials. [34]

2.1.3 van der Waals Forces: Dispersion Forces for Macroscopic Bodies-Hamakar Approach

The dispersion forces for macroscopic bodies based on the Hamakar approach are explained in chapter 4 of the dissertation. Understanding and control of the van der Waals forces between nanoparticles and nanoparticles and biological agents can be useful in being able to effectively disperse nanoparticles and biological agents.

2.2 Rheological Parameters Controlling Colloidal Dispersions

Rheology or ‘Flow-Behavior’ of suspensions plays an important role in keeping particles from agglomerating and having a high solids loading slurry so as to fabricate materials with minimal shrinkage during the fabrication process. [42] Rheology is the study of the

flow behavior of suspensions and fluids over the range of applied shear conditions. [43]
The various factors affecting this flow behavior will be explained in the later sections of this chapter.

In order to better understand the rheology of a suspension, it is also important to understand the fundamental mechanisms by which stable suspensions can be prepared. [44-46] In the following sections an introduction to the various colloidal stabilization mechanisms are discussed.

2.2.1 Mechanisms for Colloidal Stabilization

When particles are subjected to a liquid medium the van der Waals forces between them tend to flocculate the particles leading to particle agglomeration. The particles in the colloidal system collide with each other (due to the Brownian motion) and due to the strong van der Waals forces of attraction, the particles agglomerate. The particles stick together as the thermal energy is insufficient to overcome the strong attractive potential energy present in the system. [38]

Based on the system of discussion the particles may be stabilized by either of these mechanisms [22, 38, 47-49]:

1. Electrostatic stabilization
2. Steric or polymeric stabilization
3. Electro-steric stabilization

A description of each of these fundamental colloidal stabilization mechanisms are presented and discussed in the following sections.

2.2.2 Electrostatic Repulsion Based Colloidal Stabilization

The electrostatic repulsion between particles is caused by the electrostatic charge present on the particles. However, this mechanism is not as simple as it sounds-as it is not a direct repulsion between the charged particles. In this case, it is the repulsion between the diffused double layers formed around each of the particles that cause the system to be stable. [38]

The concept of the surface charge formation on particles, diffused double layer and the electrical double layer are described briefly in the following sections.

2.2.2.1 Surface Charge Formation on Particles

There are different mechanisms by which particles that are dispersed in a liquid can acquire a surface charge. The mechanisms can be any of these listed [38, 47, 48]:

1. Preferential or differential ion adsorption
2. Direct ionization of the surface groups
3. Isomorphic substitution
4. Adsorption of polyelectrolyte
5. Accumulation of electrolytes

The preferential adsorption of ions is the most common mechanism of surface charge formation for ceramic systems. [38]

2.2.2.2 Diffused Double Layer Formation and Concept

The ions that surround the particle under consideration are important parameters affecting the dispersion of the particles. The ionic layer formed by the charges around the particle is termed as the double layer. The surface charge present on the particle is neutralized by the charges present in this double layer. The oppositely charged hydrated ions present in the double layer are termed as the counter-ions and the like charged ions are termed as co-ions. [48]

Helmholtz discovered the concept of the electrical double layer by analyzing the rearrangement or arrangement of ions in two parallel planes which he termed as the molecular condenser as seen in figure (1). [48]

In the absence of any thermal motion an equal number of counter ions would adsorb onto the surface of the plate or particle and neutralize it. However, in the presence of thermal motion even though the ions will have the same tendency to neutralize, this does not happen by the formation of a compact double layer, but by the formation of a diffused double layer as seen in figure (1). [38, 48]

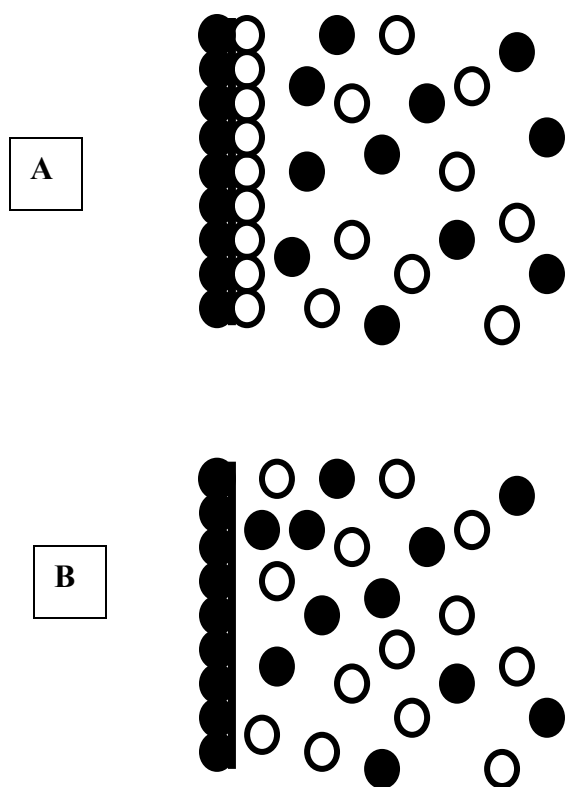


Figure 1: Schematic of the diffused double layer (molecular condenser). The cases without any thermal motion (a) and with thermal motion (b) are seen

The electrical potential in such a system varies with distance and is shown in figure (2).

These variations in the electric potential in the system are governed by [38, 48]:

1. Poisson's equation
2. Boltzmann's equation
3. Charge-density function or equation

2.2.2.3 Electrical Double Layer and Zeta-potential

Nobel laureate, Otto Stern introduced the concept that the electric double layer consists of a compact inner layer termed as the 'Stern layer' and the outer diffused layer referred to as the 'Gouy-Chapman layer' as seen in figure (3).

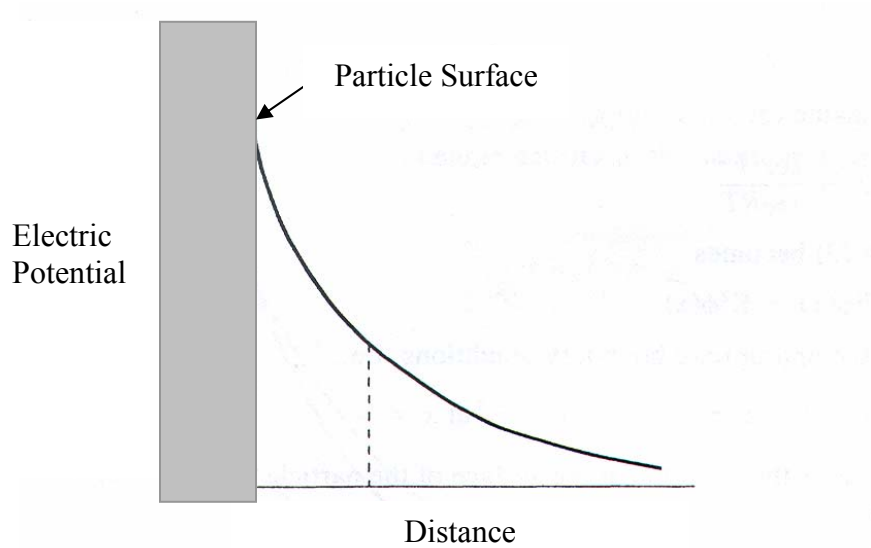


Figure 2: Schematic of the variation of the electric potential with distance from the particle surface

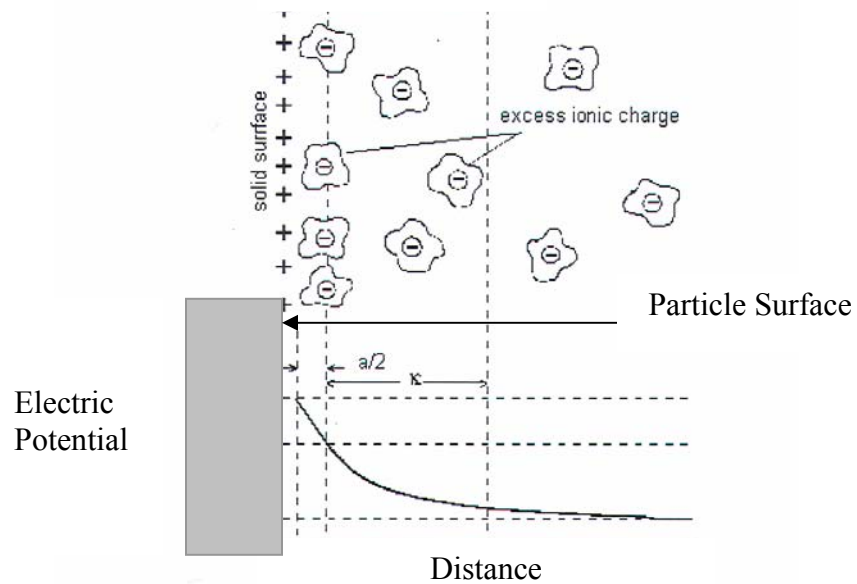


Figure 3: Schematic of the stern layer formation and the decay of the potential with distance from the particle interface

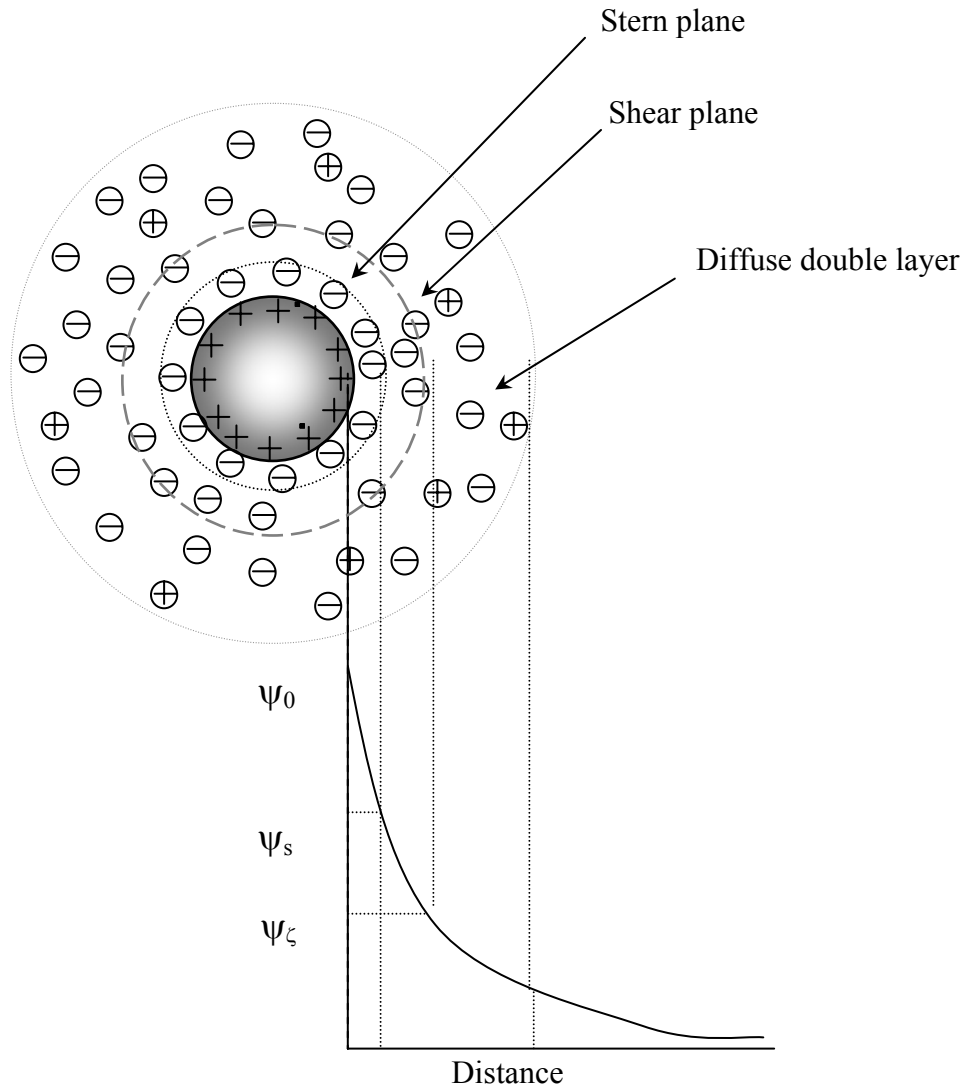


Figure 4: The EDL consisting of the three regions [22]

The shear slippage in the case of a particle experiencing the electrical double layer phenomenon occurs at a distance from the particle surface. The potential at which this occurs is termed as the zeta potential. In other words the zeta potential is the potential experienced by the surface of the electrokinetic unit while traveling in solvent as measured from its electrophoretic mobility. A schematic of the particle interface along the shear plane is seen in figure (5). [22, 38, 47, 48]

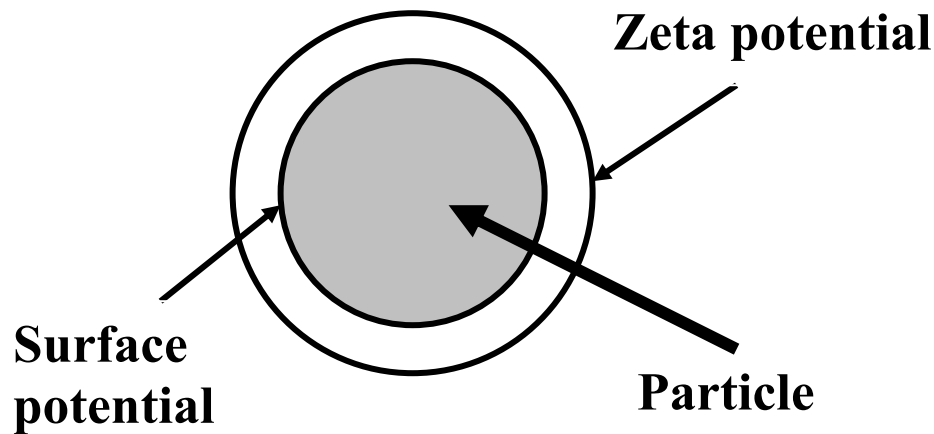


Figure 5: The particle interface along with the shear plane

When particles are dispersed in a solvent and there is the formation of the electric double layer, at some pH the adsorption of the positively charged ions is balanced by that of the negatively charged ions. This intermediate pH is termed as the point of zero charge (PZC) and in this case the particle surface becomes neutral. [22, 38]

The pH at which the zeta potential becomes zero is termed as the iso electric point (IEP). [22, 38] The iso electric points for various ceramic materials are listed in table (1). [48]

2.2.2.4 Electrical Double Layer Based Repulsion in Colloidal Systems

As the particles come closer together their electrical double layers start to overlap as seen in figure (6) and figure (7). This interaction in the double layers keeps the particles from agglomerating if the repulsive force due to the double layers is greater than the forces of attraction tending to agglomerate the particles. [50] The repulsion is due the osmotic pressure that results due to the increase in the ionic concentration. [38, 48]

Table 1: pH at the IEP for various ceramic materials

Ceramic Material	pH at the Iso Electric Point (IEP)
Alumina (Al_2O_3)	9.1 [51]
Silica (SiO_2)	2 [52]
Anatase (TiO_2)	6 [52]
Zirconia (ZrO_2)	6 [52]
Hematite (Fe_2O_3)	7.2 [53]
Lead Oxide (PbO)	10 [54]
Magnesia (MgO)	12 [54]
Silicon Nitride (Si_3N_4)	8.2 [55]
Stannic Oxide (SnO_2)	5.5 [54]
Zinc oxide (ZnO)	9 [54]

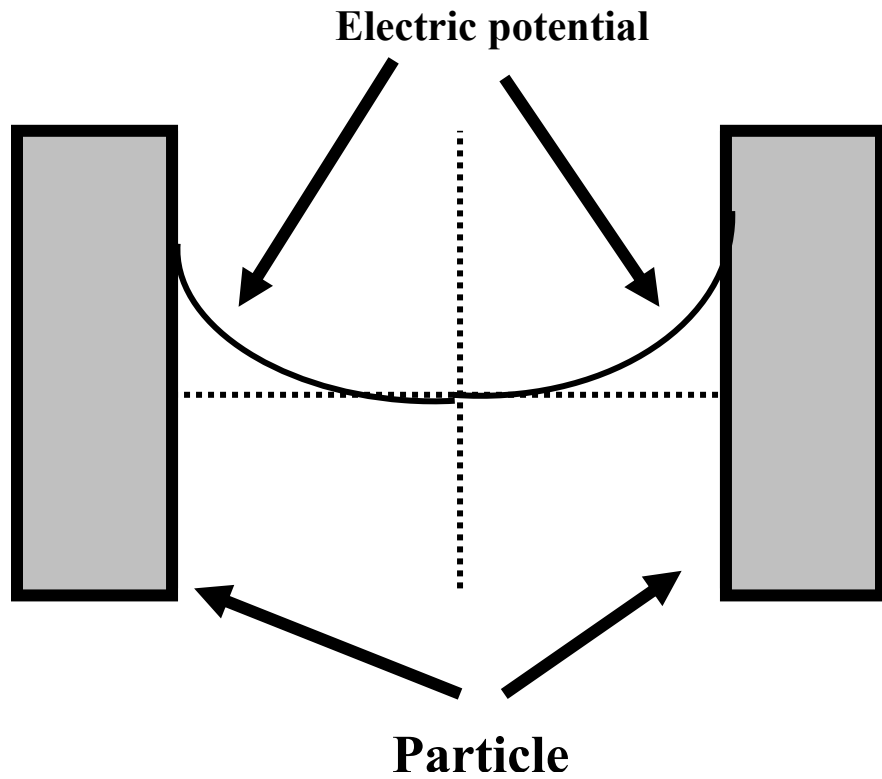


Figure 6: The interaction of the electrical double layers leading to repulsion between the particle surfaces

The repulsive interactions between the electric double layers were calculated by Derjaguin and later by Verway and Overbeek and hence called the DLVO theory which is explained in the next section. [4, 48]

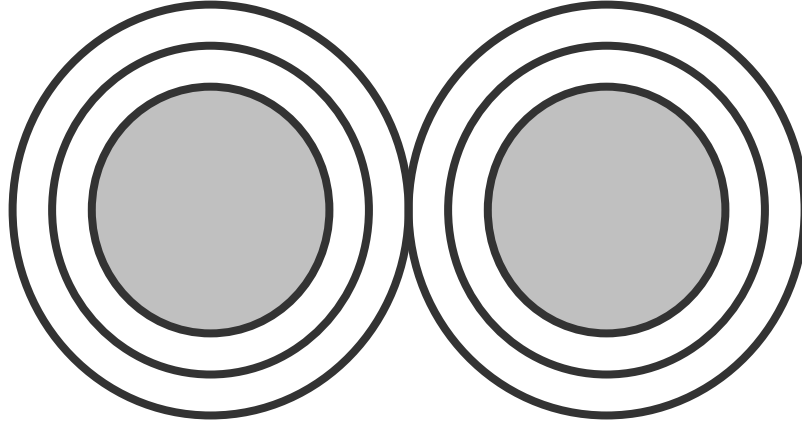


Figure 7: Electrostatic repulsion caused due to the interacting double layers as two particles come close together

2.2.2.5 Total Potential Energy of Interaction: Derjaguin, Landau, Verwey and Overbeek (DLVO) Theory

The DLVO theory explains the interaction of the electric double layers and states that the total potential energy ($E_{T(DLVO)}$) of interaction between the particles is the summation of the repulsive double layer interaction energy ($E_{R(DLVO)}$) and the attractive potential energy (E_A) as given by equation (27). [4, 22, 48, 56]

$$E_{T(DLVO)} = E_{R(DLVO)} + E_A \quad (27)$$

The variation of the electrical double layer repulsion with the van der Waals attraction is shown in figure (8). Depending on the strength of the attractive and the repulsive energies, various versions for the curve ($E_{T(DLVO)}$) in figure (8) can be obtained. In figure

(8), $E_{T(DLVO)}$ shows a case of neither a weak repulsion nor a weak attraction, but a case with two minima. (primary and secondary). [38, 48, 57, 58]

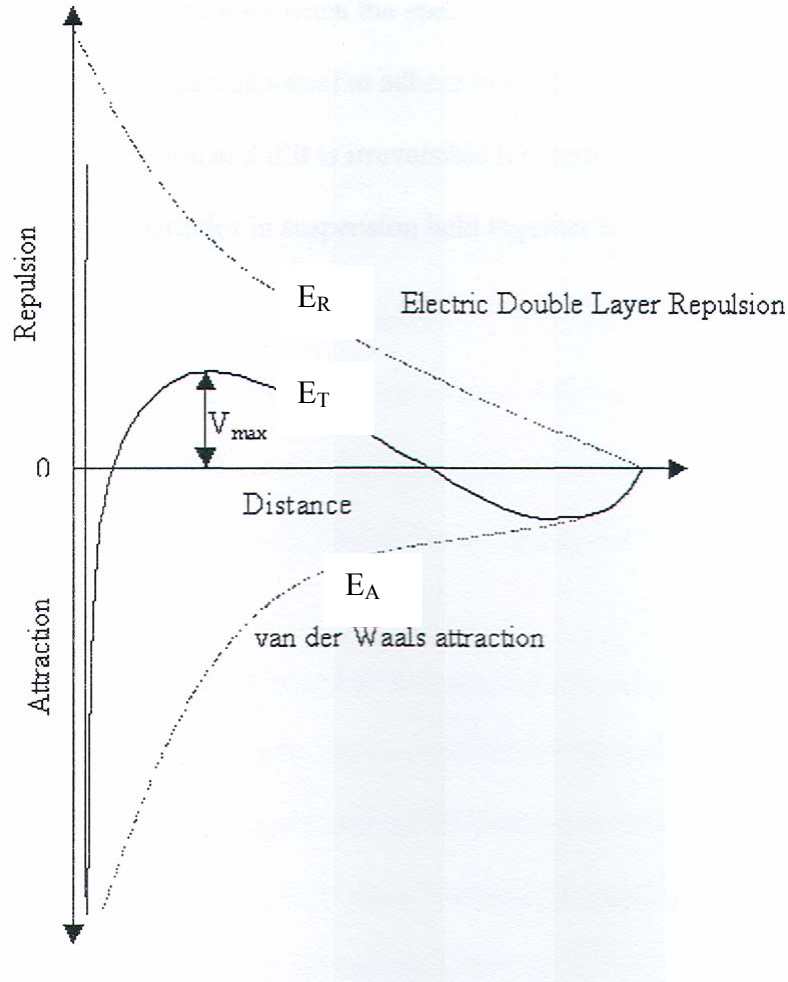


Figure 8: Interactive potential energy variation between two particles experiencing the effects of the double layer repulsion and the van der Waals attraction [22]

In non aqueous media or non polar solvents the electrostatic repulsion is minimal due to the low concentration of the ionic species and them having a low dielectric constant. [48]

Hence the steric repulsion is the major repulsive barrier in these systems. This steric repulsion based colloidal stabilization is mentioned in the following section.

2.2.3 Polymeric Repulsion Based Colloidal Stabilization

The polymeric repulsion based colloidal stabilization is the mechanism used to stabilize slurries using polymer molecules. If there is the presence of more than one repeating unit its called a co-polymer. The classifications of the co-polymers are as follows [59]:

1. Block type co-polymers:

These are co-polymers in which each of the repeating units ('A' and 'B') are present in a blocks.

Example:**AAAABBBBBBAAAA**....

2. Random type co-polymers:

These are co-polymers in which each of the repeating units ('A' and 'B') are randomly repeated in the polymer.

Example:**ABABBABAAAAB**....

3. Graft type co-polymers:

These are co-polymers in which each of the repeating units ('A' and 'B') are present in random orientations.

Example:

.....**AAAAAAAAAAAAAAAA**.....

B	B	B
B	B	B
B	B	B
B	B	B
B	B	B
B	B	B

There are two different mechanisms for polymerically stabilizing suspensions namely (a) steric stabilization and (b) depletion stabilization which are explained in the following sections. [4, 38, 48, 60-62]

2.2.3.1 Steric Stabilization

Steric stabilization occurs when macromolecules are adsorbed (by grafting or by physical adsorption) onto the particle surface hindering the attractive van der Waals forces from agglomerating them. [4, 38, 48, 60, 61]

A schematic of this stabilization mechanism is seen in figure (9).

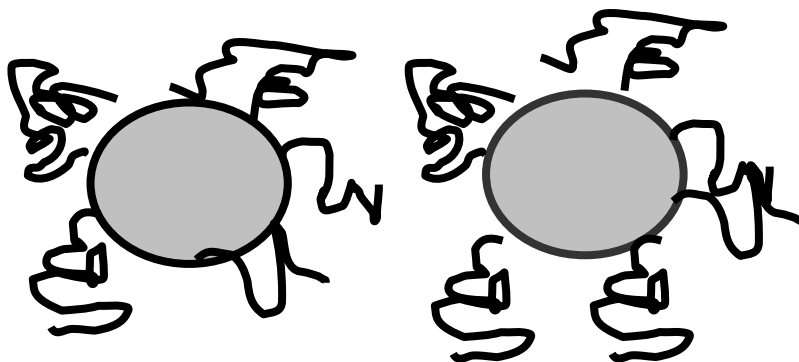


Figure 9: Schematic of the steric stabilization mechanism

When the two particles come closer together the polymer layers adsorbed on them tend to interpenetrate as shown in figure (10). In the first case in the figure the particles are separated and hence there is no interaction between them. In the second case there is little repulsion and in third case due to the penetration of the polymer layers there is strong repulsion between the particles. This interpenetration of the polymer layers leads

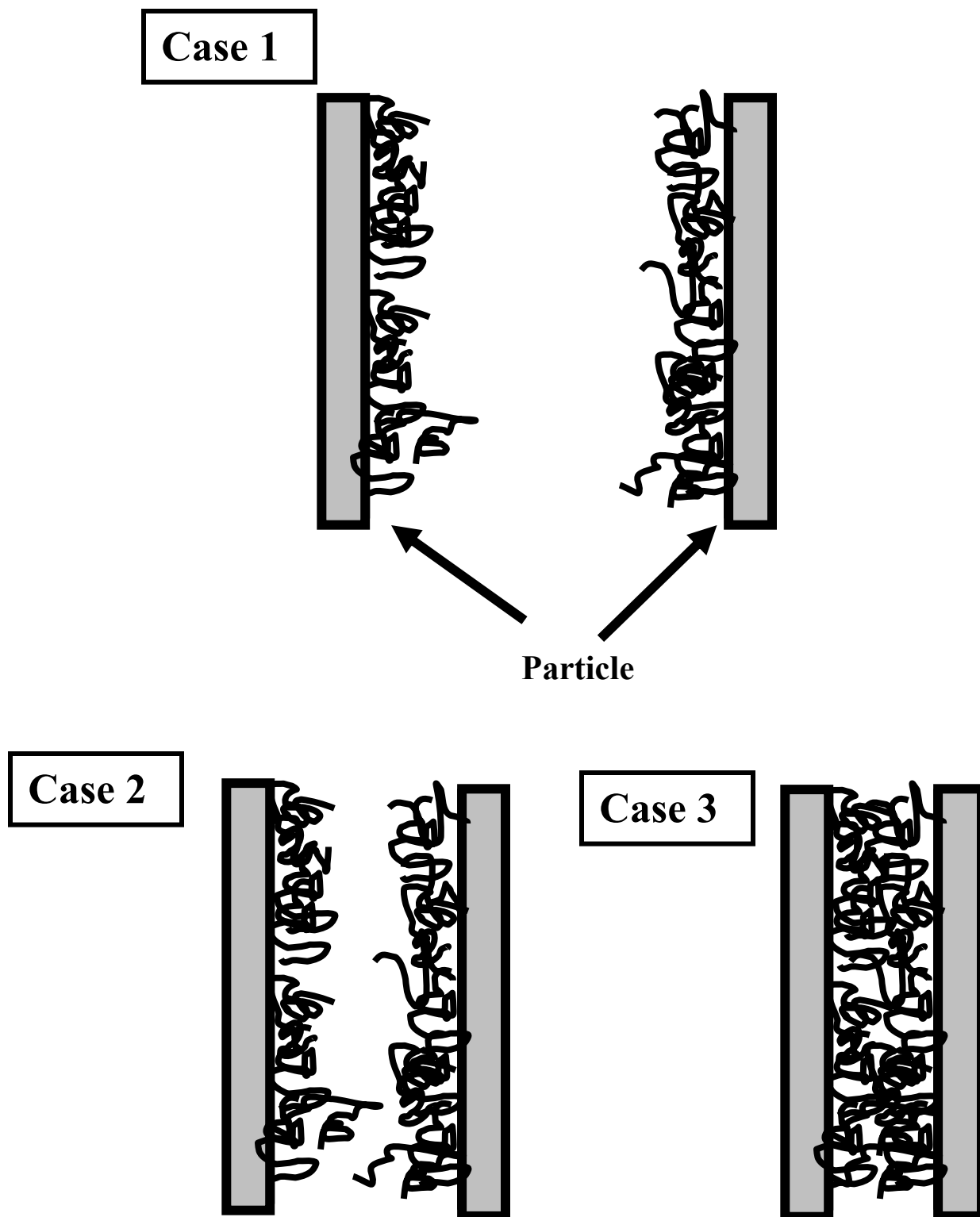


Figure 10: Interactions of the polymeric coils as the particles approach each other

to a repulsion in good solvents and an attraction in poor solvents. However at very small distances the compression of the polymer coils always leads to repulsion. [38, 48, 60]

The interactions caused due to the interpenetration of the polymer coils as the particles approach each other can have either an osmotic effect (due to increase in the local concentration of the adsorbed species) or an entropic effect (also called as the volume restriction which is caused due to the loss in the degrees of freedom due to the over crowding of the interacting species) leading to the generation of the repulsive forces. [38]

The attachment of the polymer onto the particle surface can be at a single point or at multiple points. A schematic of this is seen in figure (11). When the polymer is adsorbed onto just one site they tend to arrange in a ‘Tails’. However, when the polymer is adsorbed in multiple points on the particle surface there can be the arrangements seen in the form on ‘Trains’ or ‘Loops’ or ‘Tails’. In a typical system both of these configurations of polymer orientation will be present. [38, 47]

The potential energy curve for the steric barrier repulsion explains that the total potential energy ($E_{T(\text{steric})}$) of interaction between the particles is the summation of the repulsive steric interaction energy ($E_{R(\text{steric})}$) and the attractive potential energy (E_A) present in the system as seen in equation (28). [4, 22, 48]

$$E_{T(\text{steric})} = E_{R(\text{steric})} + E_A \quad (28)$$

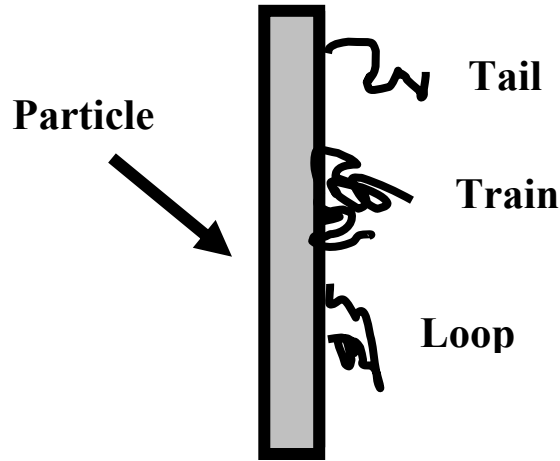


Figure 11: Schematic of the arrangement of the adsorbed polymer on the particle surface

The variation of the steric repulsion with the van der Waals attraction is shown in figure (12). Depending on the strength of the attractive and the repulsive energies, various versions for the curve ($E_{T\text{steric}}$) in figure (12) can be obtained. However, unlike the case of electrostatic repulsion, in steric repulsion systems the primary minimum does not exist (as the interactions for anchoring the stabilizers produce the repulsion necessary to eliminate the minima). [38, 48]

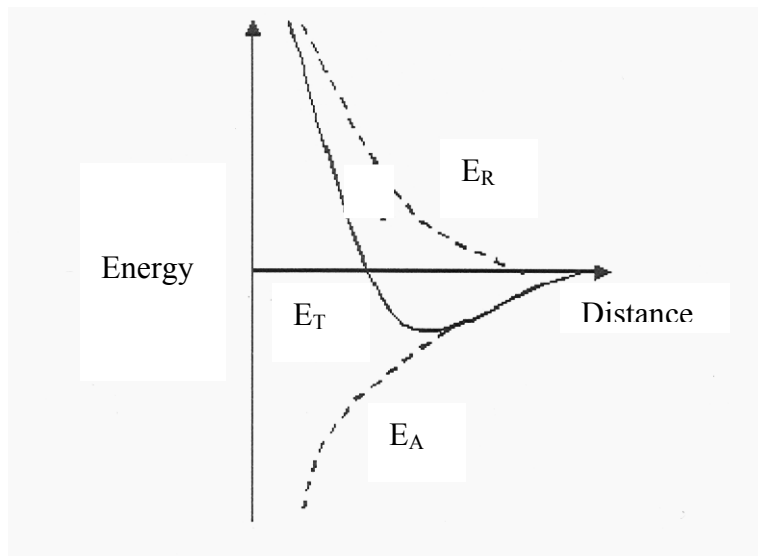


Figure 12: Schematic of the variation of the potential energy for a sterically stabilized system

Finally, the effectiveness of a steric repulsive barrier is determined by the following factors:

1. Surface coverage of the polymer
2. Configuration of the adsorbed polymer
3. Thickness of the adsorbed polymer layer

2.2.3.2 Depletion Stabilization

Depletion stabilization mechanism for stabilization of colloids occurs when the polymer molecules causing the repulsion are in the free solution. [4, 38, 48, 60, 61]

A schematic of this stabilization mechanism is seen in figure (13).

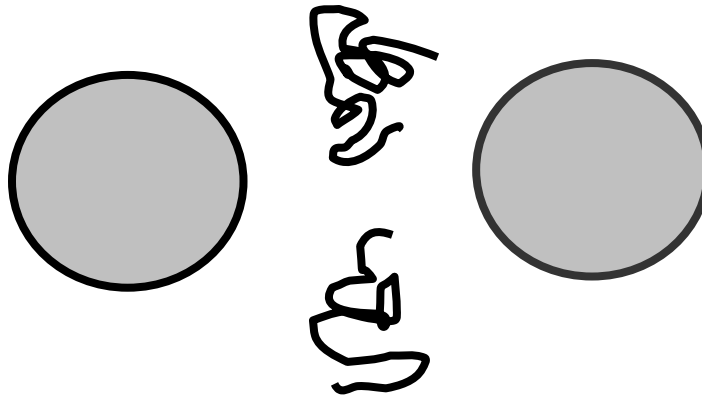


Figure 13: Schematic of the depletion stabilization mechanism between two particles

2.2.4 Electro-steric Repulsion Based Colloidal Stabilization

The electro-steric stabilization mechanism for stabilization for colloids occurs when the repulsion in the system is caused due to a combination of the steric and the electrostatic

repulsion mechanisms. This can be achieved in any of the following systems [4, 38, 48, 60, 61, 63, 64]:

1. Charged particle and neutral polymeric system
2. Neutral particle and a charged polymeric system
3. Charged particle and a charged polymeric system

A schematic of this stabilization mechanism is seen in figure (14).

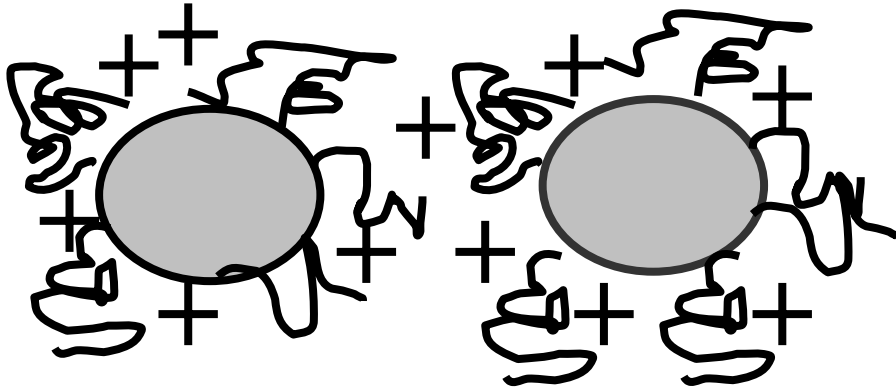


Figure 14: Schematic of electro-steric stabilization between two particles

2.2.5 Particle Agglomeration, Flocculation or Coagulation in Colloidal Suspensions

The particles in a suspension experience an attractive and a repulsive potential.

Depending on the strength of this potential the particles are agglomerated or dispersed. In coagulated systems the repulsive forces present in the system are not strong enough to overcome the attractive potential and hence the particles are agglomerated. A coagulated system is one in which the particles are held together by the van der Waals attractive

forces. When the agglomeration of the particles is irreversible it is called coagulation and if it is reversible it is termed as flocculation. [22, 48, 60]

2.2.6 Rheological Parameters Affecting Colloidal Dispersions

Rheology as mentioned earlier is the study of the flow behavior of suspensions over a full range of applied shear conditions. [43] For ceramic suspensions it is important to understand the rheological properties that affect the suspension properties, as for good suspensions there needs to be a balance between the shrinkage and its flowability. For concentrated suspension there is minimum shrinkage but low flowability. It is the opposite for dilute suspensions. Hence, there is need to control the rheological parameters so as to obtain the minimum shrinkage with good flowability characteristics. A good suspension is one that has a high solids loading that will minimize the shrinkage and a low enough viscosity to allow ease of fabrication. [4, 22, 43, 48, 61, 65]

The important property while looking at the rheology of suspensions is the suspension viscosity. In order to calculate the viscosity of the suspension the most commonly used method is to analyze the shear stresses necessary to shear the suspension at various shear rates. A typical curve (commonly called a rheogram) for the variation of shear stress of a suspension with respect to the shear rate for a Newtonian fluid is shown in figure (15). A Newtonian fluid is one in which the viscosity does not depend on the shear rate of the suspension. [22, 43, 61]

The variations of the shear stress with respect to shear rate for a Newtonian fluid as seen in figure (15) is a straight line given by the equation (29).

$$y = mx + C$$

(29)

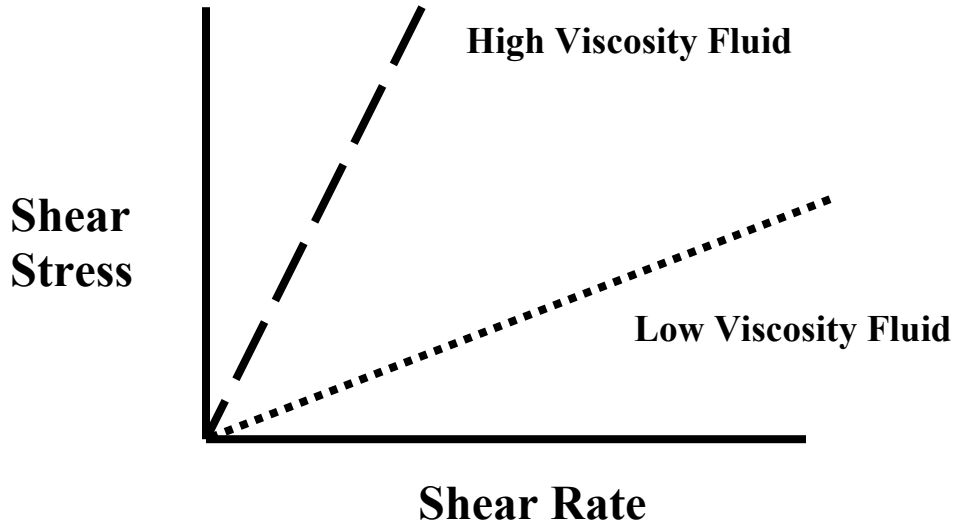


Figure 15: Variation of shear stress and shear rate based on the fluid viscosity for a Newtonian fluid

Substituting, the values for shear stress (τ), shear rate ($\dot{\gamma}$) and viscosity (η) in the appropriate locations we have the definition for the viscosity of the fluid as seen in equation (30).

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (30)$$

The viscosity of a suspension is thus defined as the ratio of the shear stress to that of the shear rate at any given applied shear rate. [22, 43, 61]

The variation of viscosity with respect to shear rate for a low viscosity fluid and a high viscosity fluid is shown in figure (16).

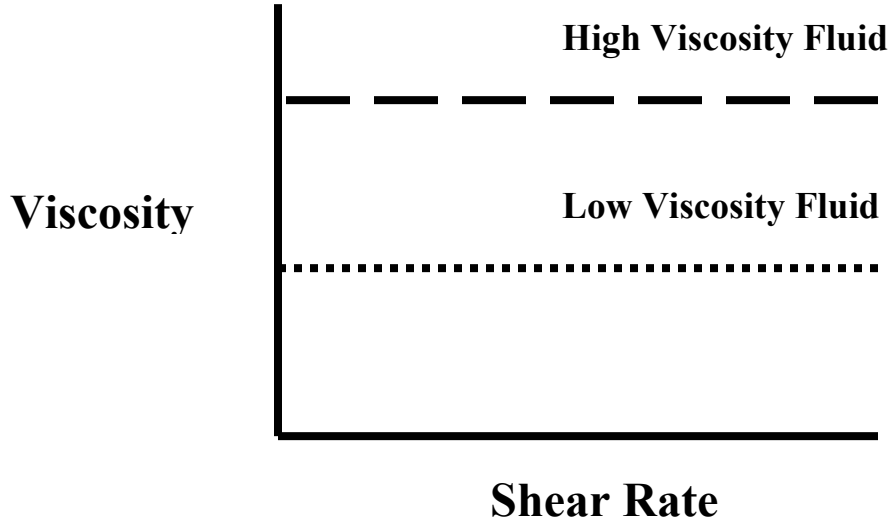


Figure 16: Variation of viscosity with respect to the shear rate for a Newtonian fluid

For most ceramic or polymer colloidal suspensions, the viscosity of the suspension is affected by the shear rate and hence the viscosity in these cases will be a function of the shear rate. These kinds of fluids are termed as non-Newtonian fluids. [22, 38, 43, 61]

Hence, equation (31) for non-Newtonian becomes

$$\eta(\dot{\gamma}) = \frac{d\tau}{d\dot{\gamma}} \quad (31)$$

where, ' $\eta(\dot{\gamma})$ ' is the viscosity of the suspension at a given shear rate.

Depending on the variation of the viscosity of the suspension with shear rate and the variation of the shear stress of the suspension with shear rate there are different kinds of liquids. The liquids whose viscosity decreases with shear rate are termed as shear thinning liquids or pseudoplastic liquids and those whose viscosity increases with shear

rate are termed as shear thickening liquids or dilatent liquids. There are other liquids whose viscosity not only varies with shear rate but also with time that are called as thixotropic or rheopexic liquids. [22, 38, 43]

For certain other liquids, the viscosity varies with shear rate after an initial threshold stress and hence are governed by equation (32).

$$\tau - \tau_y = \eta \dot{\gamma} \quad (32)$$

where, ' τ_y ' is the yield stress.

These liquids are termed as Bingham liquids (viscosity is independent of shear rate), yield-pseudoplastic (viscosity decreases with shear rate) and yield-dilatant (viscosity increases with shear rate) respectively as seen in figure (17).

The different modes of variation of shear stresses with respect to shear rate are seen in figure (18).

The amount of particles in the suspension or the solids loading of the suspension is also an important parameter controlling the rheology of the suspension. In order to understand the effect on rheological parameters due to the solids loading the particles need to be considered to be hard spheres. In this case the steric and the electric double layers on the particle surface are ignored. According to Einstein, the viscosity of the dilute suspensions

where all the interactions between the particles are neglected is given by the equation (33). [22, 38, 43, 56, 66, 67]

$$\eta = \eta_0(1 + 2.5\phi) \quad (33)$$

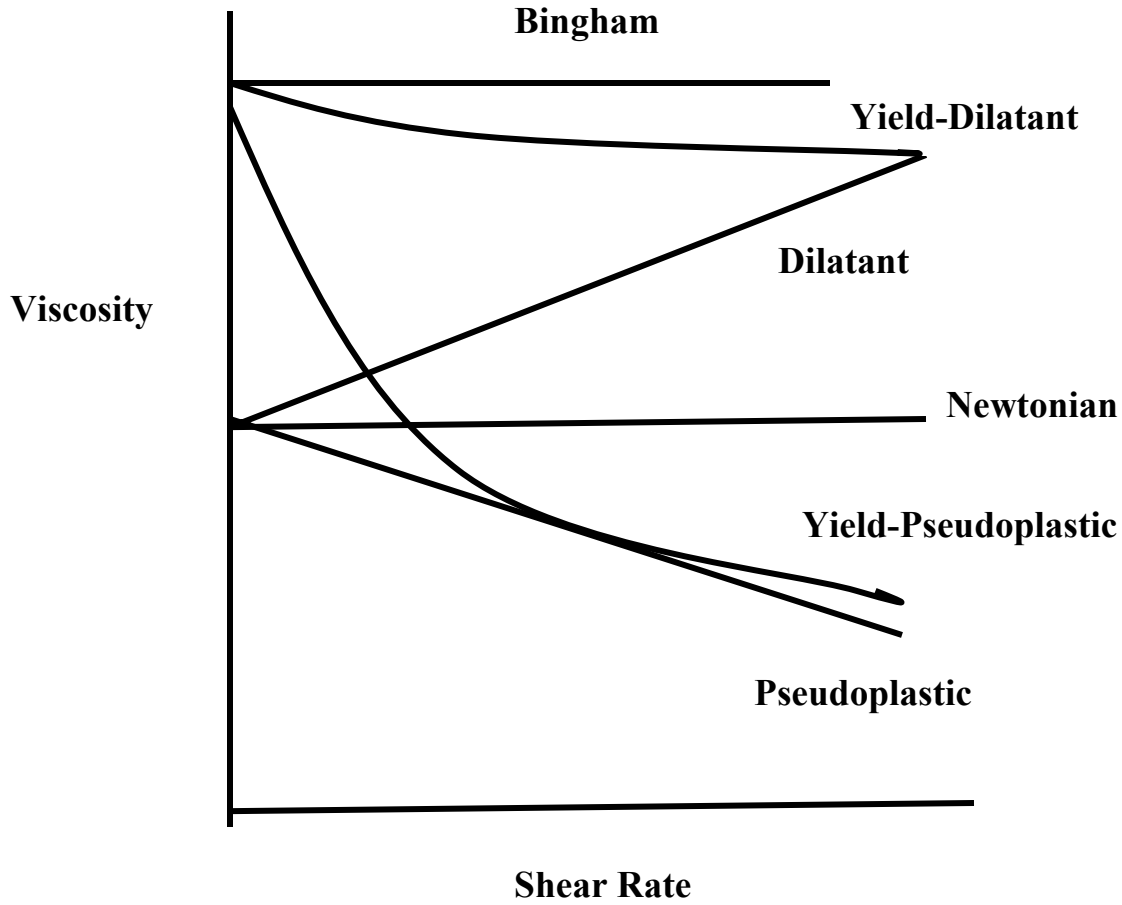


Figure 17: Different modes of variation of viscosity with respect to shear rate for liquids

where, ' η_0 ' is the viscosity of the fluid medium and ' Φ ' is the solids loading.

A more generalized form of equation (33) is seen in equation (34).

$$\eta = \eta_0(1 + k_1\phi) \quad (34)$$

where, ' k_1 ' is the Einstein's coefficient which is 2.5 in the case of hard spheres.

Equation (34) is the case wherein the suspensions are dilute. However, in the cases where the suspensions are more concentrated the dependence of the viscosity on the solids loading becomes more complex and is given by equation (35). [44]

$$\eta = \eta_0 (1 + k_1\phi + k_2\phi^2 + k_3\phi^3 + k_4\phi^4 + k_5\phi^5 + \dots) \quad (35)$$

where, ' k_1 ', ' k_2 ', ' k_3 ', ' k_4 ' and ' k_5 ' are constants of proportionality.

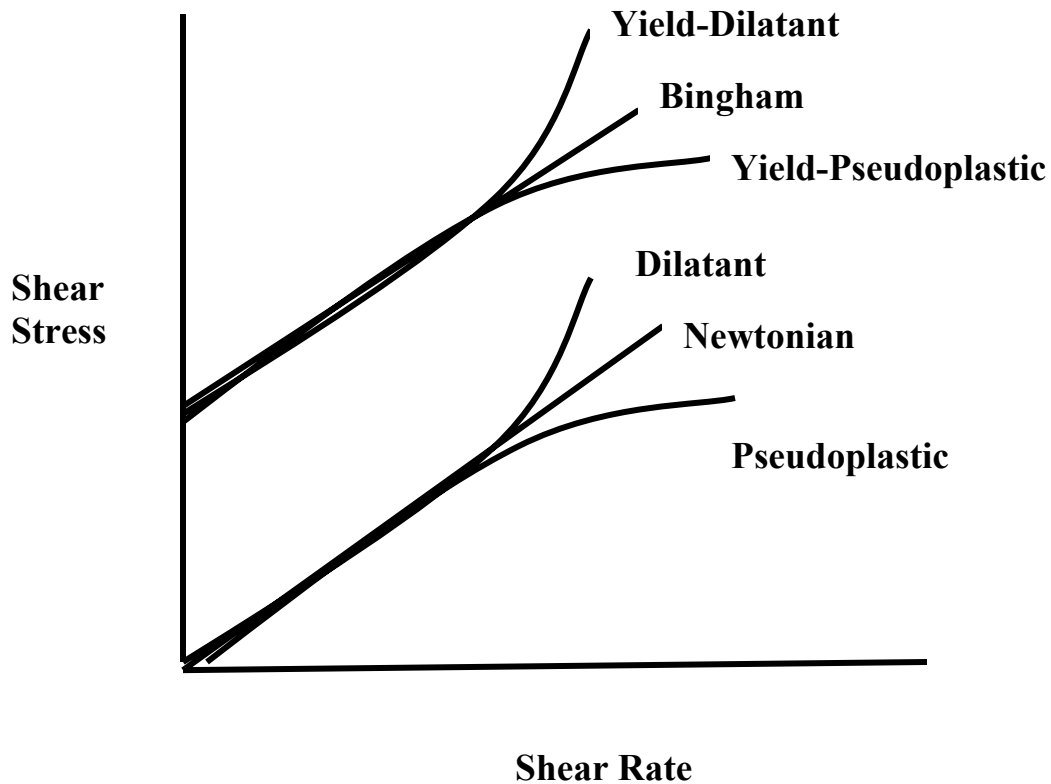


Figure 18: Different modes of variation of shear stress with respect to shear rate for liquids

The addition of particles into the suspension increases the solids loading of the suspension and also increases the suspension viscosity. The highest solids loading or the maximum solids loading are achieved when the suspension viscosity reaches infinity. When this case is achieved, the particles are so closely packed that the average separation distance between them is almost negligible. Depending on the design of the colloidal suspension, the maximum solids loading that are obtained can vary.

2.3 Colloidal Processing Methods

The forming and processing methodology utilized for the ceramic suspensions are important to obtain the structural dimensions desired. The various colloidal processing methods are listed in figure (19). These techniques can be classified into three major categories [4, 38, 60, 68]:

1. Dry processing methods
2. Wet processing methods
3. Plastic processing methods

The dry processing mechanisms are the most commonly used method in the ceramic industry. [4, 38, 60, 68]

The various parameters including cost, near net shaping, acceptable defect concentration, desired density, desired strength, processing difficulty and binder amounts acceptable; determine the colloidal processing technique to be used.

While using nanoparticles we need to use any of the wet shaping processes as the strong van der Waals forces of attraction will keep the particles agglomerated in the dry state and also the wet processing method can potentially help fabricate materials with uniform distribution of particles with a high density and a high solids loading. Hence, for micro and nano particulate dispersions the wet processing mechanism is used. The wet processing mechanisms can be divided into the direct and drained casting techniques as seen in figure (19).

2.4 Micro and Nano Porous Materials

Porous materials play a significant role in the international market and account for revenue of many billions of dollars. [69] According to the International Union of Pure and Applied Chemistry (IUPAC), any solid material that contains cavities, interstices or channels may be regarded as a porous material. [70, 71] Typically for these materials, the porosity, which is the fraction of the pore volume to the total volume, lies in the range from 20 to 95%. [72, 73]

There is a large commercial demand in today's society for porous materials. Porous materials have been of technological significance not only because of their ability to interact with atoms, molecules and ions at the surface but also within the entire bulk of the material. [74] For certain applications as mentioned in the following sections, a high porosity in the material is desired. [75]

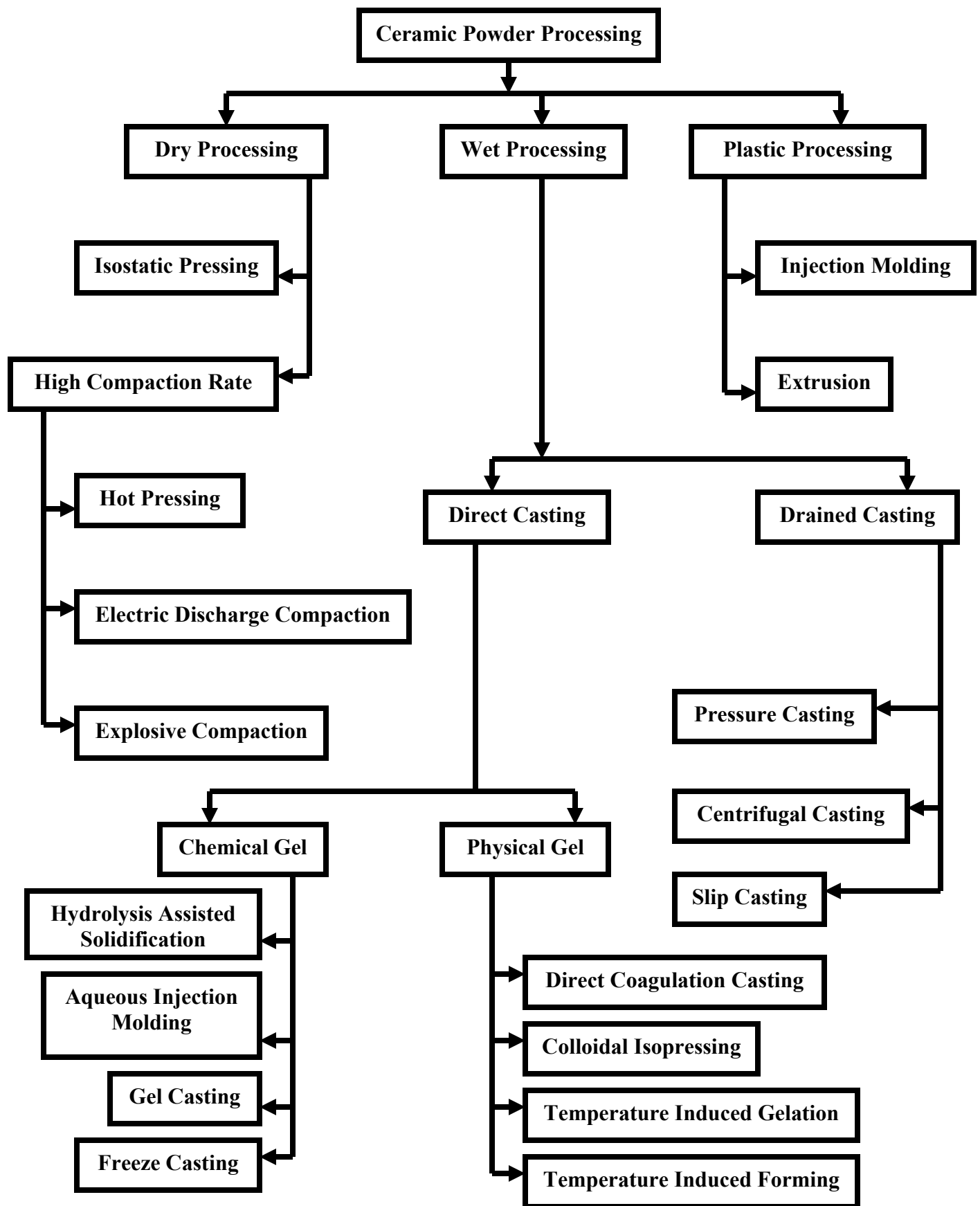


Figure 19: Schematic highlighting the various ceramic powder processing techniques

There are many important parameters for porous materials which vary greatly depending upon the desired application. These generally include pore size, size distribution, shape, extent of interconnectivity, and total amount of porosity. [74] We need to control the amount, size, location and shape of the pores so that the material has adequate strength. [74] In general as the porosity increases, the surface area of the material increases; the strength decreases; the weight is reduced; and the permeability is increased. [74, 75]

Porous materials of different compositions are increasingly being used in many industrial applications. Ceramic porous materials are very important for engineering as they have very good thermal resistance. This property helps in using them as thermal barriers. [73-75] Porosity increases the surface area of the material, reduces the weight and for bio based applications can help mechanically interconnect the implanted material with the host tissue. The porous structures can be filled with material to act as a reservoir for bioactive substances. [69, 75, 76]

The effect of introducing porosity on a particular property of a material depends upon many factors including the size; shape; percent open porosity; and total amount of porosity. There is a large diversity of porous materials which are used for many different applications throughout the world. However, there is a need to develop novel methods that can help reduce costs and simplify and improve the porous material production methods. [75, 76]

2.4.1 Classification of Porous Materials

Porous materials are characterized usually by their size distribution, shape, pore size, extent of interconnectivity and total amount of porosity [open or closed] of the pores.

[69] Pores in materials are classified as open or closed pores as seen in figure (20).

Open pores are pores that are connected to the outer surface of the material and can extend into the interior of the material. Closed pores are isolated inside the material. [73]

In open pores, the penetrating pores are permeable for the flow of liquids and hence can be used for applications such as for purifying materials (filters). [72, 75]

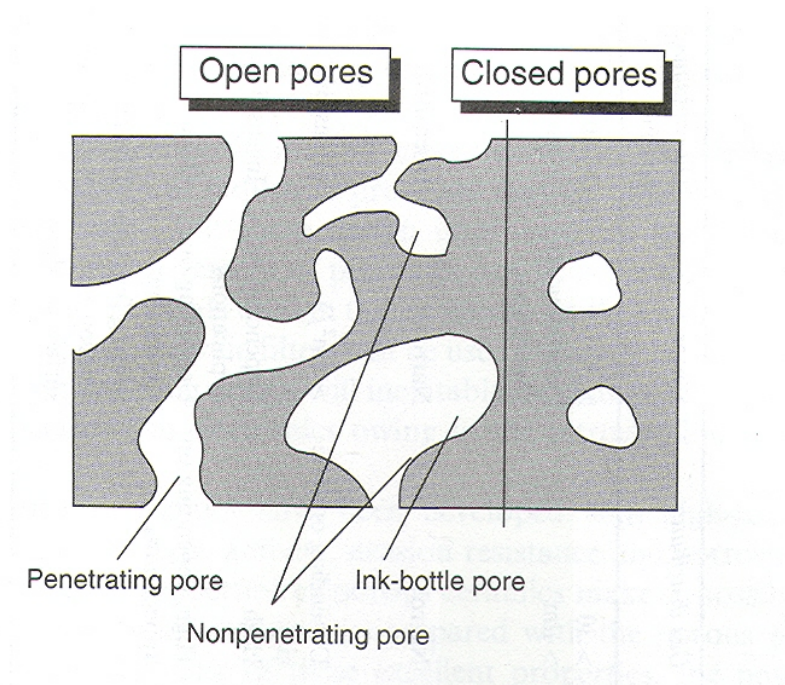


Figure 20: Schematic illustration of different morphologies of pores [72]

2.4.2 Applications of Porous Materials

Porous materials are used in thermal applications to either retain heat (as in industrial furnaces, pipe insulation, building insulation, and clothing) or to shield a component from

heat (such as space shuttle thermal tiles, cryogenic insulation, and furnace gloves). Catalytic converters in automobiles use porous materials (typically extruded monoliths) as the catalyst support and the chemical process industry utilizes reticulated ceramic foams for catalytic operations. Many sensor systems utilize porous materials, for example, photonic crystal and random hole optical fiber gas sensors (based on porous optical fibers). A large variety of porous materials are used for filtration and purification media for filtering particulates and impurities from air, water, molten metals and polymer melts. Porous materials also find wide applications in kiln furniture; waterproof, breathable apparel; silencers; aerators; absorbents; and weight reducing structural members, just to name a few. [75, 77-85] The size, size distribution, shape, extent of interconnectivity, and total amount of porosity are important factors in many of the abovementioned applications. Figure (21), shows some of the specifics of porous materials needed for few specific applications.

In recent years, nanoporous materials, which are those materials that have pores in the nanometer size range, have found applications in areas including ion exchangers; sensors; catalysts; purifiers and separators as they possess unique surface, structural and bulk properties. Porous ceramics have generated significant interest as they can be used under severe operating conditions unlike porous polymers, glasses and metals due to their excellent high temperature stability; erosion resistance; corrosion resistance; strength; and catalytic activity [73, 75, 86]. However, due to their brittleness; use of processing and sintering aids that limit toughness; lack of pore size control and lack of continuous processing methods, the true potential of these materials have not yet been fully realized

[69, 72-74, 76]. Nanoporous materials can potentially make use of the advantages associated with the nano sized porosity in the material. [73]

	<i>Filter</i>	<i>Catalyst</i>	<i>Bioreactor</i>	<i>Gas distributor</i>	<i>Sensor</i>	<i>Oil-containing bearing</i>
Open porosity (%)	> 30	> 30	> 30	> 30	> 30	20-40
Pore size	Appropriate size, depending on applications	Appropriate size, depending on applications	For bacteria: 5-30 μm For enzymes: 10-100 nm	> μm	Depending on applications	> μm
PSD ^a	Narrow	Narrow (depending on application, bimodal)	Narrow (depending on applications, bimodal)	Narrow	Narrow	Insensitive
SSA ^b	Depending on applications	1-2000 m^2/g	> 1 m^2/g	Depending on pore size	> 1 m^2/g	Insensitive
Permeability	High	Depending on applications	Depending on applications	High	Depending on applications	Insensitive
Mechanical strength	High	Depending on applications	High	High, depending on applications	Depending on applications	High
Others	Chemical resistance	Catalysis function	Appropriate surface potential		Sensing function Appropriate surface condition	Chemical and wear resistance

^a PSD = pore size distribution,
^b SSA = specific surface area per unit volume

Figure 21: Porous materials and their requirements for different applications [72]

2.4.3 Methods for Porous Material Fabrication

Many porous products are made as a result of incorporation of a fugitive phase into the article being fabricated. These fugitive phases may include sawdust, polymer spheres, open-cell polyurethane foams and carbon powder. The overall idea in fugitive-phase derived porous materials is that the fugitive phase occupies space in the structure while the article is being formed and 'set'. During firing, the fugitive phase is typically removed by oxidation (or controlled vaporization). The result is a fired part that contains a void or pore in the material of approximately the same size and shape as the fugitive phase. For most applications a large number of pores are desired. The amount of porosity that is produced (or the volume of porosity) is the same as the volume of fugitive material used (ignoring of course, the shrinkage which may occur during firing). [87] For industrial producers of porous materials, this means that a large volume of fugitive material must be purchased and stored on site for use in the production process. A significant amount of energy is consumed in removing the fugitive component. Also, during firing, this large volume of fugitive material must be removed (typically by 'burning out') thereby producing a large volume of gases that require the use of a sophisticated environmental emission control system in most cases. [88-90] A more effective way to produce the porosity may involve the use of a gas producing agent to form the voids in-situ. [76] Typically, the fugitive phase process for producing porosity, while very common in ceramic and metal systems, is much less common for polymer systems, because of the lower stability of these materials at the temperature required for typical fugitive phase removal by oxidation or 'burn-out'.

Porous polymer materials are typically produced by a ‘blowing agent’ while the polymer is in the molten state. These blowing agents may be the result of a chemical reaction, or vaporization of a low boiling point liquid. Another common method to produce porous polymers involves sintering of polymer particles. In this process, particles of the polymeric material are heated to a sufficiently high temperature that the particles partially ‘fuse’ together, leaving void spaces between the particles. The particle size distribution is carefully controlled, which in turn, controls the void size distribution produced. [91]

A large number of techniques have been developed to produce porous materials. A well known process utilizes reticulated polyurethane foam as the template for impregnation of ceramic slurries, which upon firing, produces reticulated ceramic foams. This process, while flexible in compositions which can be produced and reasonably low cost, has some limitations including inability to make very fine pore sizes (less than 100 microns) and the large amount of environmentally unfriendly byproducts which are produced from the removal of the polyurethane foam. Another process to produce porous ceramics utilizes phase separation typically in a spinodal region to form 3-dimensionally interconnected phases. After the phase separation, one of the phases can be removed by a process such as leaching. The most notable example of this may be the Vycor® process whereby a 96% silica glass can be obtained from spinodal phase separation of a sodium borosilicate glass after leaching of the soda-boron rich phase. Porous ceramics have also been produced by air injection or by high velocity stirring of a slurry; machining; etching of patterned ceramics, glasses or glass ceramics; solid freeform fabrication (or the various analogous processes) to directly ‘build’ the porosity into the part; extrusion of glasses and

ceramics; and a variety of processes such as freeze drying or soluble precipitate formation to produce crystals which can later be removed either through the vapor state or by dissolving in a suitable solvent. Porous metals can be fabricated by the dealloying process. [75, 77, 92-95] Figure (22), illustrates some of the porous materials made from different methods.

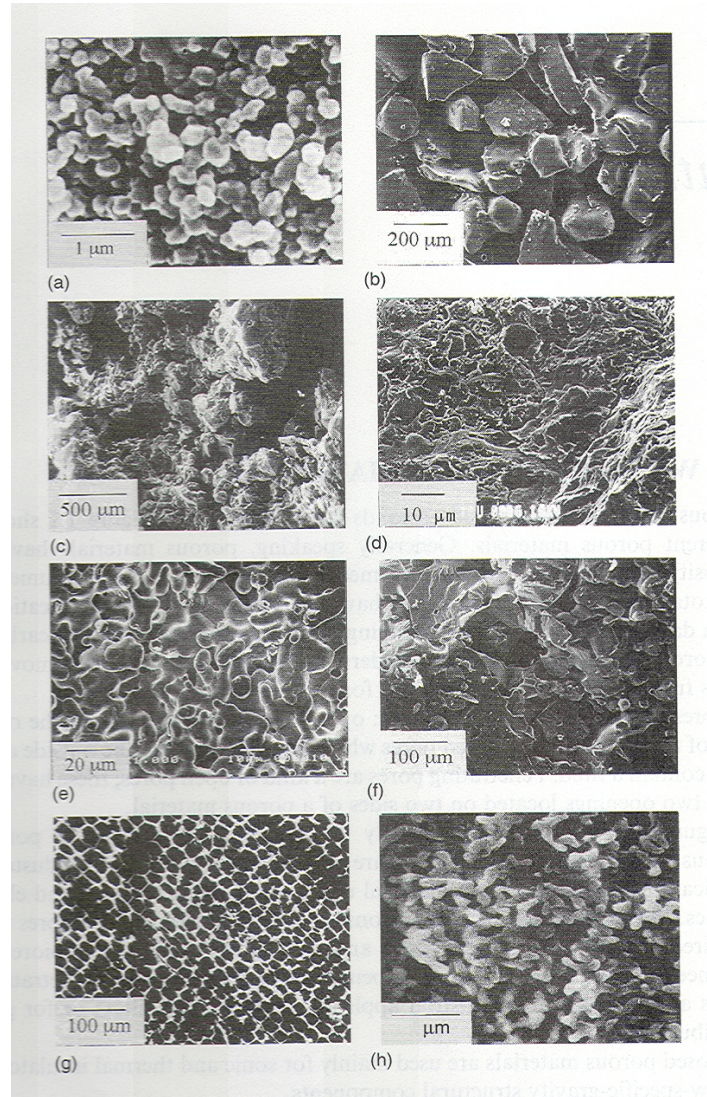


Figure 22: Examples of porous materials made by different methods: (a) porous titania sintered fine powder (b) grinding wheel, abrasive grains with a vitrified bonding agent (c) sponge titanium (d) a traditional ceramic (e) porous copper sintered electrolytic powder (f) porous silicon carbide produced by reaction sintering (g) charcoal (h) porous glass prepared by leaching method [72]

The manufacturing techniques vary depending on the application for the porous material that is to be produced. For industrial applications, it is essential that the method chosen to produce the porous material is cost effective. [75, 76, 91]

2.5 Research Motivation

The interactions of nanoparticles with nanoparticles and nanoparticles with biological agents are not clearly understood. The rheological processing parameters for dispersing nanoparticles with nanoparticles and nanoparticles with biological agents are not known either. Fundamental research into these aspects may help in a variety of different applications where biological materials are in contact with nanoparticulate materials.

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURE

In this chapter the raw materials used for the experimentation, their characterization and properties, the equipments used for the experimentation and the experimental procedure are discussed.

3.1 Materials Properties and Characterization

The different raw materials used for the experimentation are their properties and structures are discussed in this section.

3.1.1 Materials Properties and Structure

Details for the various chemicals used for the experimentation are listed in tables (2) through table (13). The chemical information for α -SiC nanoparticles are listed in table (2).

Table 2: Material properties of α -SiC nanoparticles

CHEMICAL NAME	ALPHA SILICON CARBIDE
Manufacturer or Source	Sigma-Aldrich
Chemical Structure	α -SiC
Particle Size	45-55 nm
Surface Area	70-90 m ² /g

Formula Weight	40.1
Melting Point	2700 °C
Bulk Density	0.069 g/cm ³
Appearance	Grey powder

The chemical information for Si₃N₄ nanoparticles are listed in table (3).

Table 3: Material properties of Si₃N₄ nanoparticles

CHEMICAL NAME	SILICON NITRIDE
Manufacturer or Source	Sigma-Aldrich
Chemical Structure	Si ₃ N ₄
Particle Size	15-30 nm
Surface Area	103-123 m ² /g
Formula Weight	140.29
Purity	98.5 + %
Bulk Density	0.046 g/ml
Appearance	White powder

The chemical information for SiO₂ nanoparticles are listed in table (4).

Table 4: Material properties of SiO₂ nanoparticles

CHEMICAL NAME	SILICON DI-OXIDE
Manufacturer or Source	Sigma-Aldrich
Chemical Structure	SiO ₂

Particle Size	10 nm
Surface Area	160 m ² /g
Formula Weight	60.09
Melting Point	1700 °C
Bulk Density	0.011 g/ml
Purity	99.5 %
Appearance	White powder

The chemical information for lactobacillus GG (LGG) is listed in table (5).

Table 5: Properties of lactobacillus GG

CHEMICAL NAME	LACTOBACILLUS GG (LGG)
Manufacturer or Source	ConAgra Foods
Size Feature	0.8 µm

The chemical information for porcine circovirus 2 is listed in table (6).

Table 6: Properties of porcine circovirus 2

CHEMICAL NAME	PORCINE CIRCOVIRUS 2
Manufacturer or Source	Veterinary school (Virginia Tech)
Size Feature	17-22 nm

The chemical information for pseudomonas aeruginosa is listed in table (7).

Table 7: Properties of pseudomonas aeruginosa

CHEMICAL NAME	PSEUDOMONAS AERUGINOSA
Manufacturer or Source	Civil and Environmental Engineering (Virginia Tech)
Size Feature	2 μm

The chemical details for poly acrylic acid (low molecular weight) are listed in table (8).

Table 8: Material properties of poly acrylic acid (low molecular weight)

CHEMICAL NAME	POLY ACRYLIC ACID A (PAA-A)
Manufacturer or Source	Sigma-Aldrich
Chemical Structure	$(\text{C}_3\text{H}_4\text{O}_2)_n$
Molecular Weight	1800
Appearance	White powder

The chemical details of poly acrylic acid (high molecular weight) are listed in table (9).

Table 9: Material properties of poly acrylic acid (high molecular weight)

CHEMICAL NAME	POLY ACRYLIC ACID B (PAA-B)
Manufacturer or Source	Sigma-Aldrich
Chemical Structure	$(\text{C}_3\text{H}_4\text{O}_2)_n$
Molecular Weight	450,000
Purity	$\leq 0.5\% \text{ C}_6\text{H}_6$
Appearance	White powder

The chemical information for polyethylene glycol is listed in table (10).

Table 10: Material properties of polyethylene glycol

CHEMICAL NAME	POLY ETHYLENE GLYCOL
Manufacturer or Source	Alfa Aesar
Chemical Structure	$\text{H (OCH}_2\text{CH}_2)_n \text{OH}$
Molecular Weight	8000
Melting Point	60-63 °C
Appearance	White powder

The chemical information for Duramax B-1000 is listed in table (11).

Table 11: Material properties of Duramax B-1000

CHEMICAL NAME	DURAMAX B-1020
Manufacturer or Source	Rohm and Haas
Appearance	White emulsion

The chemical information for $\text{C}_6\text{H}_{12}\text{O}_6$ are listed in table (12).

Table 12: Material properties of glucose

CHEMICAL NAME	GLUCOSE
Manufacturer or Source	Sigma-Aldrich
Chemical Structure	$\text{C}_6\text{H}_{12}\text{O}_6$
Appearance	White powder

The chemical information for NaCl are listed in table (13).

Table 13: Material properties of sodium chloride

CHEMICAL NAME	SODIUM CHLORIDE
Manufacturer or Source	Sigma-Aldrich
Chemical Structure	NaCl
Appearance	White powder

3.1.2 Electron Micrographs of Raw Materials

This section lists the characterization of the materials used for the experimentation using the scanning electron microscope (SEM) and the transmission electron microscope (TEM). The details on the instruments used are listed in the following section of the dissertation.

From the SEM images in figures (23) and (24), the particle size for α - SiC nanoparticles confirms with the industrial estimate and is expected to be approximately 55 nm.

However there is a size distribution seen in the particle sizes. The details for this are presented in later sections of the dissertation.

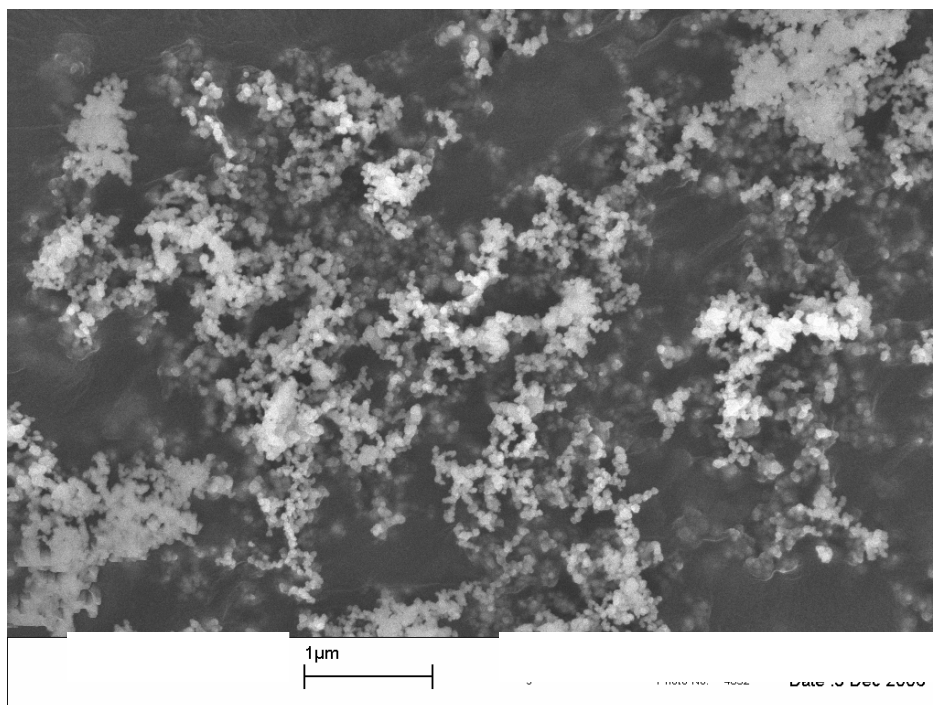


Figure 23: SEM image of α -SiC nanoparticles at 50 kX magnification

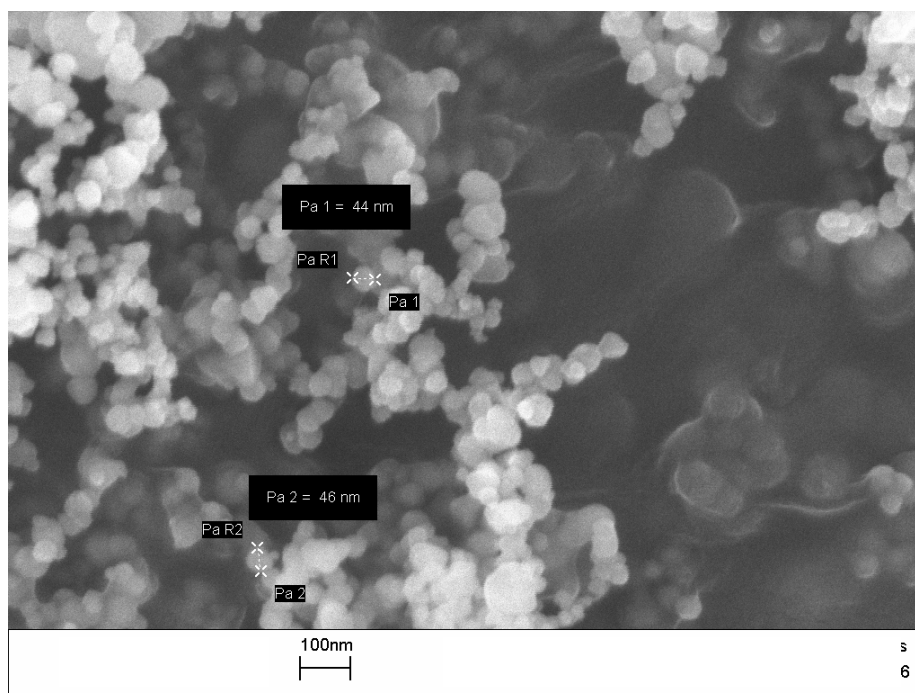


Figure 24: SEM image of α -SiC nanoparticles at 200 kX magnification

From figures (25) and (26) are the SEM and TEM micrographs of the Si_3N_4 nanoparticles. The particle size for these nanoparticles confirms with the industrial estimate and is expected to be approximately 30 nm. However there is a size distribution seen in the particle sizes.

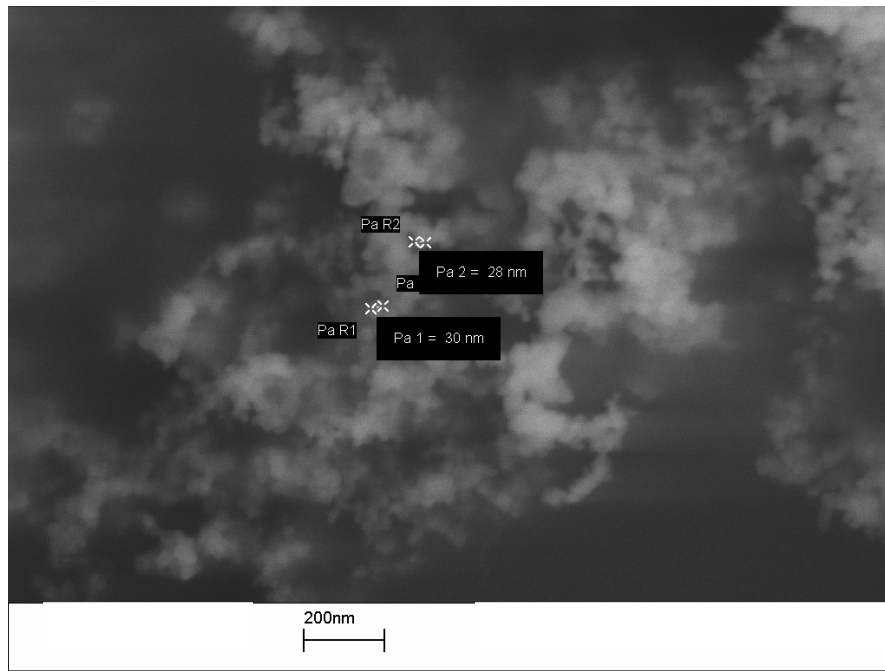


Figure 25: SEM image of the Si_3N_4 nanoparticles

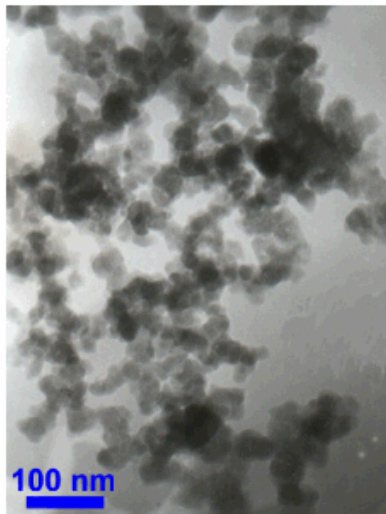


Figure 26: TEM micrograph of Si_3N_4 nanoparticles [96]

Figure (27) is the TEM micrograph of the Si_3N_4 nanoparticles from which the particle size for these nanoparticles is determined to be approximately 30 nm.

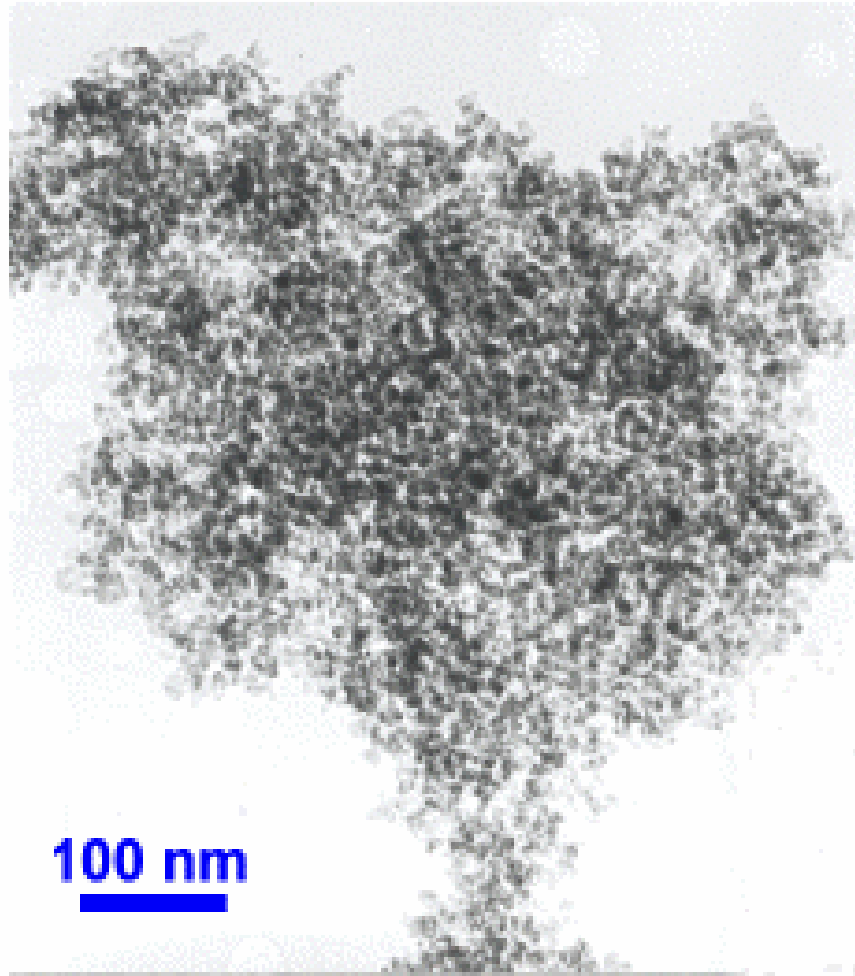


Figure 27: TEM micrograph of the SiO_2 nanoparticles [96]

Figures (28) and (29) are the SEM images of the bacteria lactobacillus GG. The size for these bacteria is expected to be approximately 0.6-1.2 μm . This value confirms with data seen in the literature. [97]

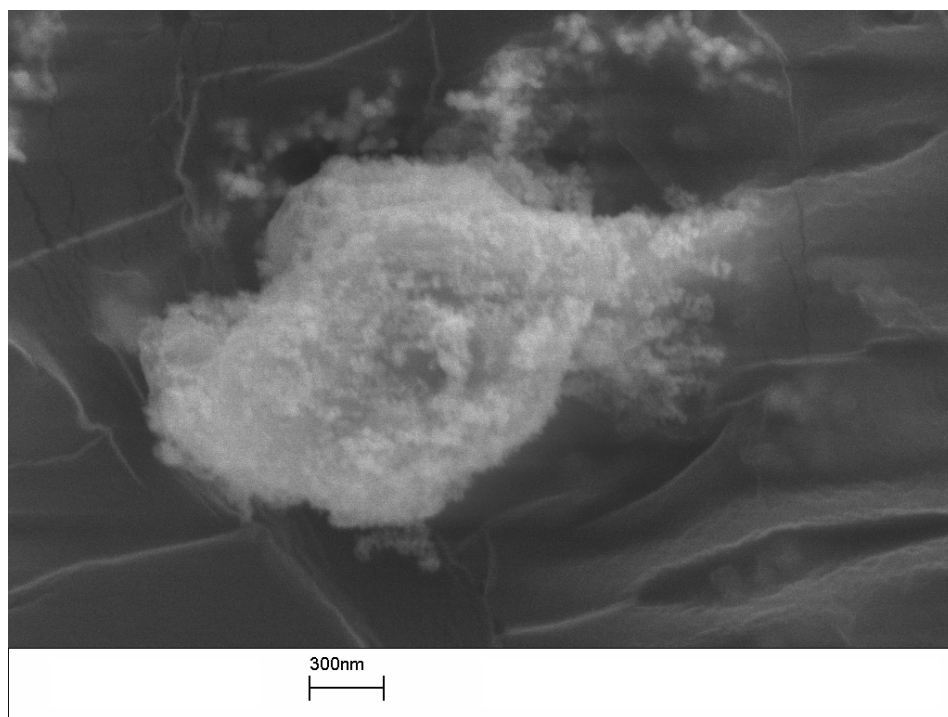


Figure 28: SEM image of LGG at 55 kX magnification

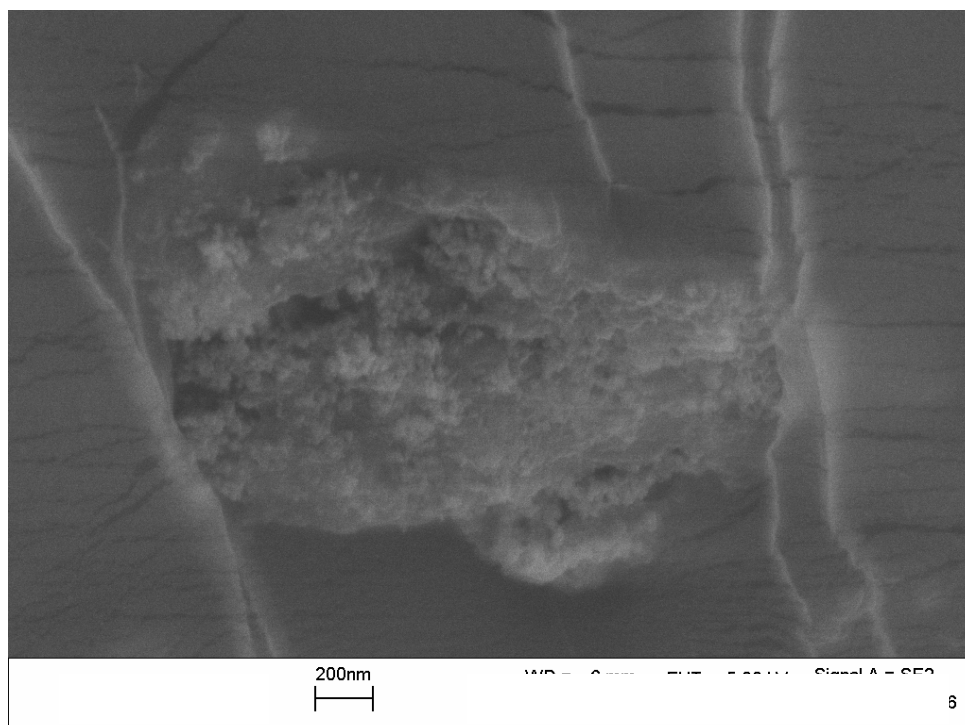


Figure 29: SEM image of LGG at 50 kX magnification

Figures (30) and (31) are the SEM images of the single celled fungi. The size for these fungus is expected to be approximately 1-2 μm .

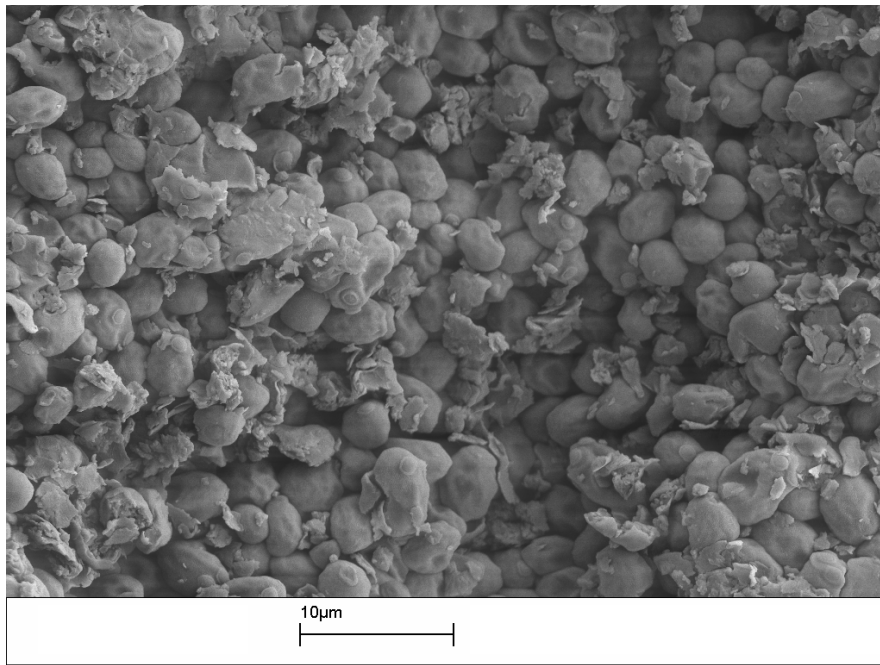


Figure 30: SEM image of single celled fungi at low magnification (6.32 kX)

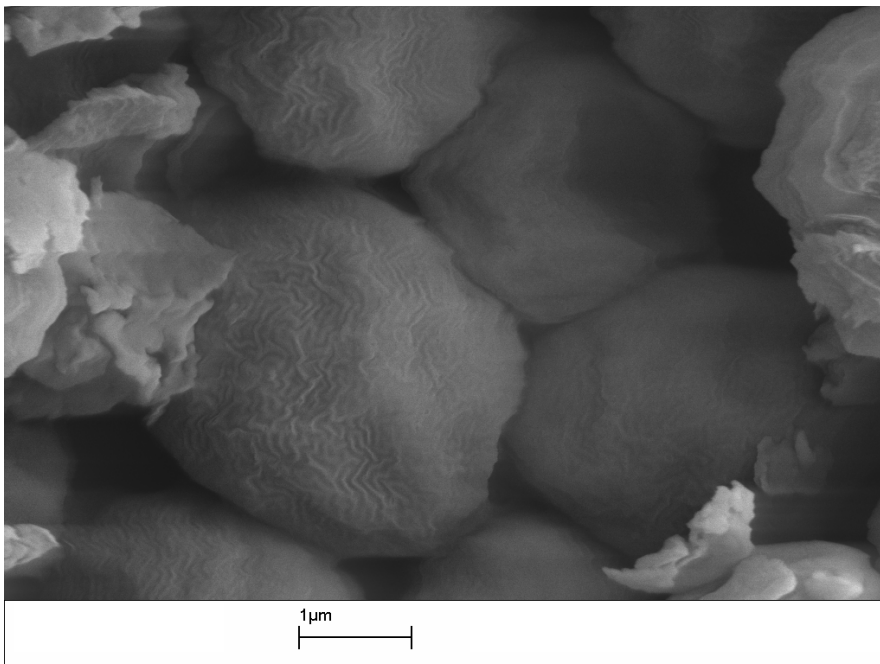


Figure 31: SEM image of single celled fungi at high magnification (46.39 kX)

Figure (32) is the electron micrographs image of the porcine circovirions. The size for these virions is expected to be approximately 17-22 nm in diameter.

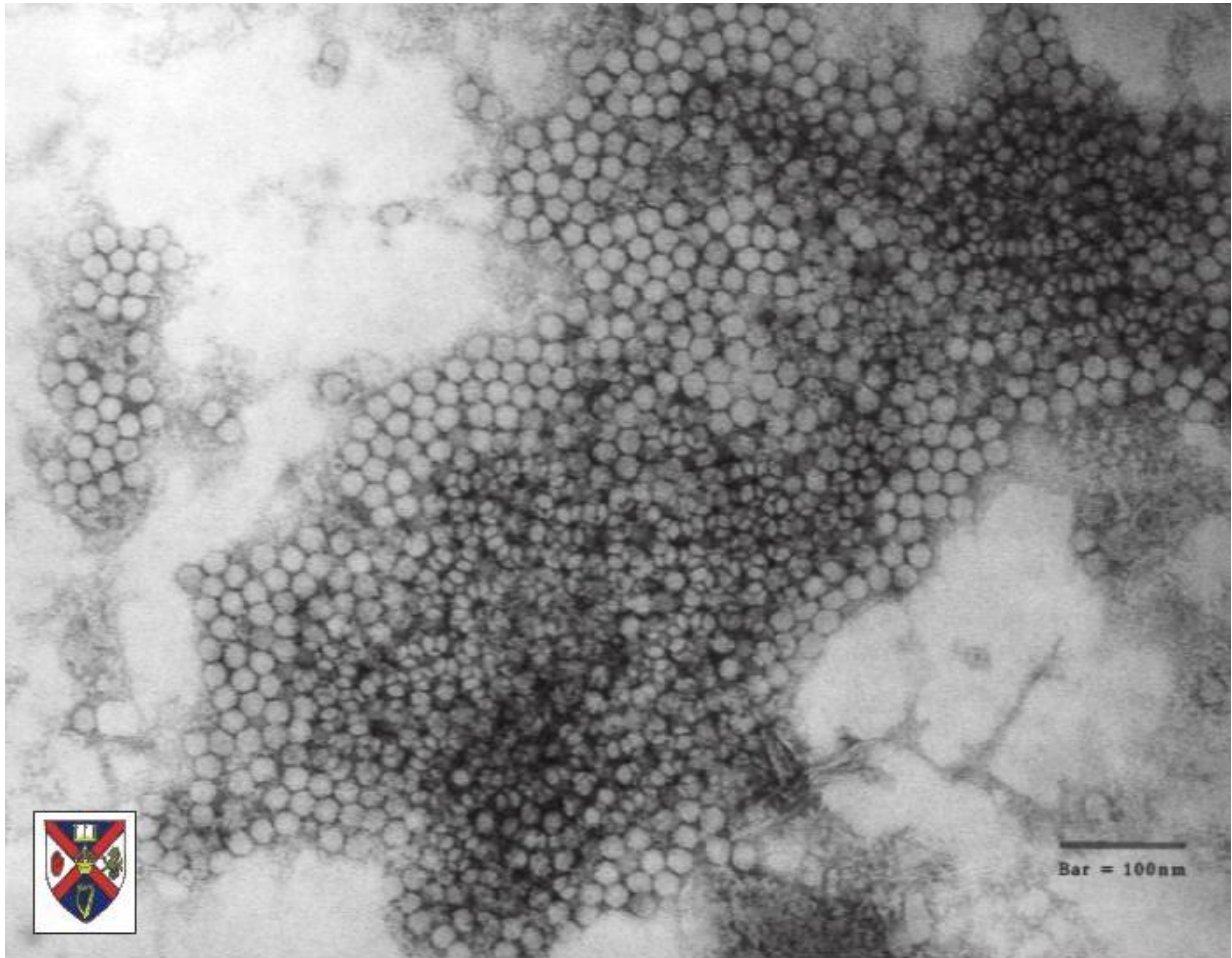


Figure 32: Porcine circovirus virions (Electron Micrographs of Animal Viruses, Veterinary Sciences, The Queen's University of Belfast, kindly provided by Prof Stewart McNulty). Copyright notice: This notice must accompany any copy of the images. The images must not be used for commercial purpose without the consent of the copyright owners. The images are not in the public domain. The images can be freely used for educational purposes.

3.1.3 Particle Size Characterization

The particle size distribution by volume for the α -SiC nanoparticles is seen in figure (33).

The majority of the particles are in the range of 45-65 nm in diameter.

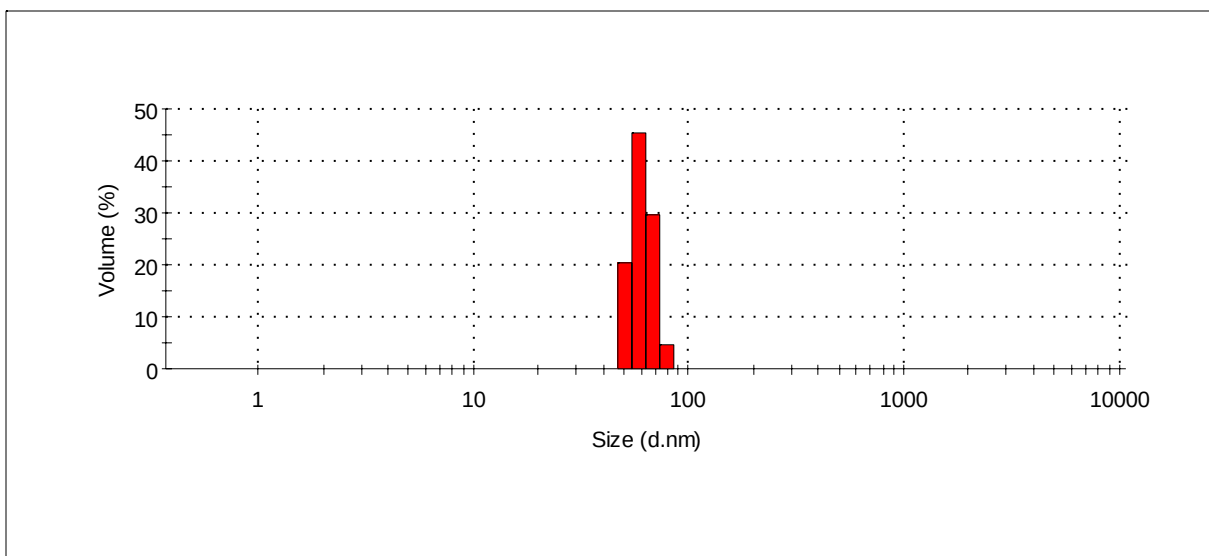


Figure 33: Particle size distribution of the α -SiC nanoparticles

3.2 Equipments and Machines

The various equipments and machines used for the experimentation highlighting their characteristics are listed in this section.

3.2.1 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) was used to probe the porosity in the material.

The images were taken using LEO 1550 field emission SEM at an accelerating voltage of 5.00 kV. The software used was LEO 32. Energy dispersive spectroscopy (EDS) was performed with an attached IXRF system, Inc Iridium Microanalysis System at an accelerating voltage of 20.00 kV. Most of the images taken are using the secondary electrons unless specified otherwise. The samples were initially sputter-coated with 15 nm of a gold-palladium alloy using the Cressington High Resolution Sputter Coater 208

HR for FE-SEM in order to reduce effects caused due to charging of the sample by providing a conducting path for the electron transfer.

3.2.2 Transmission Electron Microscope (TEM)

The transmission electron microscope used for the experimentation was the JOEL 200CX TEM with the samples on carbon grids.

3.2.3 Industrial Mixer

The mixing of the preliminary samples was performed using the Hobart mixer. Figure (34) is a digital picture of the industrial mixer.



Figure 34: Digital picture of the Hobart industrial mixer

3.2.4 Rotational Mill

The rotational mill used for the experimentation was the VS STONEWARE (S. No: 0Z03068). The machine rotational speed was controlled at 60 rpm. Due to losses in the slurry suspension and the possible destruction of the biological cells used in the slurry, no milling media was used in this process after the addition of the biological agent.

3.2.5 Ultrasonic Bath

Ultrasonic cleaner Branson 1510 was used as the ultrasonic cleaner for the experimentation. Figure (35) is a digital picture of the machine. This machine uses ultrasonic sound (sound transmitted at frequencies generally beyond the range of human



Figure 35: Digital picture of Bransonic 1510 ultrasonic bath

hearing) to facilitate breaking of the particle agglomerates in the suspension. The sound waves generated from the transducer in the machine creates high and low pressure regions in the suspension. In the low pressure stage several microscopic air bubbles are produced and this process is called as ‘cavitation’. In the high pressure case, these bubbles burst generating enormous amount of energy and these act as a scrubber for the agglomerated particles. [98]

However, on the Branson 1510 cleaner the suspensions containers cannot be placed at the bottom of the bath and hence the Cole-Parmer ultrasonic cleaner as seen in figure (36) was also used during the suspension preparation in order to break the particle agglomerates.



Figure 36: Digital picture of Cole-Parmer ultrasonic bath

3.2.6 pH Meter

The pH measurements were taken using the instrument from Denver Instruments (Model 250). The instrument was calibrated using the standard pH buffer solutions obtained from Fisher Scientific.

3.2.7 Nano Zetasizer

The particle size measurements and the suspension zeta potential was measured using the nano zetasizer ZS series from Malvern Instruments. The particle size measurements are done using a process called the Dynamic Light Scattering (DLS), also called as the Photon Correlation Spectroscopy (PCS). In this process the measurements are made of



Figure 37: Digital picture of the Malvern nano zetasizer ZS

the Brownian motion of the particles and relate it to the particle size given by the commonly known Stokes-Einstein equation. As different sized particles scatter light

differently, by comparing the intensity of light outputted from the region, the size of the particle can be determined. [99] A digital image of the nano zetasizer is seen in figure (37).

For the case of the zeta potential measurements a combination of the ‘Electrophoresis’ and ‘Laser Doppler Electrophoresis’ techniques also called the ‘Laser Doppler Electrophoresis’ (LDE) technique is used. This method helps measure the velocity of a particle motion under an applied electric field. Once these are known the zeta potential for the suspension can be determined.

The cuvettes or cells used for the particle size and zeta potential measurements are shown in figure (38).



Figure 38: Digital picture of cuvettes used for the zeta potential (left) and particle size (right) measurements

3.2.8 Viscometer

The viscometer used for the experimentation was the SV-10 Vibro Viscometer from Malvern Instruments. The digital picture of this machine is shown in figure (39).



Figure 39: Digital picture of the viscometer

3.2.9 Rheometer

The viscosity measurements were measured using the advanced rheometer, AR 300 from TA instruments with a cup and cone arrangement. The software used was the 'TA Instruments Rheology Advanced Software'. The temperature control is by a peltier heating mechanism and the machine is water cooled. The digital image of this system is

shown in figure (40). The details of the cone used for the experimentation are listed in table (14).



Figure 40: Digital picture of AR300 rheometer

Table 14: Details of the cone used for the viscosity measurements

Cone angle	2°15'
Cone diameter	40 mm
Truncation	54 μm
Material	Steel
Solvent trap	Soap water

3.2.10 Freeze Casting

The samples were freeze cast in the Labconco FreeZone[®] Stoppering Tray Dryer Freeze Dry System (model number 79480) using the lyophilization process. In the freeze drying

process the water is removed from the frozen sample by its direct conversion of frozen water into vapor without the intermediate stage of liquid water. The freeze drying sublimation process is basically a process balance between the heat absorbed by the sample to vaporize the water and the heat removed from the condenser to convert the water vapor into ice. A digital picture of the instrument is seen in figure (41).



Figure 41: Digital picture of the Labconco Freezone Stoppering Tray Dryer

3.2.11 Slip Casting

The slip casting of the samples were performed with Plaster of Paris moulds. This process is based on the capillary suction mechanism wherein the porous nature of the moulds creates a suction pressure that draws the suspension into the mould. The material to be cast is formed on the mould surface (also called as cast or cake). Due to the

shrinkage effects, once set, the sample can be removed from the mould. A schematic of the slip casting process is seen in figure (42).

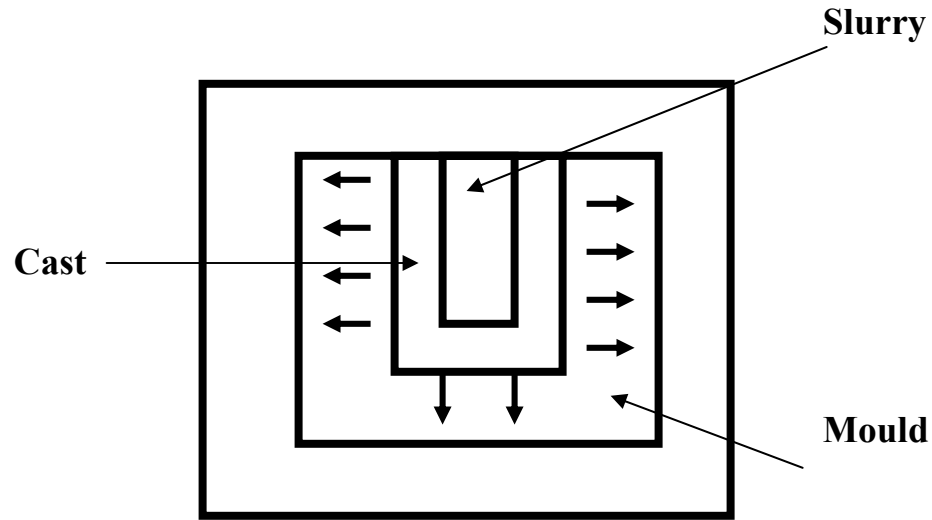


Figure 42: Schematic of the slip casting process

3.2.12 Diametric Compression Testing System

The system used for the diametric compression testing or the splitting tensile testing was the Instron 4204 compression testing machine with a 1 kN load cell attachment.

3.3 Experimental Procedure

The procedure for the experimentation and the sample preparation techniques are listed in this section.

3.3.1 Transmission Electron Microscope Sample Preparation Methodology

The procedure for preparing the biological samples to view them under the transmission electron microscope is mentioned as follows:

1. Fix cells with gluteraldehyde.
2. Spin cells in a centrifuge for five minutes at 3000 rpm to form a soft pellet.
3. Gently pull out fixative without disturbing the pellet.
4. Replace the supernatant with buffer sodium cacodylate (bacteria cannot grow).
5. Vortex sample to re-suspend the cells for 10 minutes.
6. Spin sample as in (2) and replace buffer supernatant with fresh buffer.
7. Repeat (5) through (6) three times.
8. Pull off supernatant and replace with 1% OsO₄ and vortex to re-suspend the cells for 10 min. Allow one hour fix time.
9. Spin sample again and carefully pull out the OsO₄ discarding the appropriate waste buffer.
10. Re-suspend sample in buffer sodium cacodylate for five minutes.
11. Spin down sample in centrifuge (2) and pull off as much of the buffer possible and briefly submerge the sample tube in warm (58 °C) water to warm the tube.
12. Take 2% agar and melt it in a microwave for 10-15 seconds.
13. Place the agar tube in a beaker with water preheated to 58 °C.
14. Add molten agar to the sample from (11) and quickly re-suspend them (2).
15. Sample tubes are then refrigerated for 5 minutes to solidify.
16. Add a few drops of 70% ethanol (ETOH) on top of the sample and then ream around the agar with a spatula to release the agar bullet.

17. Remove the agar to mincing dish and then dice the pelleted cells at the tip of the agar with a razor blade, placing pieces to be processed in 70% ETOH.
18. Dehydrate tissue in graded ethanol solutions increasing in concentration [70%, 95%, 100%]. Allow 15 minutes in each ETOH solution.
19. Complete dehydration by submersion in polypropylene oxide for 15 minutes.
20. Infiltrate with 50:50 solution of propylene oxide: poly/bed 812 for 20-24 hours.
21. Complete infiltration with 100% mixture of poly/bed for 10-12 hours.
22. Embed samples using freshly prepared 100% poly/bed 812 in flat embedding moulds.
23. Place moulds in 60 °C oven for at least 48 hours to cure.
24. Samples were cut 60 nm to 90 nm using a diamond knife and analyzed on the TEM.

3.3.2 Experimentation Flowchart

A flowchart explaining the experimentation procedure is shown in figure (43). The experimentation (as seen in the flowchart) can be split into four sections namely:

1. Dispersion of the particles in the solvent
2. Rheological analysis of the dispersions
3. Fabrication of the samples
4. Characterization and mechanical analysis of the samples

The specifics for each of the experiments are mentioned in chapter 4 of the dissertation.

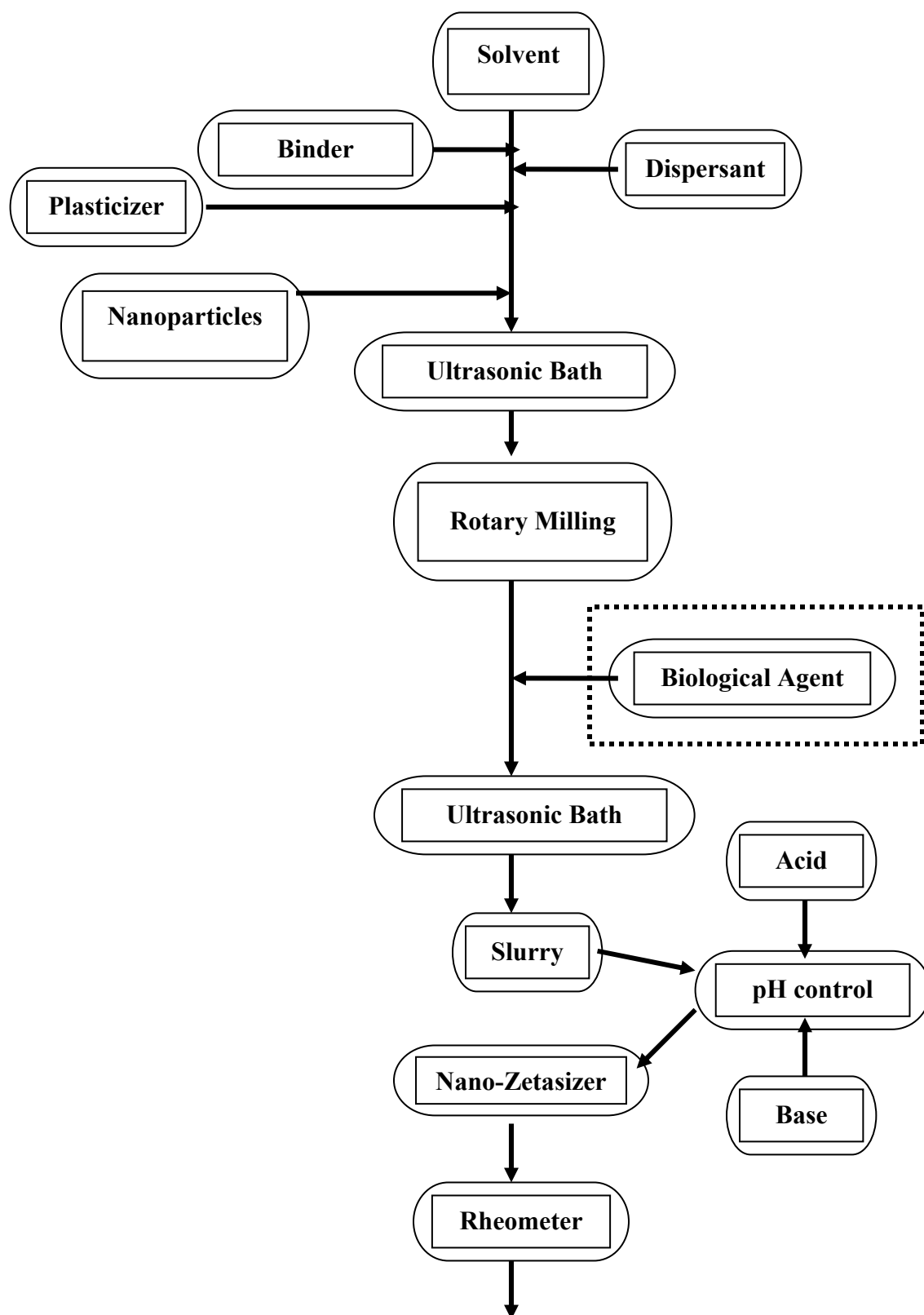


Figure 43: Flowchart of the experimentation process (continued on next page)

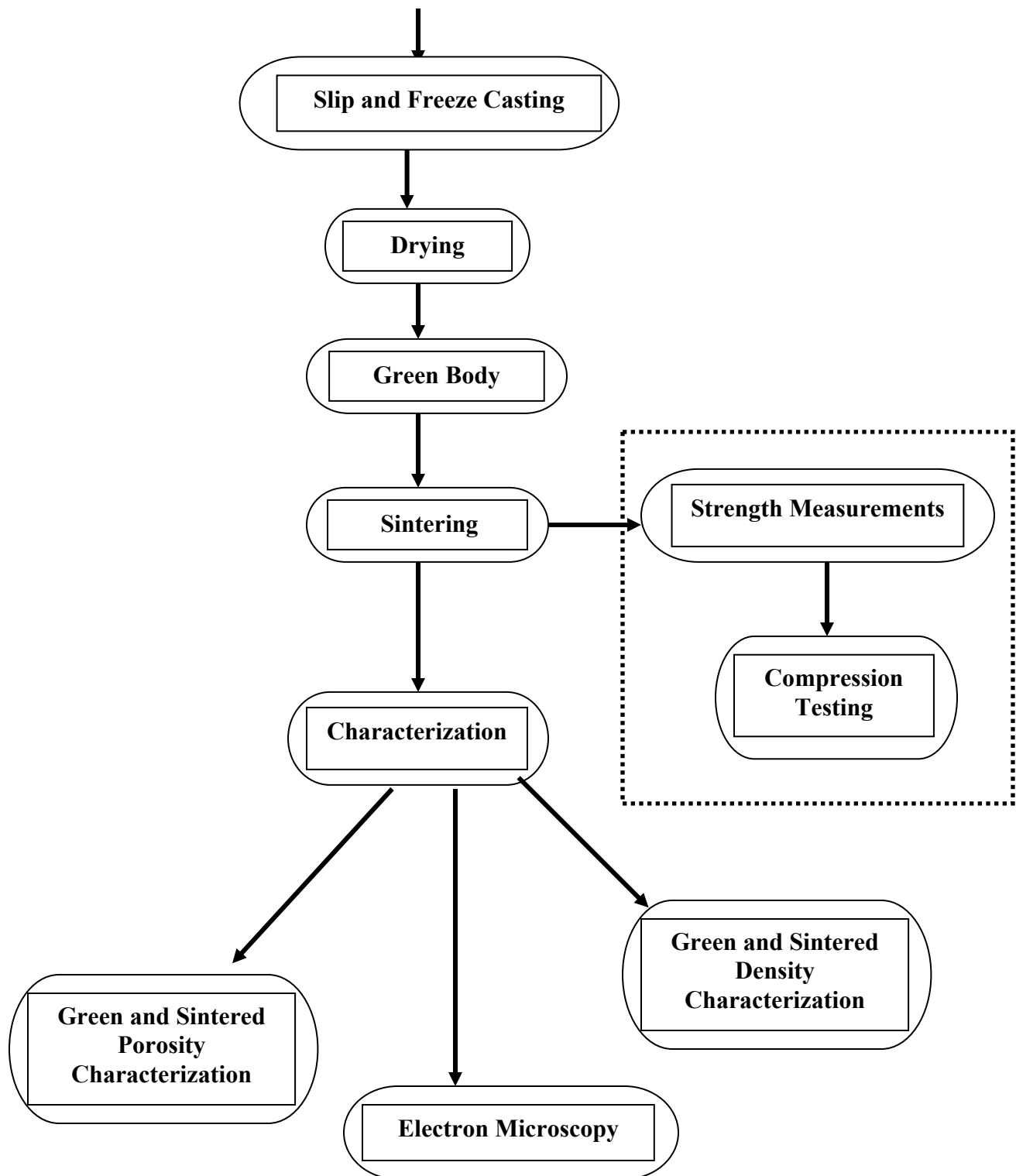


Figure 43: Flowchart of the experimentation process (continued from previous page)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 van der Waals Forces Based Mathematical Analysis for Nano-Bio Dispersions

In order to determine the mathematical relations for the nano-bio dispersions we need to consider both the polar and non polar based systems separately. In polar systems, the effects due to the electrical double layer formation and the steric repulsion required to keep the particles separated needs to be considered (which are discussed in the following sections). For non polar systems (for example: decahydronaphthalene or any iso paraffin based systems) we need to comprehend and calculate the steric hindrance necessary to keep the nanoparticles from agglomerating and a mathematical procedure to determine this is discussed in Appendix 1.

4.1.1 van der Waals Forces: Dispersion Forces for Macroscopic Bodies-Hamakar Approach for Polar Solvent Based Systems

From the discussions in chapter 2, by the summation of the pair wise interaction of the atoms in the two bodies under consideration, an expression for the energy of attraction between the bodies can be generated. [34, 37, 38] In this method however, we only have an additive effect of the individual van der Waals forces acting between the particles and do not consider the induced fields that are present. Hamakar [38] calculated the attractive potential (V') by considering an infinitely small element of matter of one body exerting an attractive potential on an infinitely small element of matter on the other body which is given by equation (36). [100]

$$V' = -\frac{c}{x^6} \rho_1 \Delta V_1 \rho_2 \Delta V_2 \quad (36)$$

where, 'C' is a constant, ' ρ_1 ' and ' ρ_2 ' are the number of molecules present in the each of the interacting bodies and ' ΔV_1 ' and ' ΔV_2 ' are the small volume elements in the two interacting bodies and 'x' is the separation distance between the two interacting volumes.

The total interaction energy or the potential energy (V_A) of the system is given by equation (37).

$$V_A = \int -\frac{c}{x^6} \rho_1 \rho_2 dV_1 dV_2 \quad (37)$$

Equation (37) according to Hamakar can be brought into the form as seen in equation (38).

$$V_A = -\frac{A}{\pi^2} \int \frac{dV_1 dV_2}{x^6} \quad (38)$$

where, 'A' is the Hamakar constant and is given by the expression in equation (39).

$$A = C\pi^2 \rho_1 \rho_2 \quad (39)$$

According to Hamakar, depending on the shape of the interacting bodies in the system, the interaction energies and the forces acting between particles are different. For

commonly seen particle interaction types, the equations are mentioned in this discussion.
[22, 37, 38, 101-104]

For the interactions between two spheres of identical diameters the interaction energy ' $W_{sph/sph}$ ' is given by equation (40).

$$W_{sph/sph} = \frac{A}{6} \left[\frac{2R^2}{H(4R+H)} + \frac{2R^2}{(2R+H)^2} + \ln \left(1 - \frac{4R^2}{(2R+H)^2} \right) \right] \quad (40)$$

where, ' R ' is the radius of the two bodies and ' H ' is the separation distance between them.

If the separation distance is large compared to the radius of the bodies (considering the bodies have different radii) equation (40) reduces to equation (41).

$$W_{sph/sph} = \frac{AR_1R_2}{6H(R_1+R_2)} \quad (41)$$

The force acting between the two bodies ' $F_{sph/sph}$ ' is given by equation (42).

$$F_{sph/sph} = \frac{AR_1R_2}{6H^2(R_1+R_2)} \quad (42)$$

In the case where the two bodies have the same radius, equation (40) reduces to equation (43).

$$W_{sph / sph} = \frac{AR}{12H} \quad (43)$$

For the interactions between two plates separated by a distance ' H ' the interaction energy ' $W_{plate / plate}$ ' is given by equation (44).

$$W_{plate / plate} = \frac{A}{12\pi H^2} \quad (44)$$

The force acting between the plates ' $F_{plate / plate}$ ' is given by equation (45).

$$F_{plate / plate} = \frac{A}{6\pi H^3} \quad (45)$$

For the interactions between a spherical body of radius ' R ' and a plate separated by a distance ' H ' the interaction energy ' $W_{sph / plate}$ ' is given by equation (46).

$$W_{sph / plate} = \frac{AR}{6H} \quad (46)$$

The force acting between the spherical body and the plate ' $F_{sph / plate}$ ' is given by equation (47).

$$F_{sph / plate} = \frac{AR}{6H^2} \quad (47)$$

For the interactions between two crossed cylinders of radius ' R_1 ' and ' R_2 ' separated by a distance ' H ' the interaction energy ' W_{cc} ' is given by equation (48).

$$W_{cc} = \frac{A\sqrt{R_1 R_2}}{6H} \quad (48)$$

The force acting between the crossed cylinders ' F_{cc} ' is given by equation (49).

$$F_{cc} = \frac{A\sqrt{R_1 R_2}}{6H^2} \quad (49)$$

For the interactions between two parallel cylinders separated by a distance ' H ' the interaction energy ' W_{pc} ' is given by equation (50).

$$W_{pc} = \frac{AL}{12\sqrt{2}} \frac{1}{H^{3/2}} \sqrt{\frac{R_1 R_2}{R_1 + R_2}} \quad (50)$$

where, ' L ' is the cylinder length.

The force acting between the two parallel cylinders ' F_{pc} ' is given by the equation (51).

$$F_{pc} = \frac{AL}{8\sqrt{2}} \frac{1}{H^{5/2}} \sqrt{\frac{R_1 R_2}{R_1 + R_2}} \quad (51)$$

In the approach used in the discussed equations, the medium separating the bodies or the particles is considered to be vacuum or air. However, in the case of microscopic bodies when we consider the interaction of an atom from one solid to the other, the intervening medium will play a major part in the analysis of the data. [22, 37, 38] In order to address

these issues, in 1956, Lifshitz [37, 38, 105, 106] suggested an alternative approach that is based on the assumption that the oscillatory and the static fields should directly affect the absorption of the electromagnetic energy of the material. He presented a method based on the interactions of the dielectric media between the materials and is given by equation (52).

$$A = C \left[\frac{\epsilon_s - \epsilon_l}{\epsilon_s + \epsilon_l} \right] \quad (52)$$

where, ‘ C ’ is the proportionality constant and ‘ ϵ_s ’ and ‘ ϵ_l ’ are the dielectric constants of the solid and the liquid respectively. [38]

This being the first attempt to look into the van der Waals attraction between macroscopic bodies was a good start however several issues could not be addressed with this approach due to the complexities arising with the measurements of the dielectric spectra for a wide range of frequencies. [37, 105, 106] Later it was found by Ninham and Parsegian, in an attempt to simplify this process mentioned, that the attraction between particles in general came from the dielectric relaxation regions. Even though the characteristic absorption frequencies are well characterized for some of the materials (for example: water), there are other materials for which this is unknown and needs to be determined. [106, 107] Hough and White suggested using the dielectric spectra in the ultraviolet (UV) and infrared (IR) regions as these were the dielectric relaxation regions that contributed most significantly to the Hamaker constant calculation. [29, 39, 108, 109]

However, the Tabor-Winterton approximation can be used to estimate the Hamakar constant for the material (A_{131}), which is a material (1) interacting with the same material in a different medium (3) using a single ultraviolet relaxation frequency and can be written as the function of the difference in the static dielectric constants, ' $\varepsilon(0)$ ' and the indices of refraction (n) in the visible region. [22, 109, 110] The Tabor-Winterton approximation equation is given by equation (53).

$$A_{131} = \frac{3kT}{4} \left(\frac{\varepsilon_1(0) - \varepsilon_3(0)}{\varepsilon_1(0) + \varepsilon_3(0)} \right)^2 + \frac{3h\omega_{uv}(n_1^2 - n_3^2)^2}{32\pi\sqrt{2}(n_1^2 + n_3^2)^{3/2}} \quad (53)$$

where, ' k ' is the Boltzmann's constant, ' T ' is the temperature and ' h ' is the Planck's constant.

The static dielectric constant with a single high absorption peak of zero bandwidth is the most common representation for the dielectric permittivity for ceramics and other insulating materials. [38] Considering the frequencies at which the absorption peaks arise are the same for the materials and we ignore the contributions due to the static dielectric constant, the approximation for the Hamakar constant (A_{132}) for the two materials (1) and (2) separated by the medium (3) is given by equation (54). [20, 111]

$$A_{132} = \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2}((n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2})} \quad (54)$$

where, ' ν_e ' is the common absorption frequency for the three materials, ' h ' is Planck's constant and the refractive indices of the three materials are ' n_1 ', ' n_2 ' and ' n_3 ' respectively.

A modified form of the equation (54) where the dielectric constants are taken into account is given by equation (55). [109, 112, 113]

$$A_{132} = \frac{3}{4} k_b T \frac{(\varepsilon_1 - \varepsilon_3)(\varepsilon_2 - \varepsilon_3)}{(\varepsilon_1 + \varepsilon_3)(\varepsilon_2 + \varepsilon_3)} + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2}((n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2})} \quad (55)$$

where, ' k_b ' is the Boltzmann's constant and ' T ' is the temperature.

The Hamakar constant combining rules for two materials namely (1) and (2), singly or together embedded or immersed in a medium (3) are given by the equations (56) to equations (61). [34, 36, 114]

$$A_{12} = \sqrt{A_{11}A_{22}} \quad (56)$$

Equation (56) is the case when the constant is being calculated between two different particles.

$$A_{131} \cong A_{313} \cong A_{11} + A_{33} - 2A_{13} \quad (57)$$

Equation (57) is the case when the Hamakar constant is being calculated between two similar particles separated by a medium.

$$A_{131} \cong (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \quad (58)$$

Equation (58) is also the case for determining the Hamakar constant between two identical particles which have a medium of separation between them.

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (59)$$

Equation (59) is the case when the constant is being calculated between two different particles that are separated by an interacting medium.

$$A_{132} \cong \sqrt{A_{131} A_{232}} \quad (60)$$

Equation (60) is the case when the Hamakar constant can be calculated between two different particles which have a medium of separation between them.

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (61)$$

Equation (61) is the case when the constant is being calculated between two different particles separated by an interacting medium.

When materials are in contact with a liquid that is highly polar (as in the case of water), the surface of the material experiences or acquires a surface charge that is caused due to the preferential adsorption of ions from the surface; the disassociation of ions from the surface of the material; the isomorphic substitution; the adsorption of polyelectrolyte or due to the accumulation of electrolytes. [24, 38] However, the preferential adsorption of ions from the surface of the material is the most common method for ceramics materials. [24, 38]

In solution, the surface charge on the material is balanced by the layer of oppositely charged ions at a distance from the surface of the material and this distance is called the Debye length and its inverse is the Debye-Huckle parameter (D_H) which is given in equation (62). [24, 66]

$$D_H = \left(\frac{2A_v q^2 Z}{\epsilon_r \epsilon_0 K_B T} \right)^{1/2} \quad (62)$$

where, ' A_v ' is the Avogadro number, ' q ' is the electron charge, ' Z ' is the counter ion valency, ' K_B ' is the Boltzmann constant, ' T ' is the temperature, ' ϵ_r ' is the relative dielectric constant of the medium and ' ϵ_0 ' is the permittivity of free space.

The Debye length (D_L) is given by the inverse of equation (62) as seen in equation (63).

$$D_L = \frac{1}{D_H} \quad (63)$$

The Debye length is related to the surface charge density (G_C) of a surface to the electrostatic surface potential or the stern potential (ψ) via the Grahame equation as seen in equation (64). [24, 26, 115]

$$G_C = (8\varepsilon_r\varepsilon_0 A_V ZK_B T)^{1/2} \sinh\left(\frac{Zq\psi}{2K_B T}\right) \quad (64)$$

The electrostatic force (E_{SF}) as a function of the separation distance of the particles is given by equation (65).

$$E_{SF} = \pi \left(\frac{2G_{C1}G_{C2}}{\varepsilon_r\varepsilon_0 D_H} \right) \exp(-D_H H) \quad (65)$$

where, ' H ' is the separation distance between the particles.

The van der Waals force per unit radius (V_R) from equation (43) is given by equation (66).

$$V_R = \frac{A}{12H} \quad (66)$$

In order to obtain well dispersed α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar systems we need to calculate the forces that are acting on the particles in the system, and balance the forces, so that the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems do not aggregate. For simplifying the

mathematical and theoretical calculations for dispersing the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems in a polar solvent, let us make the following assumptions: [a] the van der Waals forces acting between the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems are attractive in nature, [b] the α -SiC and LGG particles are perfectly spherical in shape [c] the biological agent (LGG) shape does not change with applied shear and external parameters.

The van der Waals forces are the main forces for coagulation of nanoparticles in a non polar solvent, where only steric repulsion is present. [116] In a polar solvent the van der Waals force needs to be balanced by the double layer repulsion (and steric hindrance-if necessary) to have a dispersed slurry. Hence in the systems of the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems, an appropriate balance [V_T] between the van der Waals attractive force [V_A], steric repulsive forces [V_R] and electrostatic force [V_E] are needed to disperse the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems in a polar solvent as seen in equation (67).

$$V_T = V_A + V_R + V_E \quad (67)$$

Thus, when the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems come close together, the attractive van der Waals forces become significant and this is the major component for causing particle agglomeration in the system. However, if we balance this attractive force [V_A] with a

steric barrier [V_R] and the electrostatic force [V_E] as shown in equation (67), a stable suspension should result. [44, 117]

A schematic of the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems being separated by a electro-steric barrier potential is shown in figure (44) and figure (45) respectively. When the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems are covered with the adsorbed polymer layer and approach each other there is the interaction between the adsorbed polymer layers. Due to this inter-

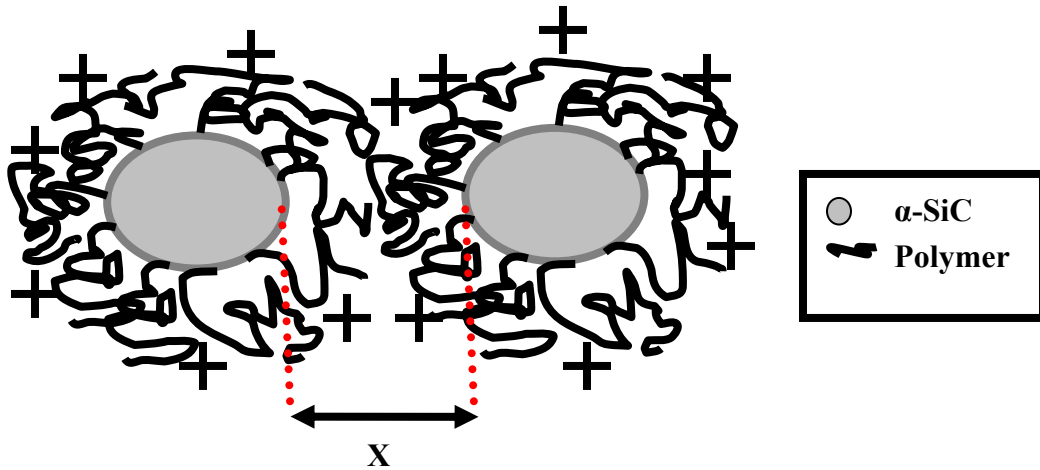


Figure 44: Sketch showing two α -SiC nanoparticles being separated by a electro-steric barrier potential in the α -SiC/H₂O/ α -SiC polar solvent based systems

penetration of their polymer layers, a repulsive force is produced (steric stabilization) [116]. When this happens a balance between the repulsive and attractive forces will result and some optimum separation distance will be achieved. As shown in figure (44) and figure (45), if we keep the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems at a distance of 'X' and 'Y'

from each other respectively, then the system is balanced with respect to the criteria mentioned above.

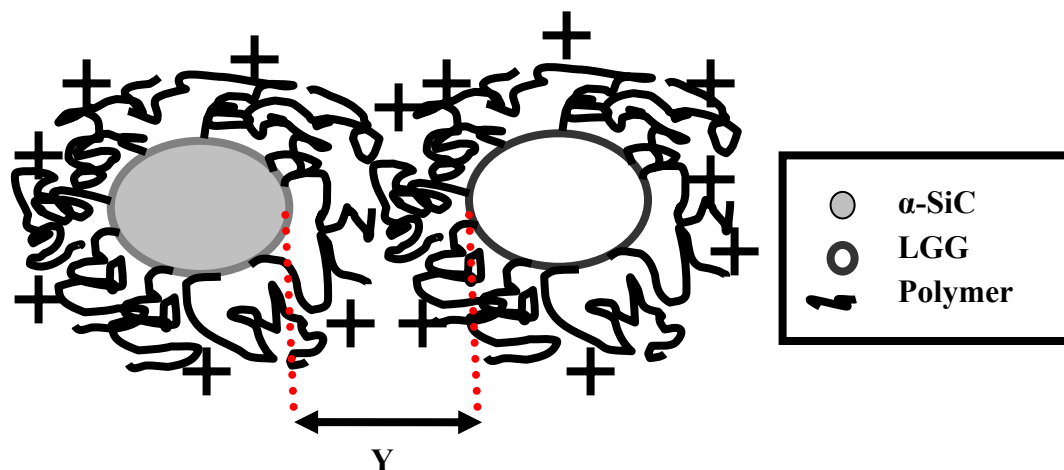


Figure 45: Sketch showing the α -SiC and LGG particles being separated by a electro-steric barrier potential in the α -SiC/H₂O/LGG polar solvent based systems

For steric stabilization of a colloidal suspension the following criteria need to be met: (a) the polymer should firmly adhere to the surface of the particle, (b) the stabilization moieties should have a good solvent condition, (c) the adsorbed dispersant should be thick enough to overcome the attractive van der Waals forces, and (d) the polymer must cover the particle completely. [116] However, the attractive van der Waals forces are difficult to quantitatively measure with any surface force technique [116], since the forces increase by orders of magnitude close to the surface. This causes a jump in the measuring probe and no data can be collected. Hence, it is useful to mathematically calculate the force balance as discussed in the sections earlier.

Since the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems are assumed to be spherical in shape, by

using their radius values in equation (43) we can calculate the attractive van der Waals interaction energy between the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems. The Hamaker constants for a α -SiC (1)/H₂O(2)/ α -SiC(1) system and the α -SiC(1)/H₂O(2)/LGG(3) systems (A_{131}) and (A_{132}) respectively can be obtained from the Tabor-Winterton approximation as shown in equation (53) and (55). [118, 119]

This is the first time a biological material has been used in such a system to develop the Hamakar constant.

However, if the radius of the particles is greater than the separation distance between the particle surfaces, the expression in equation (40) can be reduced to the commonly used form represented as seen in equation (43). [120]

Using equation (43), we can predict the variation of van der Waals separation distance between the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system and α -SiC and LGG nanoparticles in the α -SiC/H₂O/LGG systems. An inverse function curve will result when plotting equation (43), since the van der Waals interaction varies inversely with separation distance. From this curve, we can approximately determine the minimum distance ($2r$) to keep the particles separated which will be the point on the curve the attraction becomes significant. Using this knowledge we can determine the molecular weight of the dispersant selected for experimentation based on similarities in solubility parameters of the solvent and the dispersant. [119] Since the dispersant consists of

repeated monomer units, calculating segment lengths between atoms by incorporating the radius of gyration equation as seen in equation (68), with ' r ' being half the minimum van der Waals distance calculated earlier, we can determine the appropriate order of magnitude for the molecular weight of the dispersant that can be used for experimentation. [38, 119, 121]

$$r^2 = cnl^2 \quad (68)$$

where ' l ' is the segment length, ' c ' is a constant [~ 5] and ' n ' is the number of segments.

From these figures and the equations described in the earlier section we can obtain the appropriate molecular weights of the dispersants needed to obtain a well dispersed slurry as mentioned in the earlier section. The balance of the van der Waals forces with a combination of the steric barrier and the electrostatic forces is the governing condition to keep the particles dispersed in the medium.

The calculated values for the force balance in the α -SiC/H₂O/ α -SiC and the α -SiC/H₂O/LGG polar based systems are presented and discussed in the following sections.

4.1.2 van der Waals Forces Based Analysis for α -SiC/H₂O/ α -SiC Polar Solvent Based Dispersions

Based on the analysis discussed in the previous section, the force balance curves for the α -SiC/H₂O/ α -SiC polar based systems are discussed in this section. The Hamaker constant (A_{131}) for the system based on the refractive indices values and dielectric

constants for the α -SiC nanoparticles in the polar solvent was taken to be 1.9×10^{-19} J. [122] Since the values for the Hamakar constants for the α -SiC/H₂O/ α -SiC system were available in the literature the Tabor-Winterton Approximation as described in equation (53) was not used for the calculation. The calculated variation of the electrostatic part of the DLVO interaction energy with respect to the approaching α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system at the IEP are plotted in figure (46).

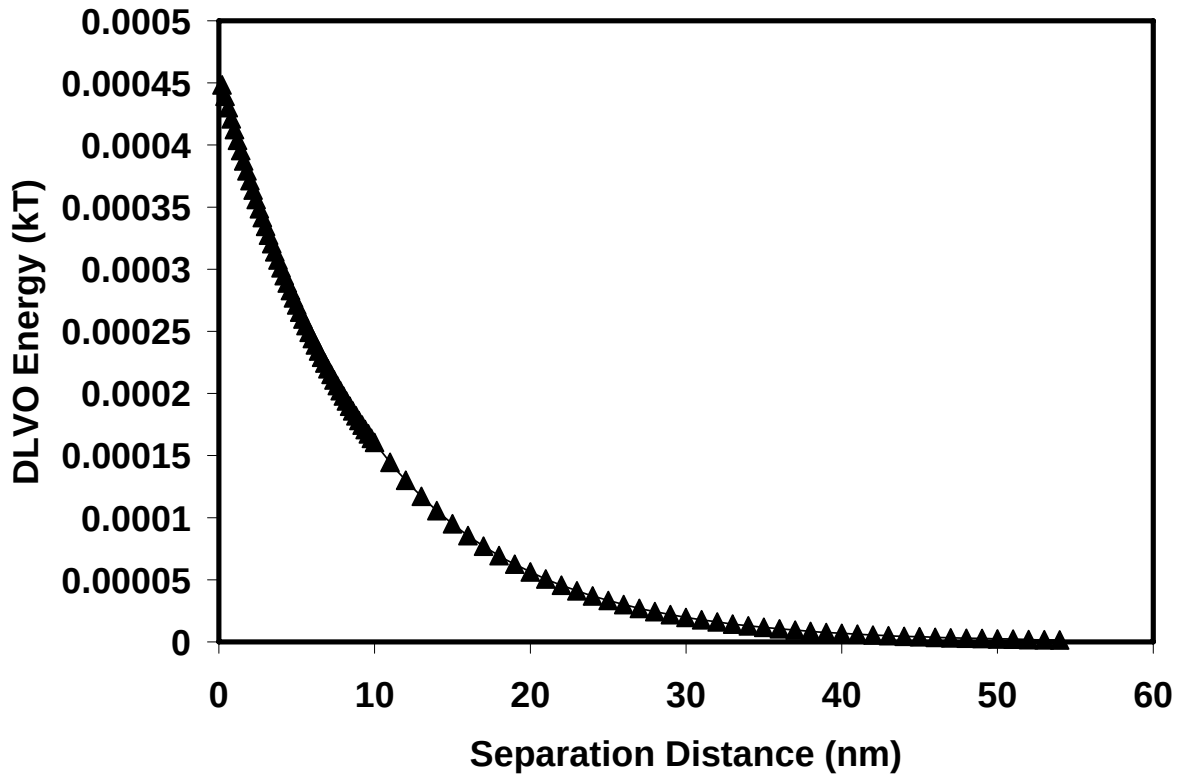


Figure 46: Calculated repulsive electrostatic interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at the IEP

From figure (46) it can be seen that in the absence of the van der Waals forces and the steric hinderance the electrostatic interaction energy tends to keep the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system separated due to the electric double layer formation around the particles. The calculated variation of the van der Waals part of the

DLVO interaction energy with respect to the approaching α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system at the IEP are plotted in figure (47).

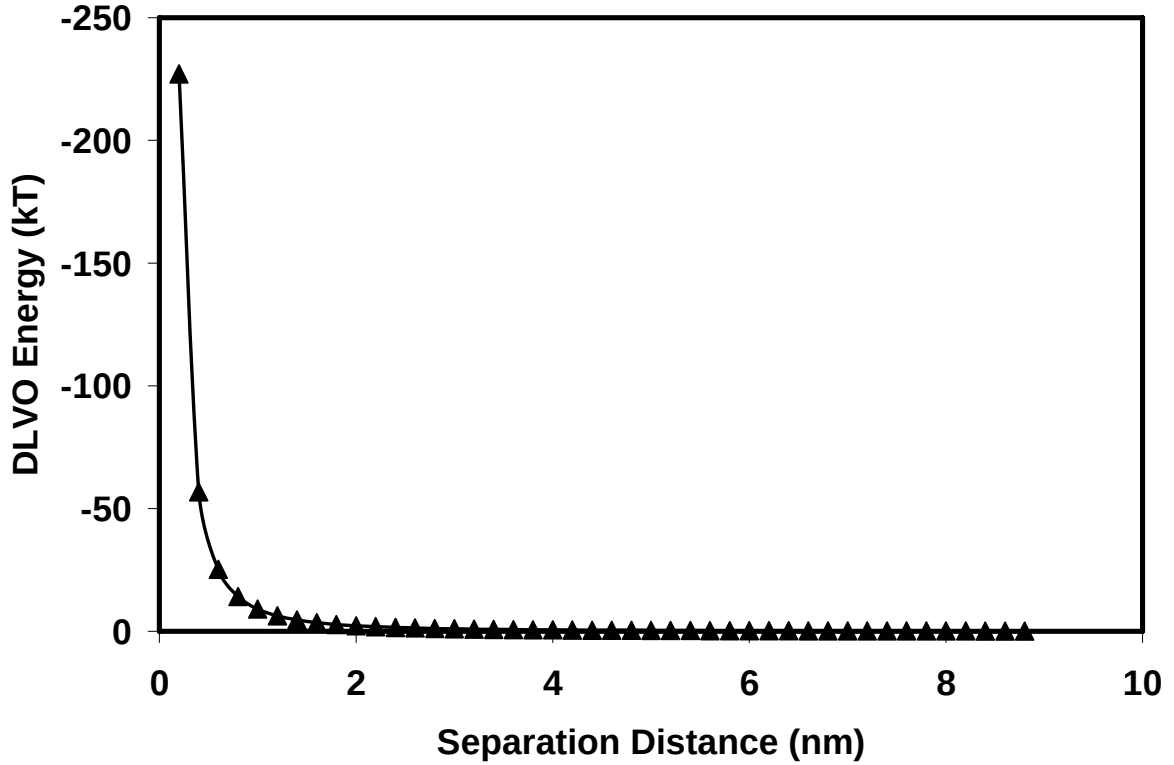


Figure 47: Calculated attractive van der Waals interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at the IEP

From figure (47) it can be seen that in the absence of the electrostatic and other surface forces including the steric hindrance the van der waals interaction energy tends to keep the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system agglomerated due to the strong attractive behavior. Hence, in order to determine the balance between the van der waals and the electrostatic interaction energies for the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system, the calculated variation of the total DLVO interaction energy with respect to the approaching α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system at the IEP are

plotted in figure (48). An expanded graph for this interaction energy variation with respect to the nanoparticle separation distance is seen in figure (49).

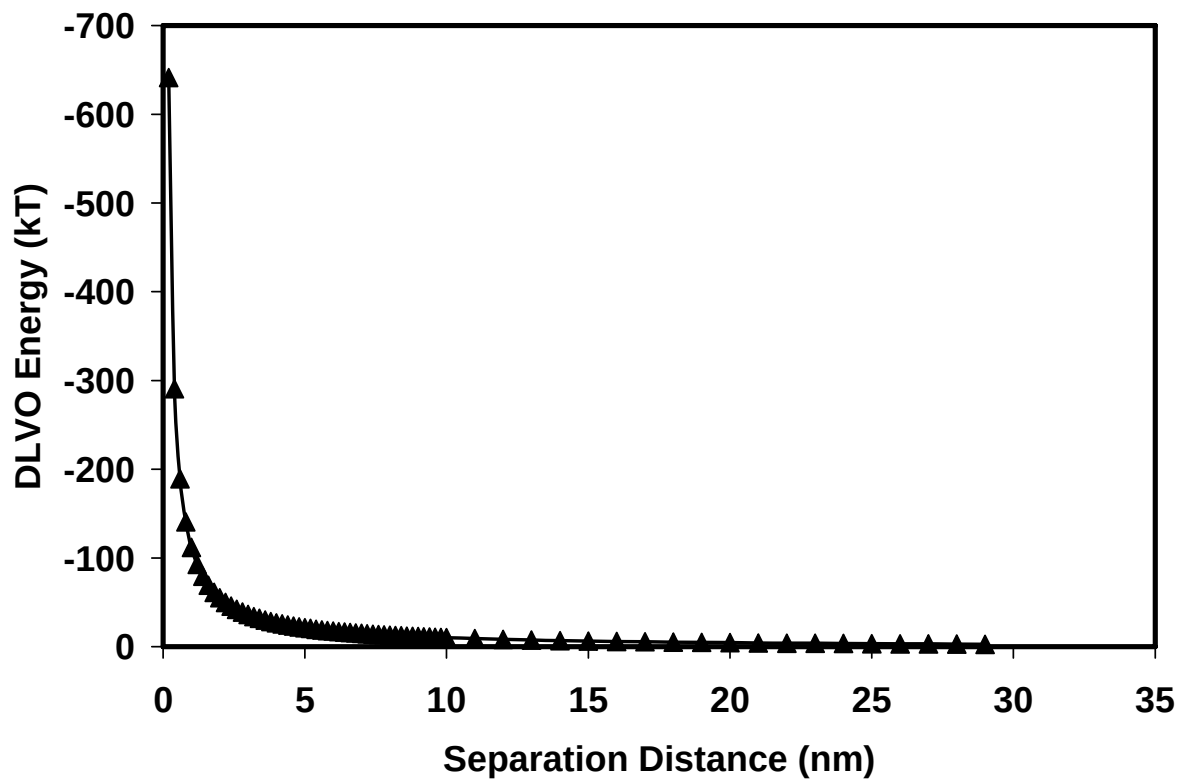


Figure 48: Calculated total interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at the IEP

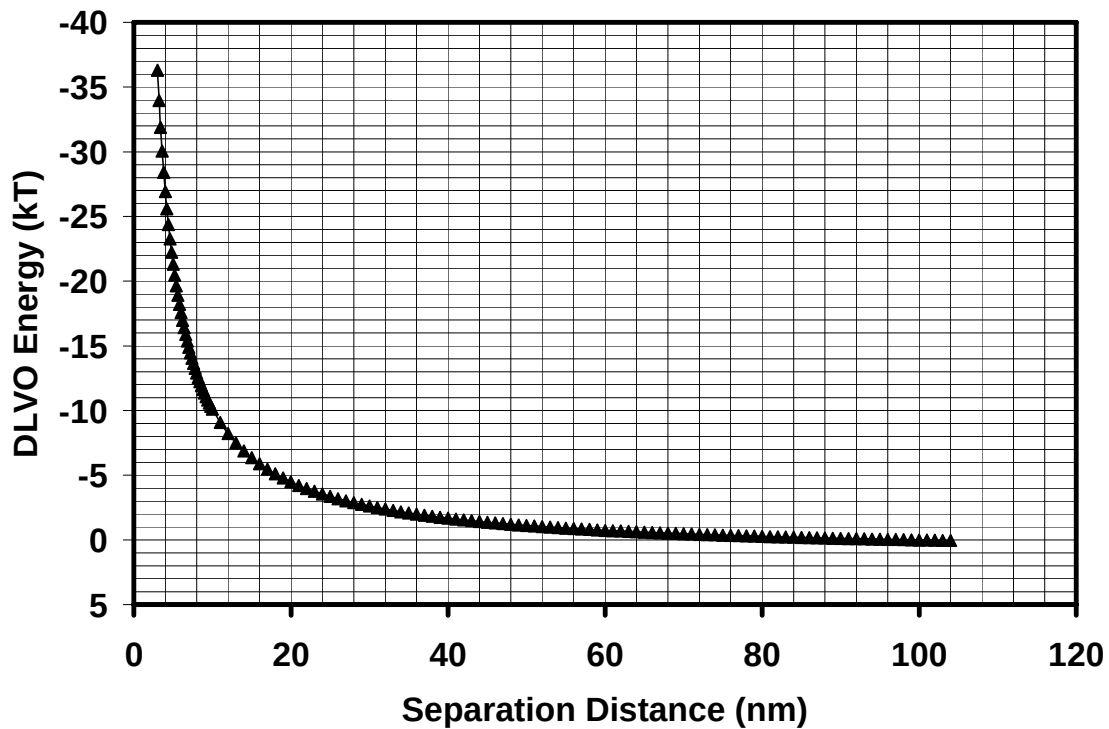


Figure 49: Expanded view of the calculated data for the total interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at the IEP from figure (48)

From figure (48) and figure (49) it can be seen that in the absence of a steric barrier potential the van der Waals interaction energy is strong enough to overcome the electrostatic interaction potential and tends to keep the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system agglomerated due to their strong attractive behavior. Hence, in order to determine the balance between the van der Waals and the electrostatic interaction energies for the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system, a steric barrier is needed to create the necessary repulsion to keep the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system from agglomerating. From figure (49) it can be seen that the increase in the van der Waals interaction energy starts at the particle separation distance of about 26 nm (the case with DLVO energy as 3 kT). This means that if we can create a

steric barrier that can keep the particles separated at 26 nm we could avoid the coagulation of the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system caused to the strong attractive van der Waals interaction potential. Based on the solubility parameters from the solubility parameter handbook and the literature reference and using equation (68), the approximate molecular weight of the poly acrylic acid dispersant to be used to create the necessary steric hindrance for the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system is calculated. [22, 38, 123] From the calculations the average molecular weights required for the poly acrylic acid were in the order of 10^5 . The solubility tests were conducted and they showed concurrence to the mathematical calculations with the dispersant being soluble in the polar solvent. Hence, PAA-A was used as the dispersant to disperse α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system. The calculated variation of the electrostatic part of the DLVO interaction energy with respect to the approaching α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system at a zeta potential value of 20 mV is plotted in figure (50). 20 mV was selected as this is the case for most ceramic systems to be dispersed.

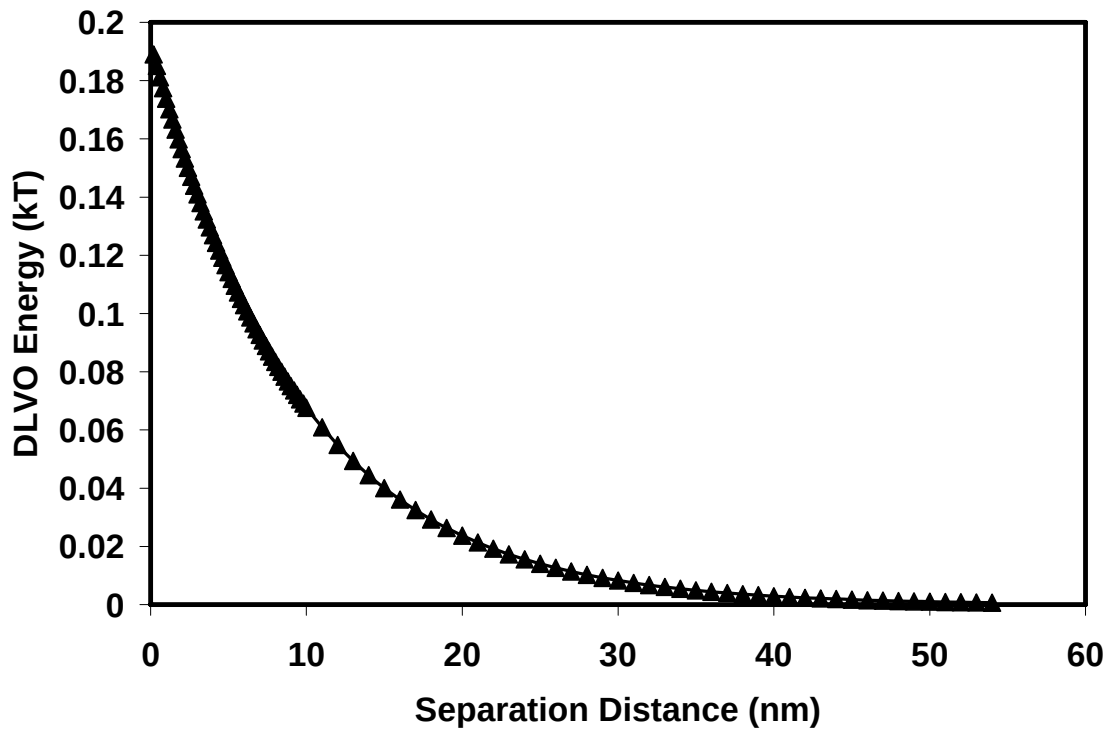


Figure 50: Calculated repulsive electrostatic interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at 20 mV

Due to the electric double layer formation around the particles, from figure (50) it can be seen that in the absence of the van der Waals forces and the steric hindrance the electrostatic interaction energy tends to keep the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system separated. The calculated graph showing the variation of the van der Waals part of the DLVO interaction energy with respect to the approaching α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system at the zeta potential value of 20 mV are plotted in figure (51).

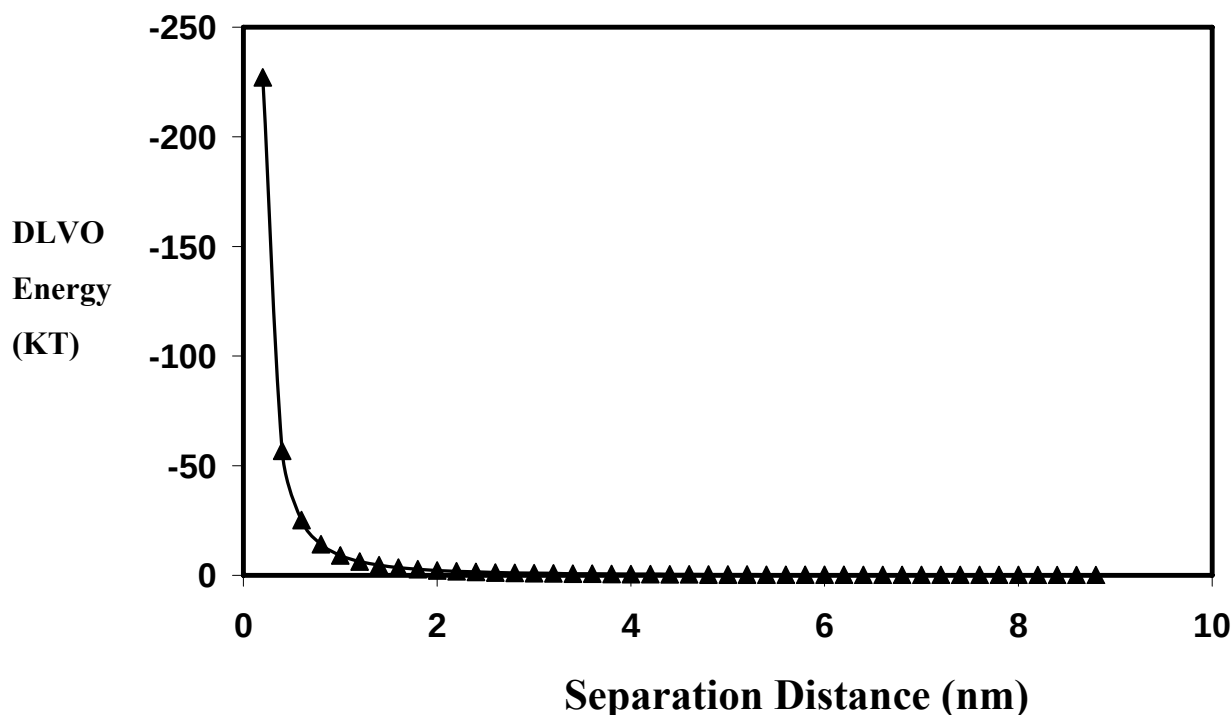


Figure 51: Calculated attractive van der Waals interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at 20 mV

Due to the strong attractive van der Waals forces, from figure (51) it can be seen that in the absence of the electrostatic and other surface forces including the steric hindrance the van der Waals interaction energy tends to keep the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system agglomerated. Therefore, to determine the balance between the van der Waals and the electrostatic interaction energies for the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system, the calculated variation of the total DLVO interaction energy with respect to the approaching α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system at a zeta potential value of 20 mV are plotted in figure (52). The expanded version of this

interaction energy variation graph with respect to the nanoparticle separation distance is seen in figure (53).

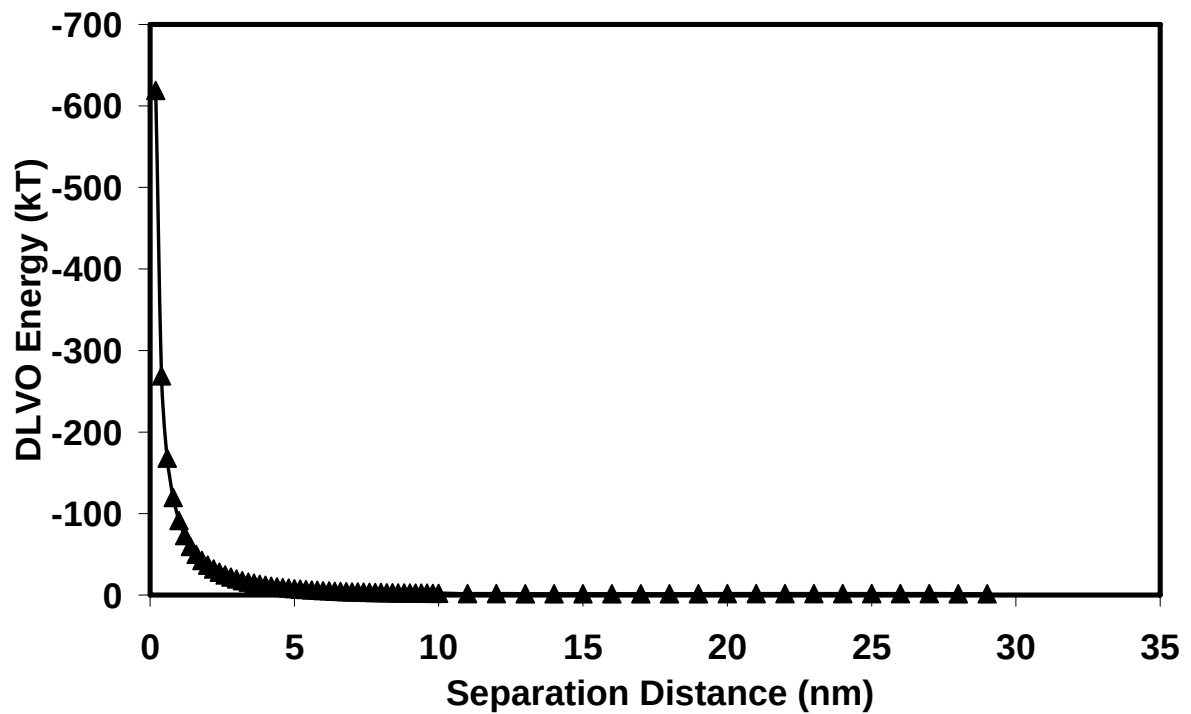


Figure 52: Calculated total interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at 20 mV

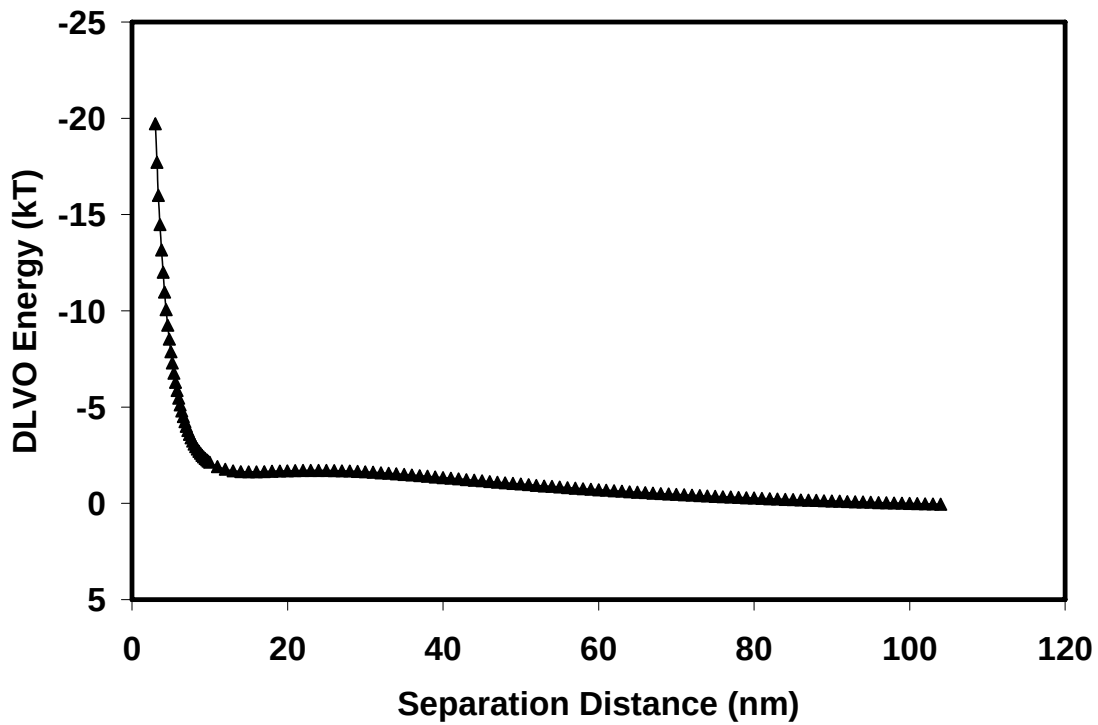


Figure 53: Expanded view of the calculated total interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at 20 mV from figure (52)

In the absence of a steric barrier potential, as seen in figure (52) and figure (53), the van der Waals interaction energy overcomes the electrostatic interaction potential and tends to agglomerate the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system. Therefore the balance between the van der Waals and the electrostatic interaction energies for the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system, a steric barrier is necessary to create the required repulsion to keep α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system from agglomerating. From figures (48), (49), (50) and (51) it is also seen that with an increment in the value of the zeta potential the electric double layer interactions becomes significant and hence the steric barrier necessary to create the repulsion between the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system is lowered. The variation of total

DLVO interaction energy (calculated) with respect to the approaching α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC system at a zeta potential value of 40 mV are plotted in figure (54), which is in agreement with the discussion presented earlier.

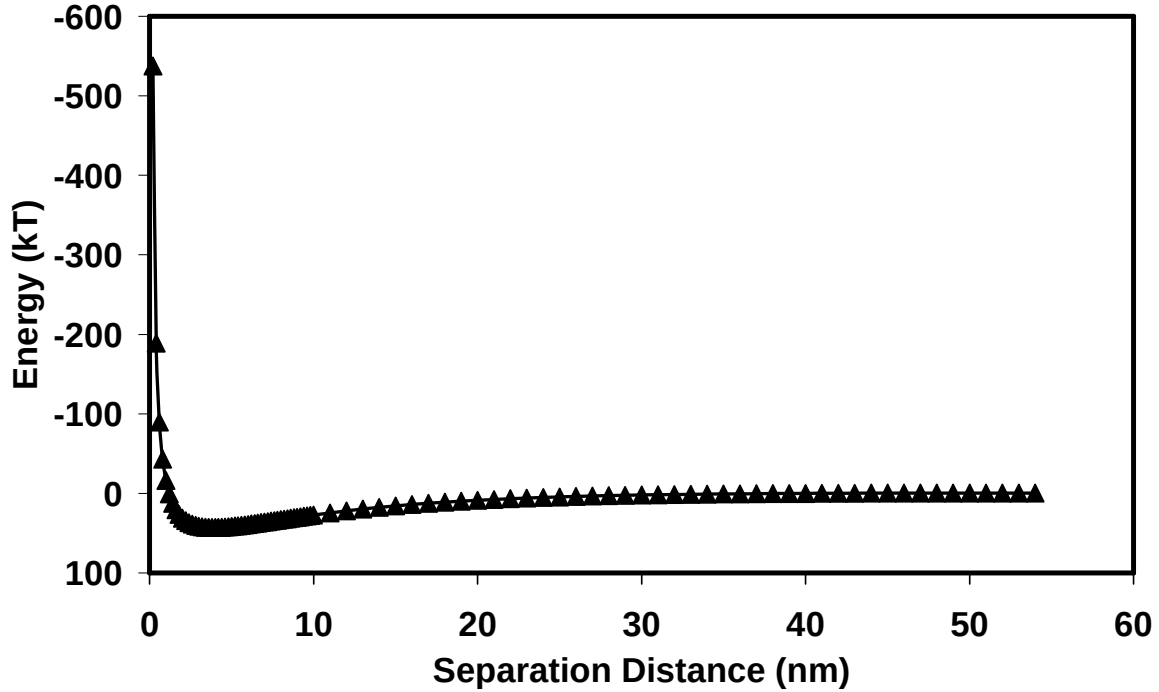


Figure 54: Calculated total interaction potential energy variation with particle separation distance for α -SiC/H₂O/ α -SiC based dispersions at 298 K at 40 mV

4.1.3 van der Waals Forces Based Analysis for α -SiC/H₂O/LGG Polar Solvent Based Dispersions

The force balance curves for the α -SiC/H₂O/LGG polar based systems using the analysis discussed in the previous section is presented here. The Hamaker constant (A_{132}) for the system based on the refractive index values and dielectric constants for the α -SiC and LGG particles in the polar solvent was calculated to be 0.27×10^{-21} J. However, the values for the Hamaker constants for the α -SiC/ α -SiC, LGG/LGG and H₂O/H₂O systems were

available in the literature, incorporating these values and by using equations (59) and (61) the Hamakar constant for the α -SiC/H₂O/LGG polar based system was calculated. The Tabor-Winterton Approximation as described in equation (55) was not used for the calculation. The calculated variation of the electrostatic part of the DLVO interaction energy with respect to the approaching α -SiC and LGG particles in the α -SiC/H₂O/ α -SiC system at the IEP are plotted in figure (55).

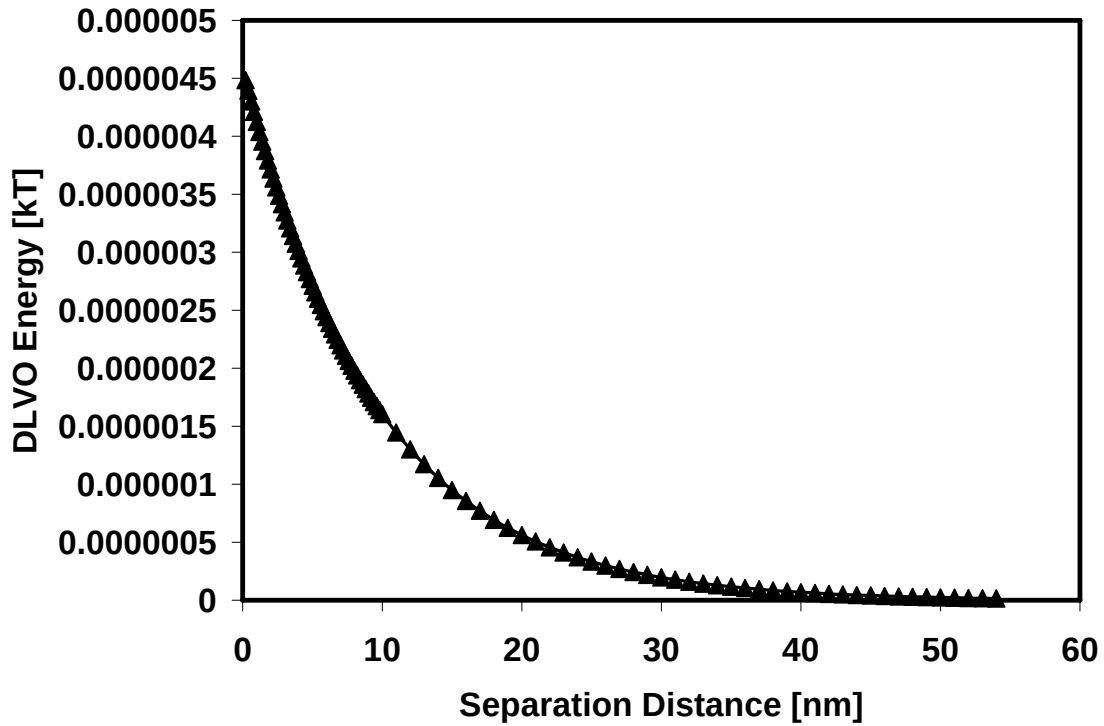


Figure 55: Calculated repulsive electrostatic interaction potential energy variation with particle separation distance for α -SiC/H₂O/LGG based dispersions at 298 K at the IEP

It is seen from figure (55) that the electrostatic interaction energy tends to keep the α -SiC and LGG particles in the α -SiC/H₂O/LGG system separated due to the electric double layer formation around the particles in the absence of the van der Waals forces and the steric hindrance . In figure (56) the calculated variation of the van der Waals part of the

DLVO interaction energy with respect to the approaching α -SiC and LGG particles in the α -SiC/H₂O/LGG system at the IEP are plotted.

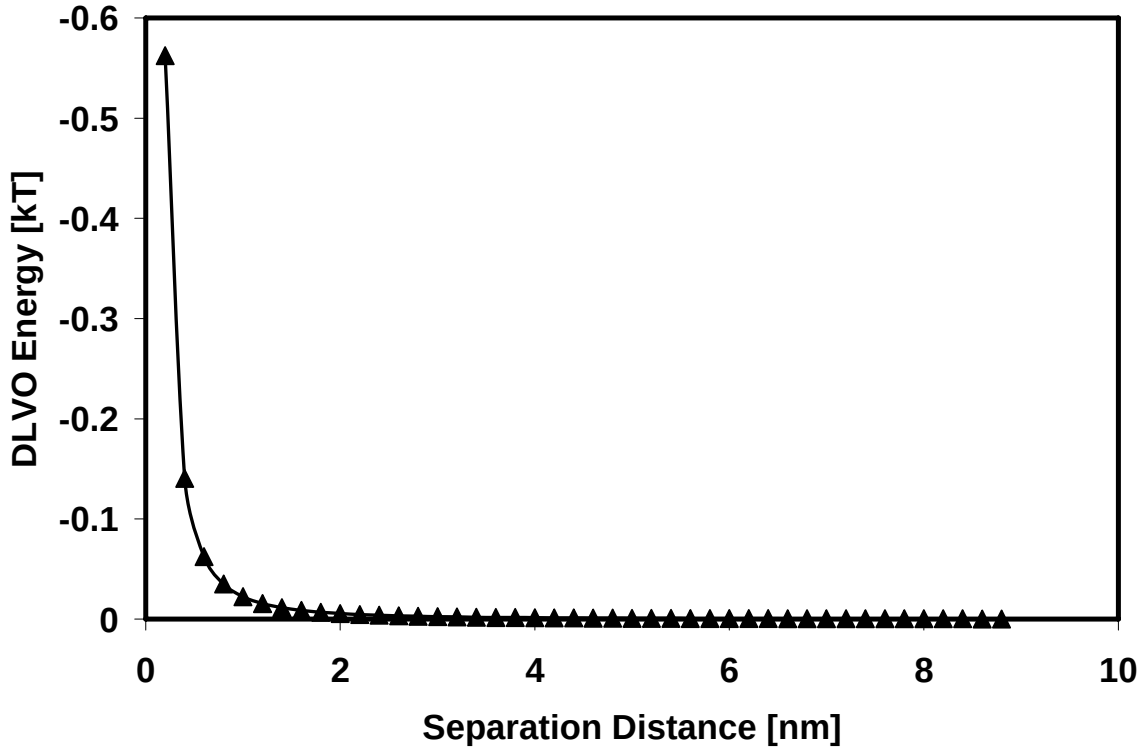


Figure 56: Calculated attractive interaction potential energy variation with particle separation distance for α -SiC/H₂O/LGG based dispersions at 298 K at the IEP

In the absence of the electrostatic and other surface forces including the steric hindrance, the van der Waals interaction energy tends to keep the α -SiC and LGG particles in the α -SiC/H₂O/LGG system agglomerated due to their strong attractive behavior as seen in figure (56). Therefore, to determine the balance between the van der Waals and the electrostatic interaction energies for the α -SiC and LGG particles in the α -SiC/H₂O/LGG system, the calculated variation of the total DLVO interaction energy with respect to the approaching α -SiC and LGG particles in the α -SiC/H₂O/LGG system at the IEP are plotted in figure (57).

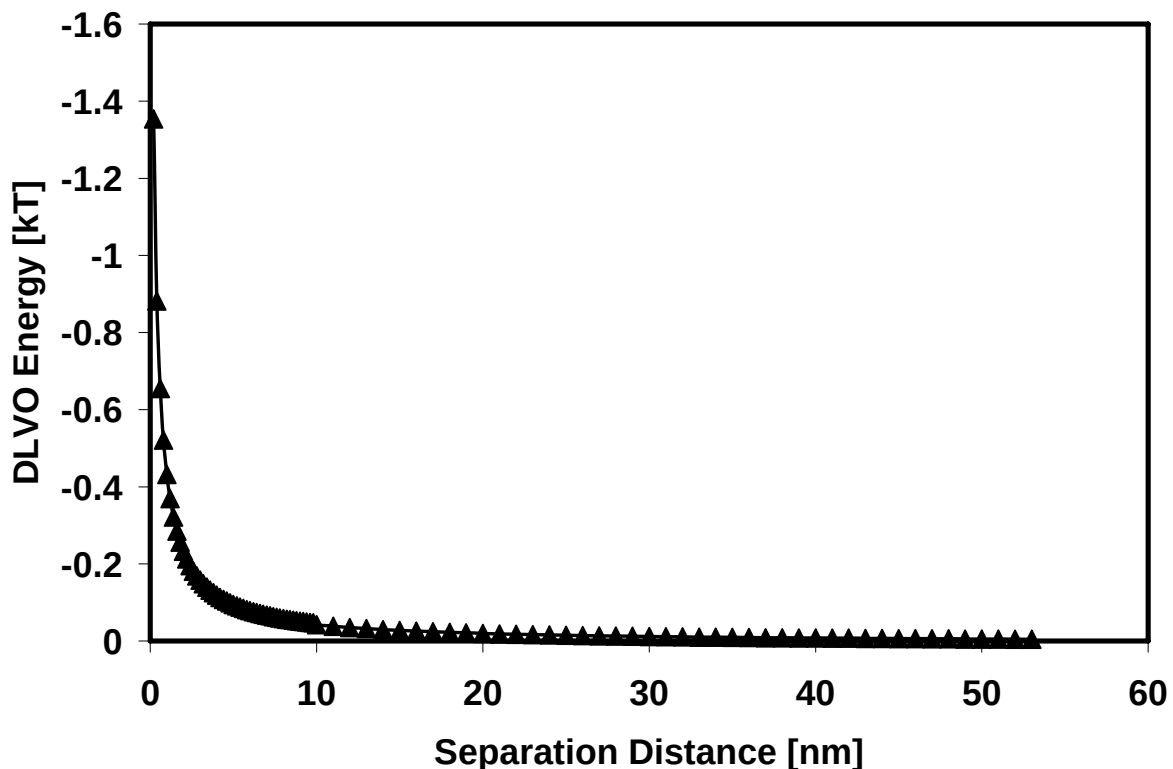


Figure 57: Calculated total interaction potential energy variation with particle separation distance for α -SiC/H₂O/LGG based dispersions at 298 K at the IEP

In the absence of a steric barrier potential, the van der Waals interaction energy is strong enough to overcome the electrostatic interaction potential and tends to keep the α -SiC and LGG particles in the α -SiC/H₂O/ α -SiC system agglomerated due to their strong attractive behavior as seen in figure (56) and figure (57). Therefore, to determine the balance between the van der Waals and the electrostatic interaction energies for the α -SiC and LGG particles in the α -SiC/H₂O/LGG system we need to create a steric barrier so as to generate the necessary repulsion to keep the α -SiC and LGG particles in the α -SiC/H₂O/ α -SiC system from agglomerating. The van der Waals interaction energy starts to increase at the particle separation distance of about 10 nm as seen in figure (57).

Therefore, a steric barrier potential generated that can keep the particles separated at 10

nm would potentially avoid the coagulation of the α -SiC and LGG particles in the α -SiC/H₂O/LGG system caused by the strong attractive van der Waals interaction potential. Determining and comparing the solubility parameters from the solubility parameter handbook, utilizing the literature reference and using equation (68), the calculations were done to determine the approximate molecular weight of the poly acrylic acid dispersant to be used to create the necessary steric hindrance for the α -SiC and LGG particles in the α -SiC/H₂O/LGG system. [22, 38, 123] The average molecular weights calculated for the poly acrylic acid in this system were in the order of 10^3 . Solubility tests conducted showed agreement to the mathematical analysis with the dispersant being soluble in the polar solvent. Therefore the dispersant used to disperse α -SiC and LGG particles was PAA-B.

4.1.4 Comparison of the van der Waals forces for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Polar Solvent Based Dispersions

From the mathematical calculations and the discussions in the previous sections it is seen that there is a difference in the order of the magnitude for the Hamaker constants for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar solvent based dispersions. It can also be seen that the α -SiC/H₂O/LGG systems are more repulsive than the α -SiC/H₂O/ α -SiC systems at the same zeta potential. The experimental analysis of this data is presented in the later sections of the chapter.

4.2 Rheology of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Polar Solvent Based Dispersions

In order to understand the rheological properties of the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar solvent based dispersions it is important to clearly understand the parameters that govern the dispersions including the shear stress, shear rate, viscosity and zeta potential. In this section, the results from the experimental rheological analysis carried out for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar solvent based dispersions are presented and discussed. It must be noted that in the figures the error in measurement has been incorporated by the size of the dot marker used

4.2.1 Determination of the Optimum Amount of Poly Acrylic Acid for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Polar Dispersions

Measured amounts of H₂O and PAA-A (in the case of α -SiC/H₂O/ α -SiC suspensions) and PAA-B (in the case of α -SiC/H₂O/LGG suspensions) are taken in a beaker and placed on a hot stirrer till the polymer dissolves in the solvent. This is followed by the addition of the α -SiC nanoparticles and the slurry is placed on the rotating mill for 24 hours at an rpm of 60 with alumina milling media. For one set of samples, LGG is added after this period. Once added the samples are placed once again on the rotating mill for another 24 hours with an rpm of 60. For the samples with LGG no milling media are added in the process. This is followed by placing the samples on the Cole-Parmer ultrasonic bath for 6 hours followed by placing them on the Branson ultrasonic bath for 30 minutes. The desired suspension is thus prepared and the viscosity measurements are carried out. For

the viscosity measurements the temperature for the shear flow measurements is set to 298 K. The slurry is pre-sheared at 800 s^{-1} and allowed to rest for 60 seconds before the rheological analysis is recorded. The measurements are carried out from a shear rate of 0.001 to 1000 s^{-1} . The relative viscosity of the slurry is calculated as the ratio of the slurry viscosity to that of the solvent (in this case H_2O) at the same temperature. The viscosity of water is calculated using the equation (69). [68, 124]

$$\eta_{\text{water}} = 0.0017 - (4.73 * 10^{-5}) T + (7.45 * 10^{-7}) T^2 - (6.25 * 10^{-9}) T^3 + (2.13 * 10^{-11}) T^4 \quad (69)$$

4.2.1.1 α -SiC/ H_2O / α -SiC Based Polar Dispersions

For the α -SiC/ H_2O / α -SiC based polar dispersions the rheological data obtained is presented in this section. In order to keep the α -SiC nanoparticles in the α -SiC/ H_2O / α -SiC system well dispersed, it is essential for the polymer to coat the particles well so that the steric hindrance effect produced will be sufficient to overcome the van der Waals forces of attraction between the α -SiC nanoparticles. In this regard the amount of dispersant added into the suspension should be sufficient to cover the α -SiC nanoparticles completely. Based on the rheological variations (particularly the viscosity) of the suspensions with various amounts of dispersants, the optimum amount of the weight of the dispersant needed for preparing well dispersed suspensions can be determined. Figure (58) is the variation of the viscosity of the suspension with respect to the amount of PAA-A added to the α -SiC/ H_2O / α -SiC based polar dispersion system.

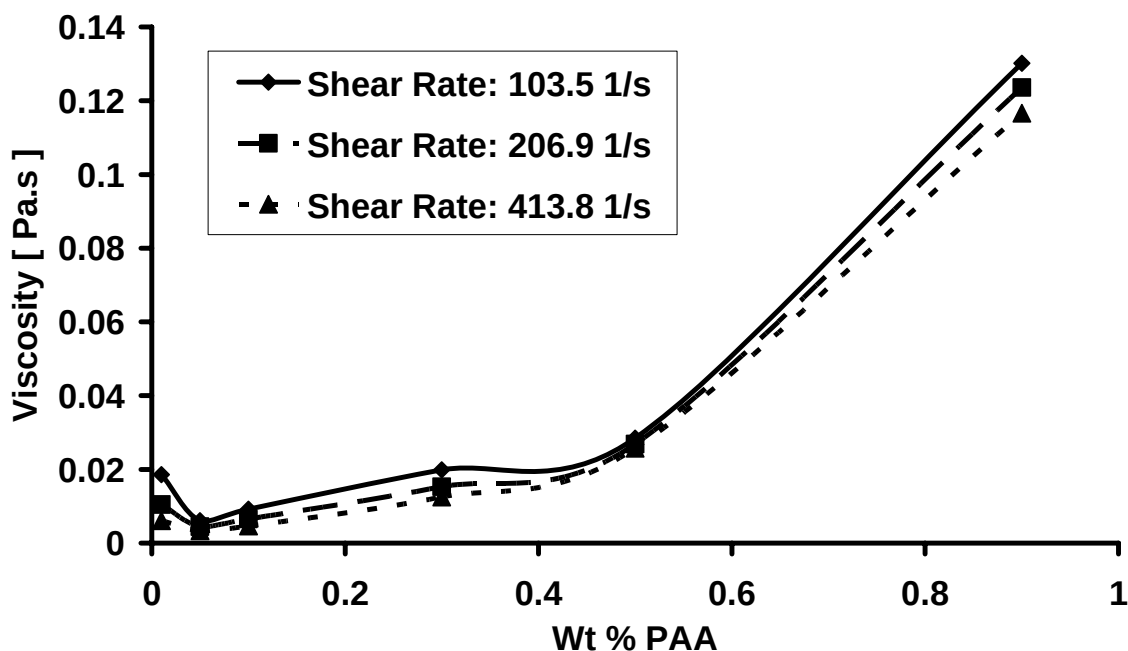


Figure 58: Experimentally determined variation of the viscosity with respect to the wt% PAA-A for the α -SiC/H₂O/ α -SiC based polar dispersion system at different shear rates

The amount of the PAA-A added to the α -SiC/H₂O/ α -SiC based polar dispersions system must be just enough so that it covers the α -SiC nanoparticle surface completely. In the case of excess amount of PAA-A in the system, it may increase the viscosity of the system due to depletion flocculation. However, if less than the required amount is added, the repulsive steric barrier potential is not strong enough to overcome the strong van der Waals forces of attraction for the α -SiC/H₂O/ α -SiC based polar dispersions system. Upon the addition of the optimum amount of the PAA-A into the α -SiC/H₂O/ α -SiC based polar dispersion system, the repulsive barrier potential is high enough to overcome the attractive potential and hence a stable α -SiC/H₂O/ α -SiC based polar dispersion is obtained. [22, 38, 65, 125] The optimum amount of PAA-A necessary to completely cover the α -SiC nanoparticle surface in the α -SiC/H₂O/ α -SiC based polar dispersions

system is the lowest point on the graph plotted between the weight percent of dispersant and viscosity as from the figure (58) is taken to be 0.1 wt%. Figure (59) is the variation of the zeta potential of the suspension with respect to the amount of PAA-A added to the α -SiC/H₂O/ α -SiC based polar dispersion system.

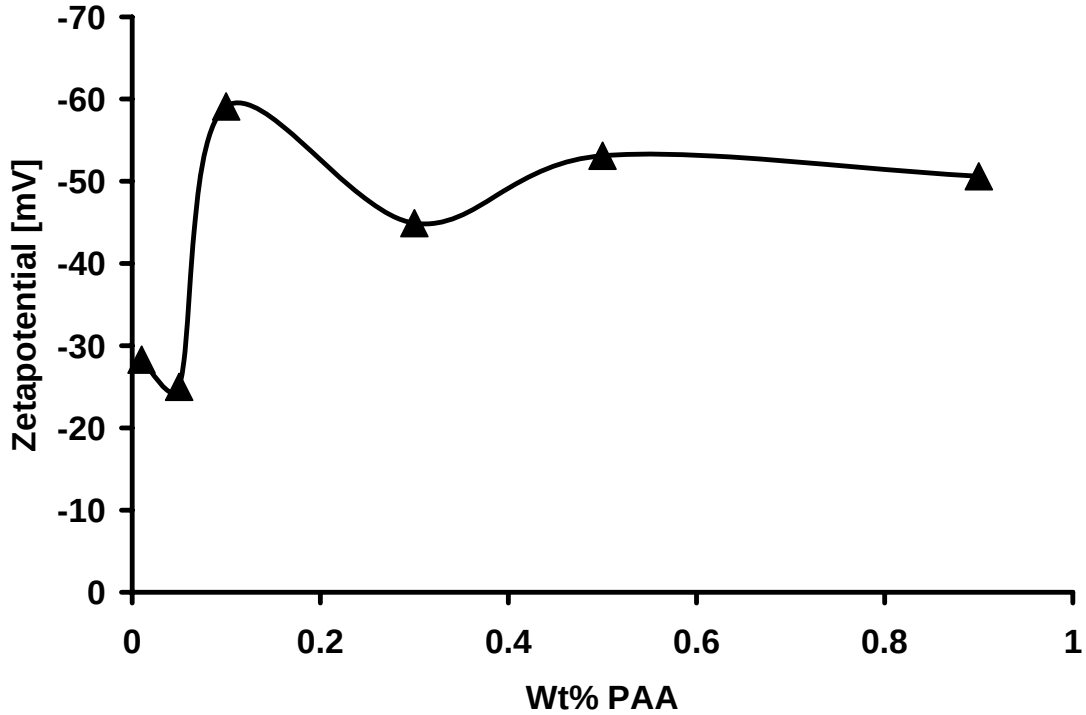


Figure 59: Experimentally determined variation of the zeta potential with respect to the wt% PAA-A for the α -SiC/H₂O/ α -SiC based polar dispersion system

From figure (59) it can be seen that the data obtained is in agreement with the data from figure (58) and the discussion mentioned earlier. It can be seen that at the optimum weight percent of PAA-A the α -SiC/H₂O/ α -SiC based polar dispersion system has the highest zeta potential value signifying the formation of a well dispersed suspension system. But at other amounts of the additions of PAA-A into the α -SiC/H₂O/ α -SiC based polar dispersion system the zeta potential values for the system are lower, signifying that

the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC based polar dispersion system is not well dispersed. Figure (60) and figure (61) show the experimentally determined variation of the shear stress with respect to shear rate and the viscosity with respect to shear rate for the various amounts of PAA-A added to the α -SiC/H₂O/ α -SiC based polar dispersion system.

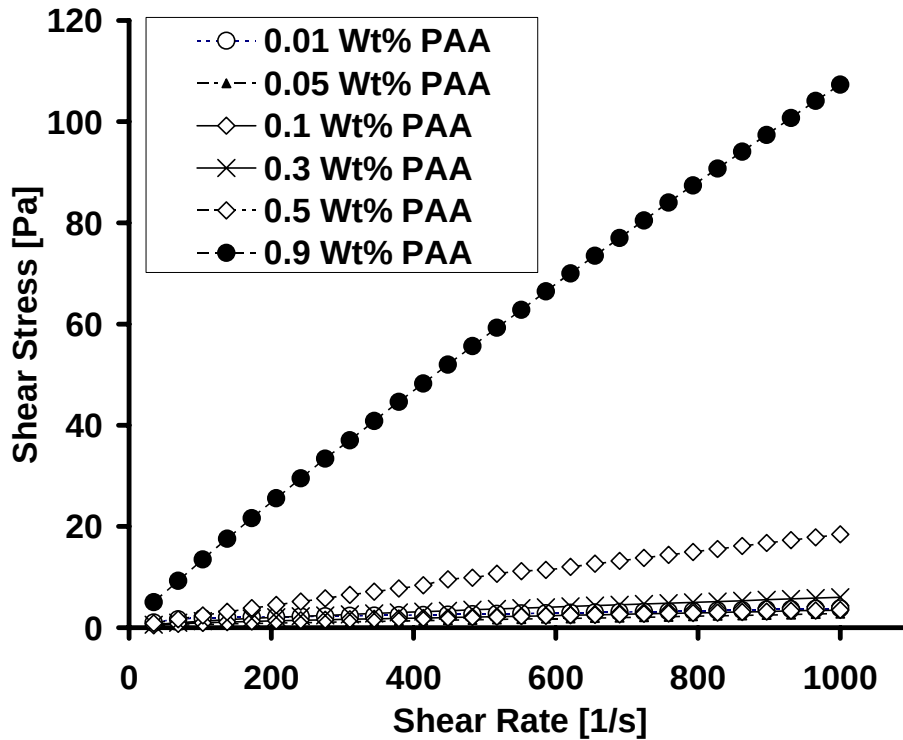


Figure 60: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system with different PAA-A amounts

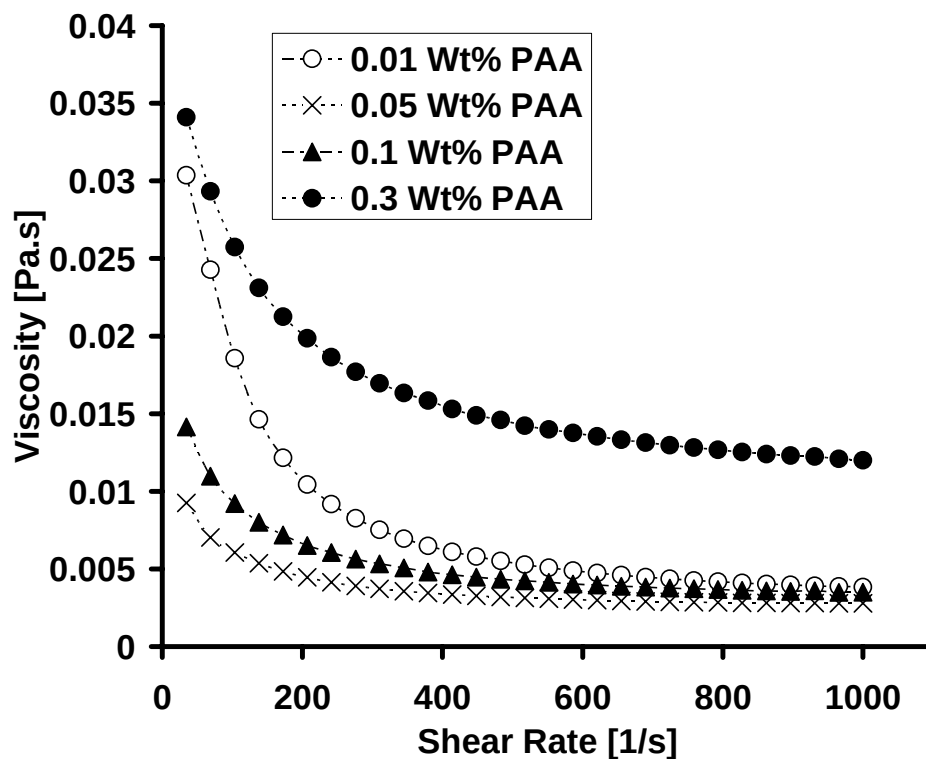


Figure 61: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system with different PAA-A amounts

From figure (60) and figure (61) it can be seen that the α -SiC/H₂O/ α -SiC based polar dispersions system with different PAA-A amounts show a shear thinning behavior which means that the viscosities of this system depend on the shear rate being applied on the system. It can also be seen that with small additions in the amount of PAA-A into the α -SiC/H₂O/ α -SiC based polar dispersions systems there is a decrease in the viscosity of the suspensions until an optimum value is reached after which the suspension viscosity again increases as discussed in the previous sections.

4.2.1.2 α -SiC/H₂O/LGG Based Polar Dispersions

The rheological data for the α -SiC/H₂O/LGG based polar dispersions is presented in this section. For the α -SiC and LGG particles in the α -SiC/H₂O/LGG system to be well dispersed, it is essential for PAA-B to coat the particles well. By this the steric hindrance produced will be sufficient to overcome the van der Waals forces of attraction between the α -SiC and LGG particles, thus preventing particle agglomeration. Hence, the amount of dispersant added into the suspension is critical and should be sufficient enough to cover the α -SiC and LGG particles completely. Based on the rheological variations (particularly the viscosity) of the suspensions with various amounts of PAA-B the optimum amount of the weight of the dispersant needed for preparing well dispersed suspensions can be determined. Figure (62) is the variation of the viscosity of the suspension with respect to the amount of PAA-B added to the α -SiC/H₂O/LGG based polar dispersion system.

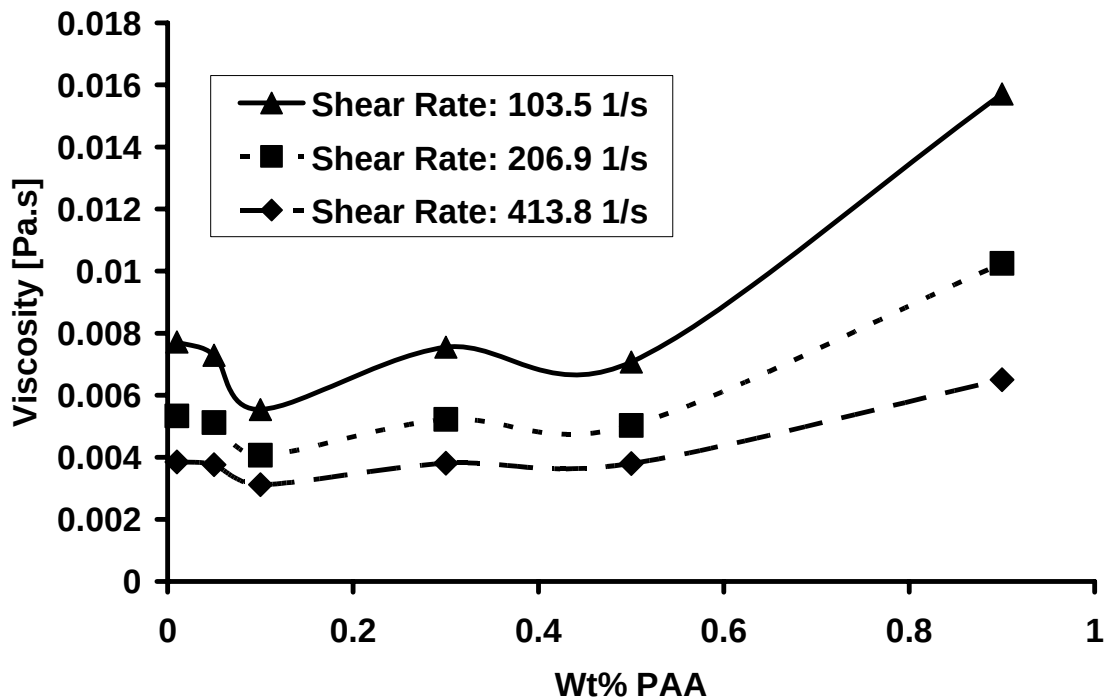


Figure 62: Experimentally determined variation of the viscosity with respect to the wt% PAA-B for the α -SiC/H₂O/LGG based polar dispersion system at different shear rates

As discussed earlier, the amount of the PAA-B added to the α -SiC/H₂O/LGG based polar dispersions system is critical and should cover the α -SiC and LGG particle surface completely to have good dispersions. Excess amounts of PAA-B will cause an increase in the viscosity of the system due to the depletion flocculation leading to particle agglomeration. Also, if less than the required amount is added, the repulsive steric barrier potential is not strong enough to overcome the strong van der Waals forces of attraction for the α -SiC/H₂O/LGG based polar dispersions system. Upon the addition of the optimum amount of the PAA-B into the α -SiC/H₂O/LGG based polar dispersion system, the repulsive barrier potential is high enough to overcome the attractive potential and hence a stable α -SiC/H₂O/LGG based polar dispersion is obtained. [22, 38, 65, 125] The optimum amount of PAA-B necessary to completely cover the α -SiC and LGG particle

surface in the α -SiC/H₂O/LGG based polar dispersions system is the lowest point on the graph plotted between the weight percent of dispersant and viscosity as from the figure (62) is taken to be 0.1 wt%. In figure (63) the graph shows the change in the zeta potential values of the suspension with respect to the amount of PAA-B added to the α -SiC/H₂O/LGG based polar dispersion system.

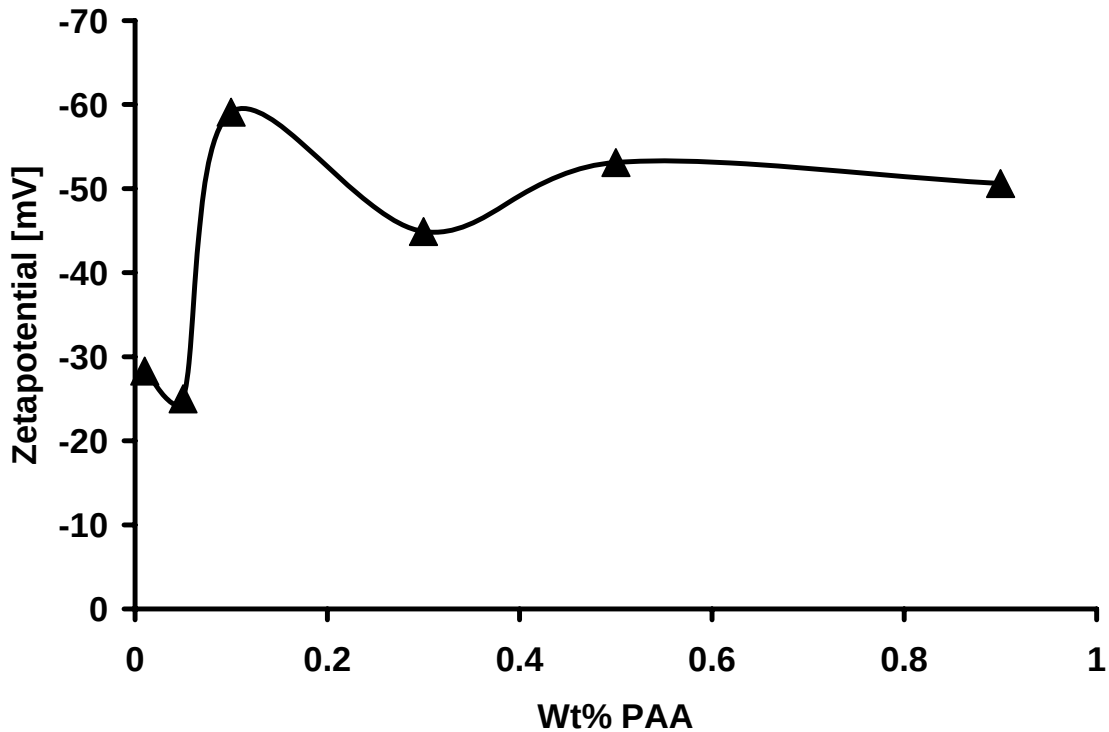


Figure 63: Experimentally determined variation of the zeta potential with respect to the wt% PAA-B for the α -SiC/H₂O/LGG based polar dispersion system

The data obtained from figure (63) is in agreement with the data from figure (62) and the discussion mentioned earlier. At the optimum weight percent of PAA-B the α -SiC/H₂O/LGG based polar dispersion system has the highest zeta potential value signifying the formation of a well dispersed suspension system. Also, at other amounts of the additions of PAA-B into the α -SiC/H₂O/LGG based polar dispersion system the

zeta potential values for the system are lower signifying that the α -SiC and LGG particles in the system is not well dispersed. The experimentally determined variation of the shear stress with respect to shear rate and the viscosity with respect to shear rate for the various amounts of PAA-B added to the α -SiC/H₂O/LGG based polar dispersion system is seen in figure (64) and figure (65).

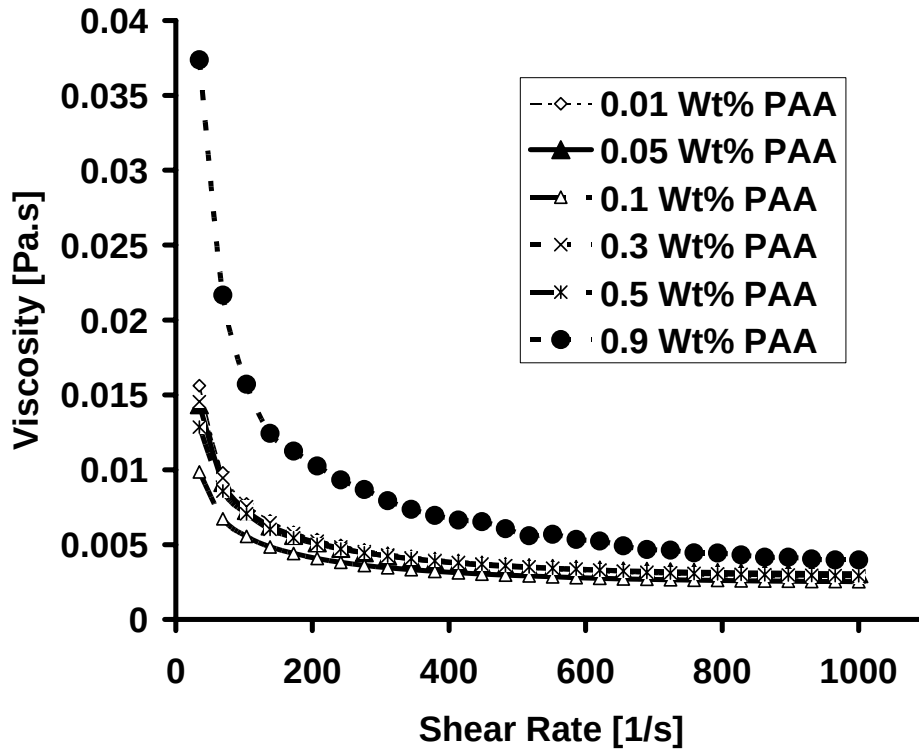


Figure 64: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/LGG based polar dispersion system with different wt% PAA-B amounts

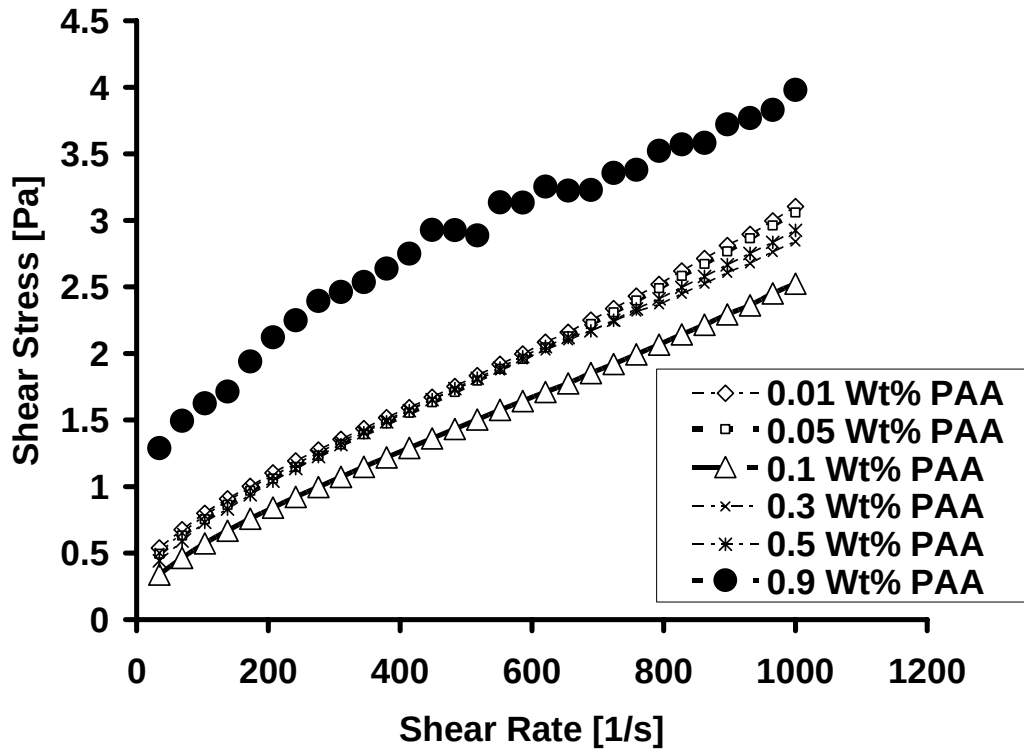


Figure 65: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/LGG based polar dispersion system with different wt% PAA-B amounts

The α -SiC/H₂O/LGG based polar dispersions system with different PAA-B amounts, show a shear thinning behavior as seen in figure (64) and figure (65) which signifies that the viscosities of these α -SiC/H₂O/LGG based polar dispersions systems depend on the shear rate being applied on the system. It is seen that with small additions of PAA-B into the SiC/H₂O/LGG based polar dispersions systems there is an decrease in the viscosity of the suspensions until a optimum value is acheived after which the suspension viscosity again increases as discussed in the previous sections.

4.2.1.3 Comparison of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

The analysis of the rheological data for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions is presented in this section. A control for the experimentation with α -SiC/H₂O/ α -SiC based polar dispersions for the α -SiC/H₂O/LGG based rheological data obtained can be seen in figures (66), (67) and (68). Figure (66) is the variation of the viscosity of the suspension with respect to the amount of dispersant added to the α -SiC/H₂O/ α -SiC (control) polar based dispersion system.

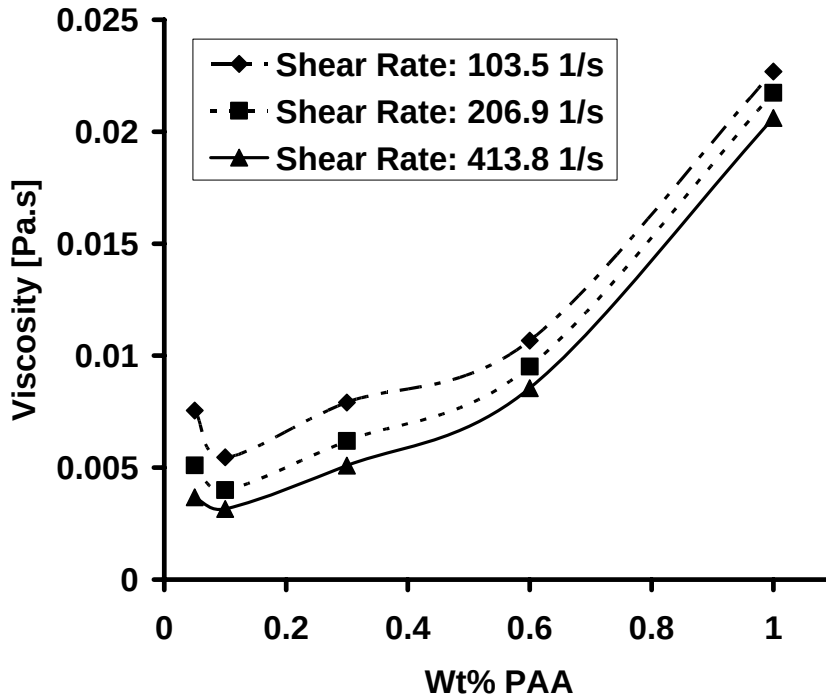


Figure 66: Experimentally determined variation of the viscosity with respect to the wt% PAA-A for the α -SiC/H₂O/ α -SiC based polar dispersions system (control) at different shear rates

For the α -SiC/H₂O/ α -SiC (control) polar based dispersion system the variation of the amount of dispersant to the viscosity of the suspension is significantly different from the α -SiC/H₂O/LGG polar based dispersion system which is discussed in the later section of

this discussion. The viscosity versus the shear rate and the shear stress versus the shear rate for the α -SiC/H₂O/ α -SiC (control) polar based dispersion system is shown in figure (67) and figure (68). For the control equal vol% of α -SiC and LGG were taken to make the total solids loading value.

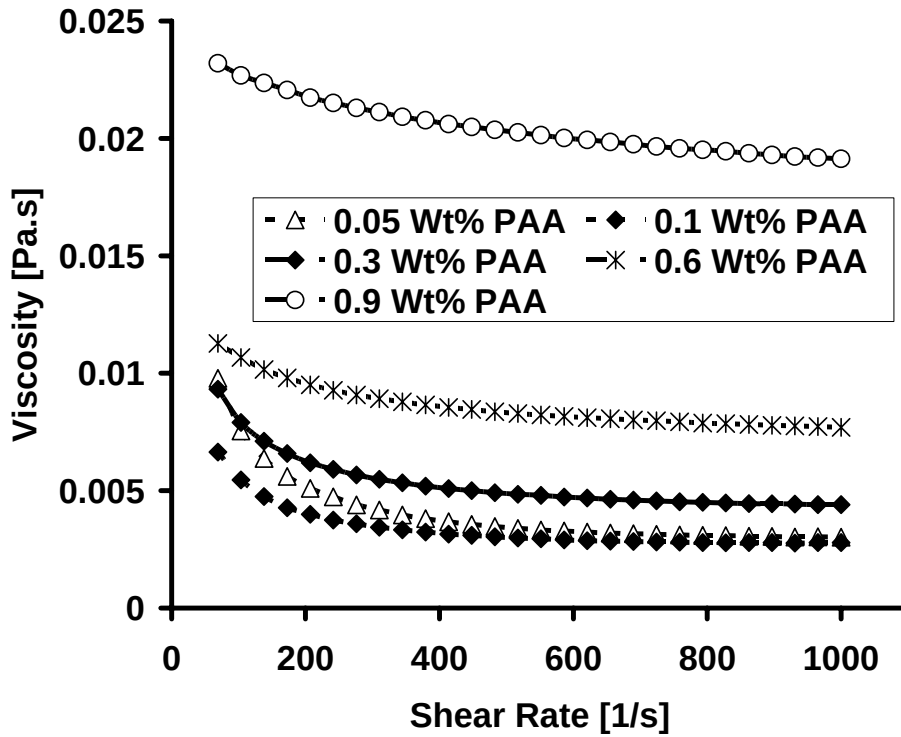


Figure 67: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersions system (control) at different wt% dispersant

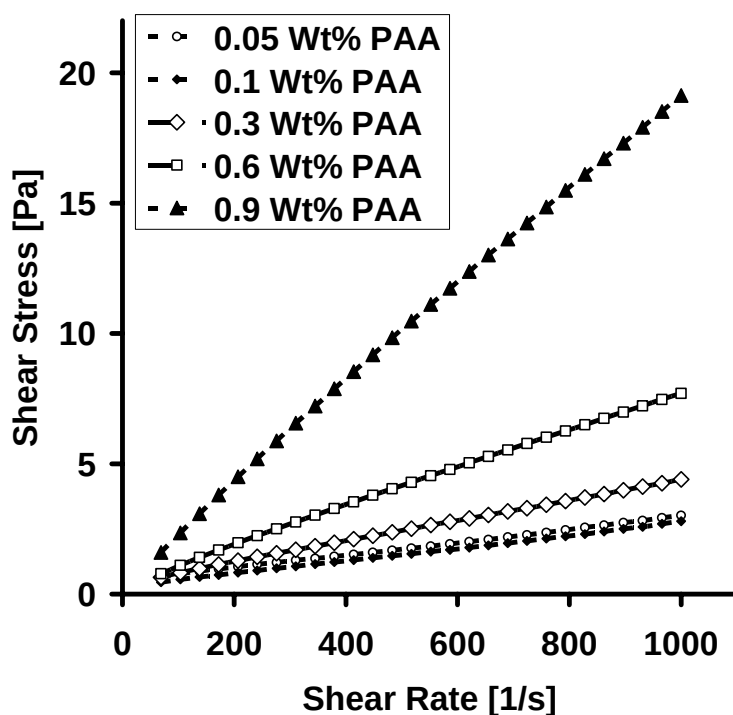


Figure 68: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersions system (control) at different wt% dispersant

For the α -SiC/H₂O/ α -SiC (control) polar based dispersion system, the variation of the suspension viscosity versus the shear rate and the shear stress versus the shear rate show a shear thinning behavior as well. Figures (69), (70) and (71) shows the comparison to the variation of the suspension viscosity with the dispersant amounts for the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) polar based dispersion systems at different shear rates of 103.5 s⁻¹, 206.9 s⁻¹ and 413.8 s⁻¹.

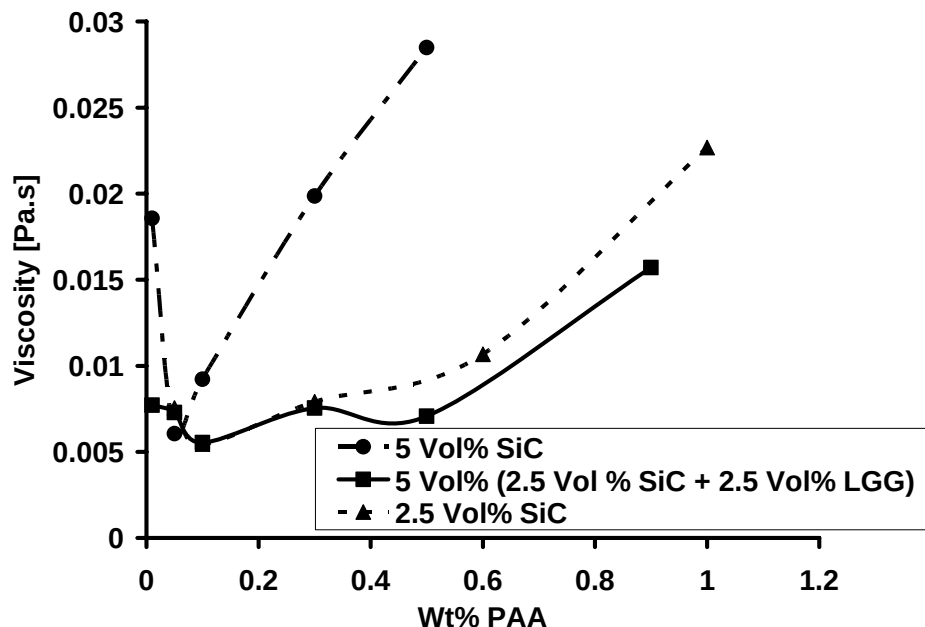


Figure 69: Experimentally determined variation of the viscosity with respect to the wt% dispersant for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions systems at a shear rate of 103.5 s⁻¹

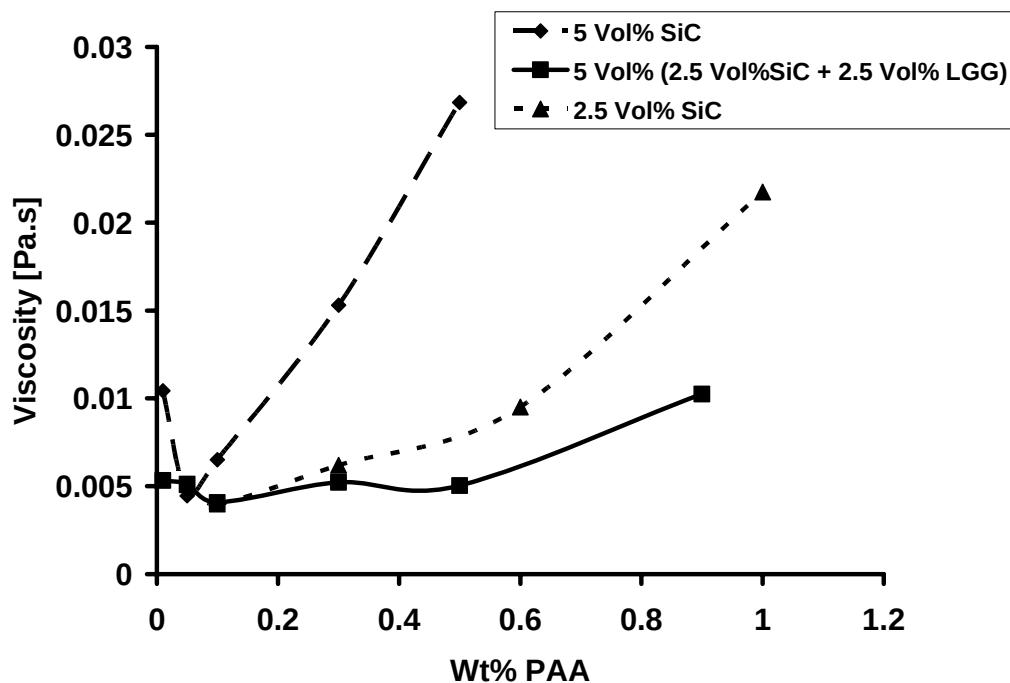


Figure 70: Experimentally determined variation of the viscosity with respect to the wt% dispersant for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions systems at a shear rate of 206.9 s⁻¹

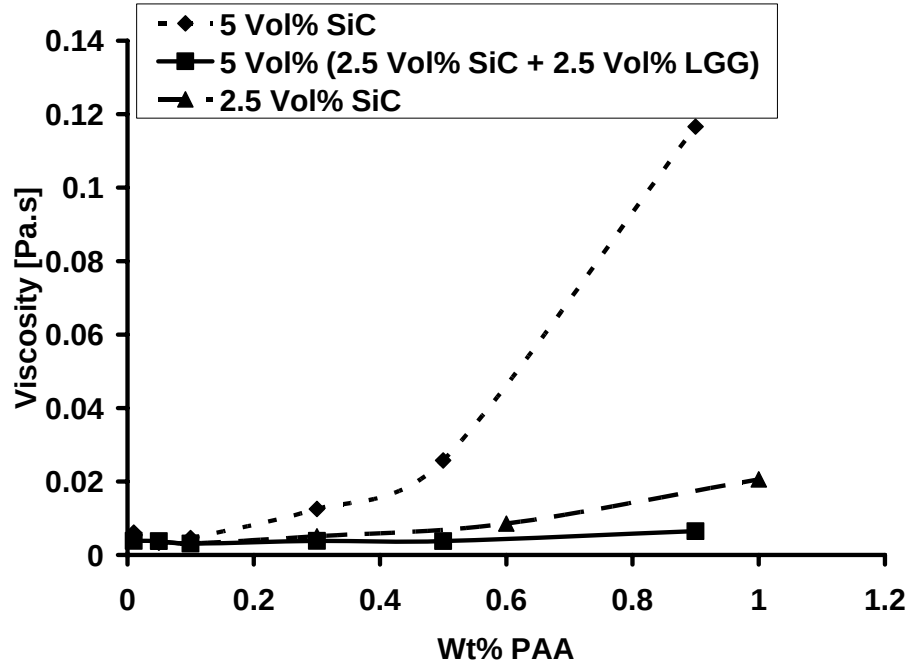


Figure 71: Experimentally determined variation of the viscosity with respect to the wt% dispersant for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions systems at a shear rate of 413.8 s⁻¹

From figures (69), (70) and (71) it can be seen that there is a significant difference in the viscosity for the amounts of the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) polar based dispersion systems. It can be seen that at lower shear rates the variations for viscosity for the α -SiC/H₂O/ α -SiC polar based dispersions is very significant and a minima can be clearly obtained. However, with an increase in the shear rate, the curve tends to broaden. In the case of the α -SiC/H₂O/LGG polar based system it is seen that the variation with respect to the dispersant amounts is smaller as compared to the α -SiC/H₂O/ α -SiC polar based dispersions. Figure (72) and figure (73) shows the comparison for the variation of the suspension viscosity with the shear rate and the suspension shear stress with respect to the shear rate for the α -SiC/H₂O/ α -SiC and α -

SiC/H₂O/LGG polar based dispersion systems at the optimum wt% PAA amounts selected for these dispersion systems.

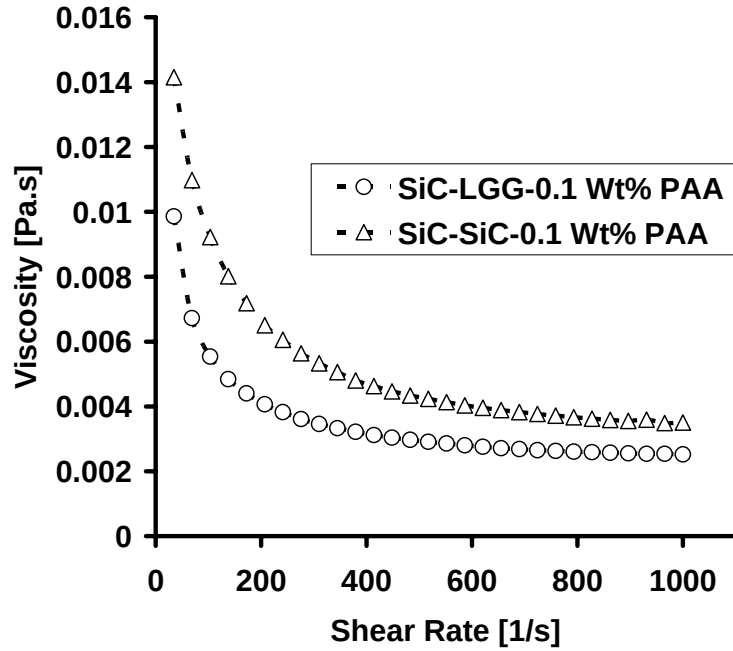


Figure 72: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions systems

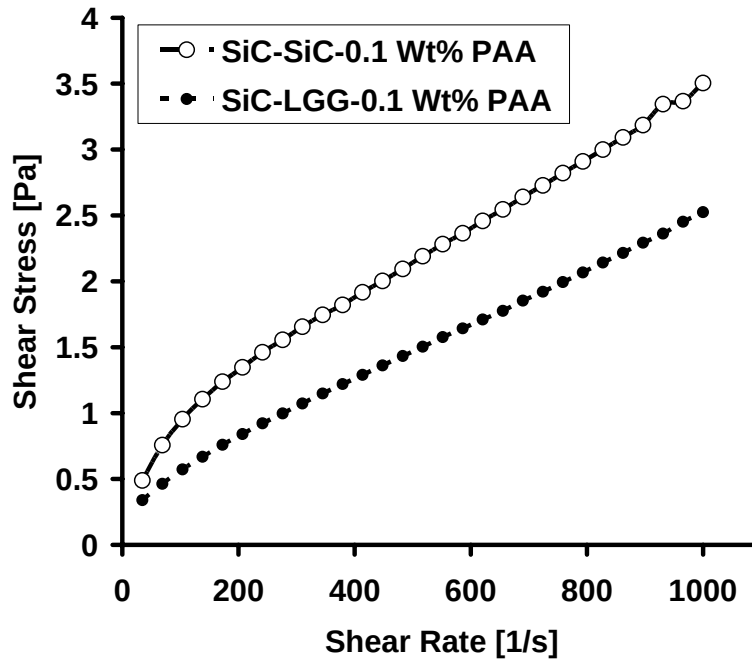


Figure 73: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions systems

From the data it is seen that these systems show a shear thinning behavior and the α -SiC/H₂O/ α -SiC polar based dispersion systems have a higher viscosity than the α -SiC/H₂O/LGG polar based dispersion systems at all shear rates. It is also seen that the α -SiC/H₂O/ α -SiC polar based dispersion systems have a higher shear stress values than the α -SiC/H₂O/LGG polar based dispersion systems at all shear rate values.

4.2.2 Determination of the Optimum pH and Zeta Potential for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

The calculated and measured amounts of H₂O and PAA-A (in the case of α -SiC/H₂O/ α -SiC suspensions) and PAA-B (in the case of α -SiC/H₂O/LGG suspensions) are taken in a beaker (in the case where the dispersant is used) and placed on a hot stirrer till the polymer dissolves in the solvent. α -SiC nanoparticles are then added to the system and the slurry is placed on a rotating mill for 24 hours at an rpm of 60 with alumina milling media. For the case when PAA is not used this step is done directly. For a set of samples, LGG is added after this period. The samples are then placed once again on the rotating mill for another 24 hours at 60 rpm. No milling media were used for the samples with LGG. This is followed by placing the samples on the Cole-Parmer ultrasonic bath for 6 hours and followed by the Branson ultrasonic bath for 30 minutes. The desired suspension is thus prepared and the pH and zeta potential measurements are determined.

4.2.2.1 α -SiC/H₂O/ α -SiC Based Polar Dispersions

For the α -SiC/H₂O/ α -SiC based polar dispersions the rheological data obtained is presented in this section. Figure (74) and figure (75) show the variation of the zeta

potential of the suspension with respect to the pH and the variation of the mobility of the particles with respect to the pH for the α -SiC/H₂O/ α -SiC based polar dispersions system for the case without the addition of PAA-A. In this case the mechanism for the dispersion is only due to the repulsion between the electrical double layers (electrostatic) of the α -SiC nanoparticles. The pH at the IEP for the α -SiC/H₂O/ α -SiC based polar dispersions system for the case without the addition of PAA-A is determined to be 3.6 from figure (74).

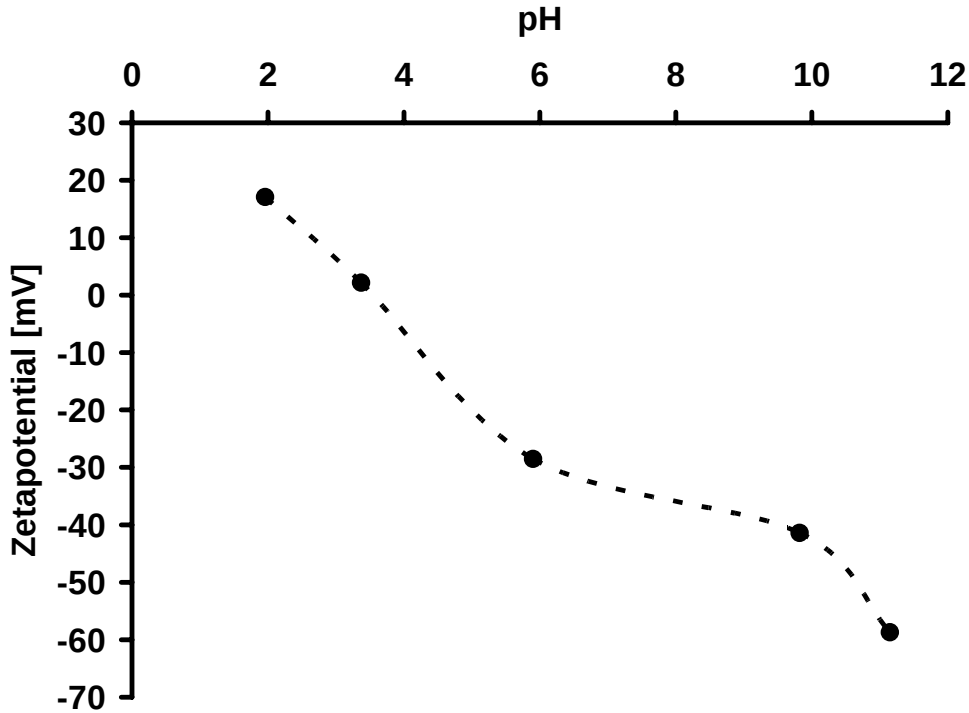


Figure 74: Experimentally determined variation of the zeta potential with respect to pH for the α -SiC/H₂O/ α -SiC based polar system

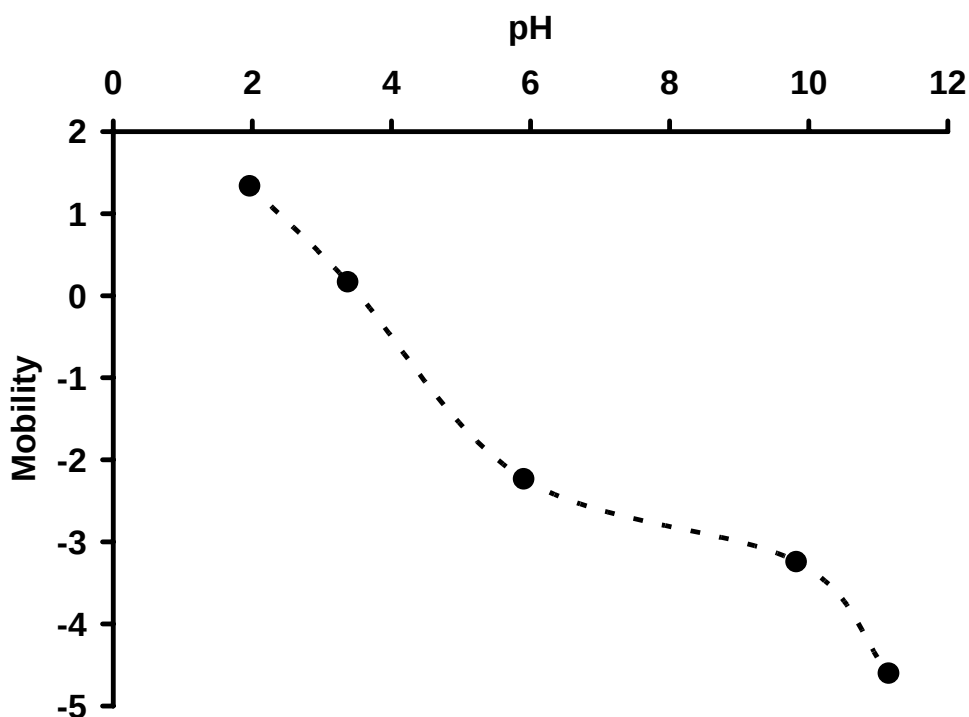


Figure 75: Experimentally determined variation of the mobility with respect to pH for the α -SiC/H₂O/ α -SiC based polar system

Figure (76) and figure (77) show the variation of the zeta potential of the suspension with respect to the amount of pH and the variation of the mobility of the particles with respect to the pH for the α -SiC/H₂O/ α -SiC based polar dispersions system for the case with the addition of PAA-A. In this case the mechanism for the dispersion is due to the repulsion between the electrical double layers (electro-steric) of the α -SiC nanoparticles and the steric hindrance created in the system due to the addition of PAA-A. The pH at the IEP for the α -SiC/H₂O/ α -SiC based polar dispersions system for the case with the addition of PAA-A is determined to be 1.5 from figure (76).

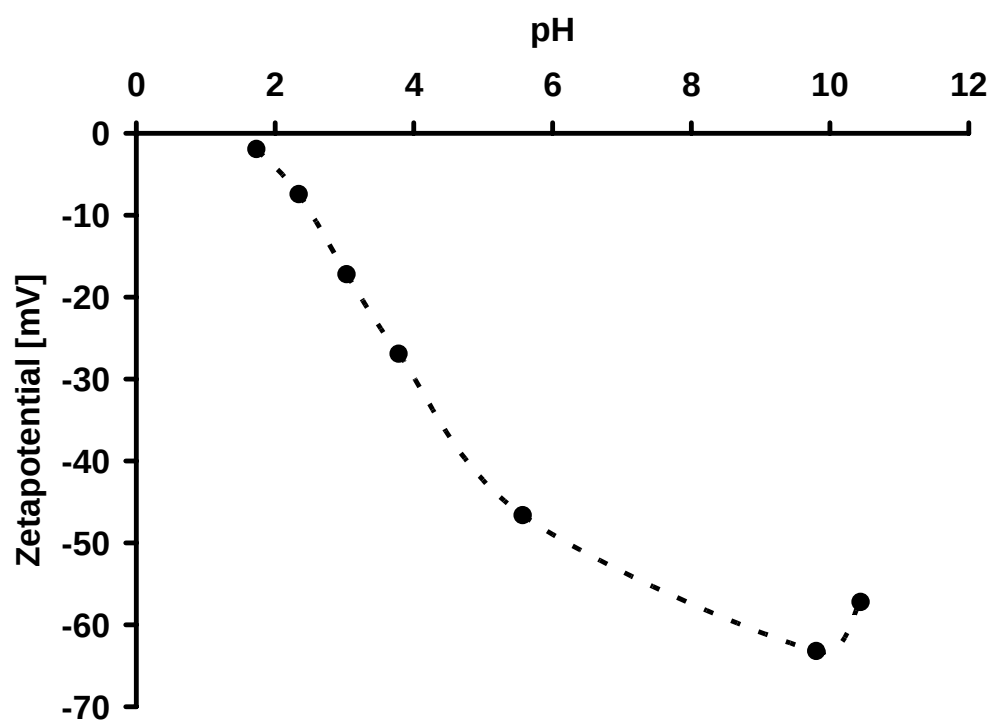


Figure 76: Experimentally determined variation of the zeta potential with respect to pH for the α -SiC/H₂O/ α -SiC polar system with PAA-A

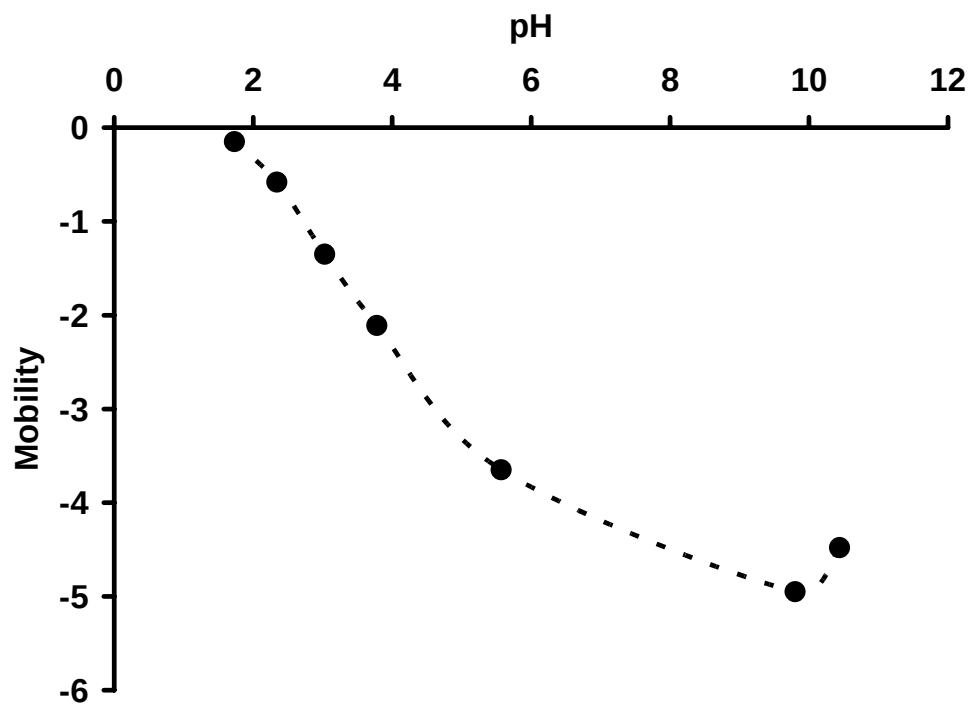


Figure 77: Experimentally determined variation of the mobility with respect to pH for the α -SiC/H₂O/ α -SiC based polar system with PAA-A

4.2.2.2 LGG/H₂O/LGG and α -SiC/H₂O/LGG Based Polar Dispersions

The rheological data for the LGG/H₂O/LGG and α -SiC/H₂O/LGG based polar dispersions is presented in this section. The variation of the zeta potential of the suspension with respect to the pH and the variation of the mobility of the particles with respect to the pH for the LGG/H₂O/LGG based polar dispersions system for the case without the addition of a dispersant are seen in figure (78) and figure (79). The mechanism for the dispersion in this case is only based on the repulsion between the electrical double layers (electrostatic) of the LGG particles. From figure (78) the pH at the IEP for the LGG/H₂O/LGG based polar dispersions system for the case without the addition of a dispersant is determined to be 2.7.

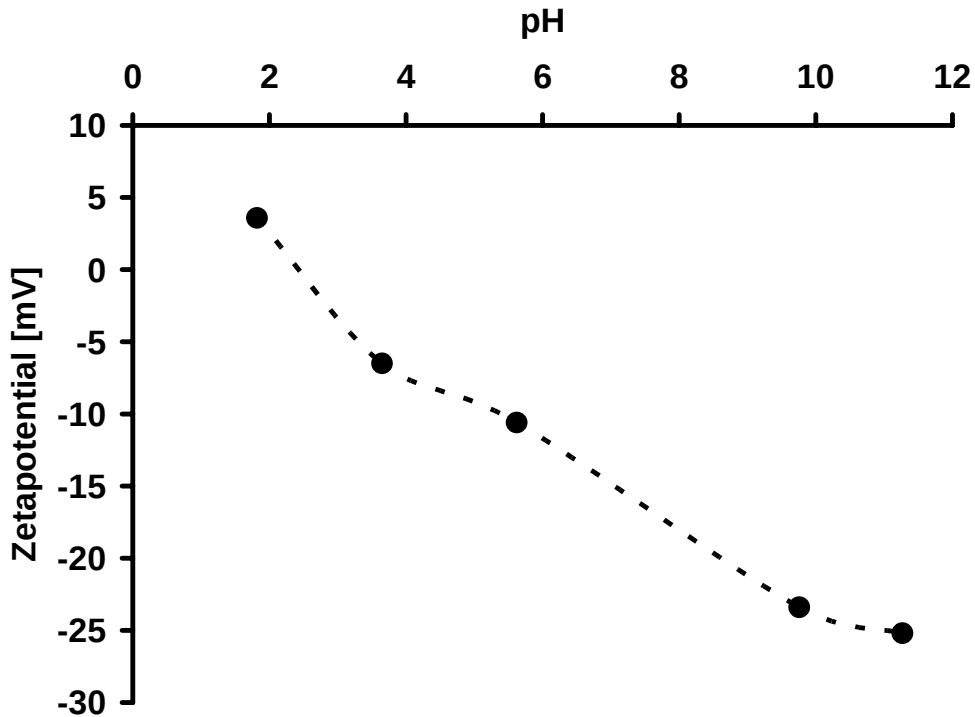


Figure 78: Experimentally determined variation of the zeta potential with respect to pH for the LGG/H₂O/LGG polar system

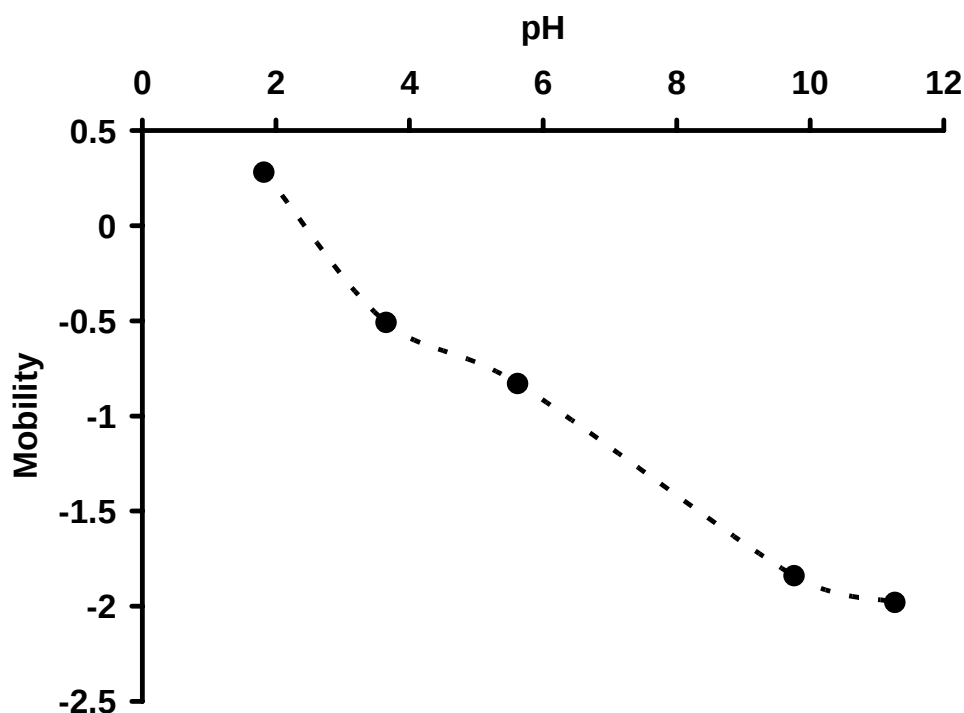


Figure 79: Experimentally determined variation of the mobility with respect to pH for the LGG/H₂O/LGG polar system

The variation of the zeta potential of the suspension with respect to the amount of pH and the variation of the mobility of the particles with respect to the pH for the α -SiC/H₂O/LGG based polar dispersions system for the case without the addition of PAA-B are seen in figure (80) and figure (81). The mechanism for the dispersion in this case is only due to the repulsion between the electrical double layers (electrostatic) of the α -SiC and LGG particles. From figure (80) the pH at the IEP for the α -SiC/H₂O/LGG based polar dispersions system for the case without the addition of PAA-B is determined to be 1.4.

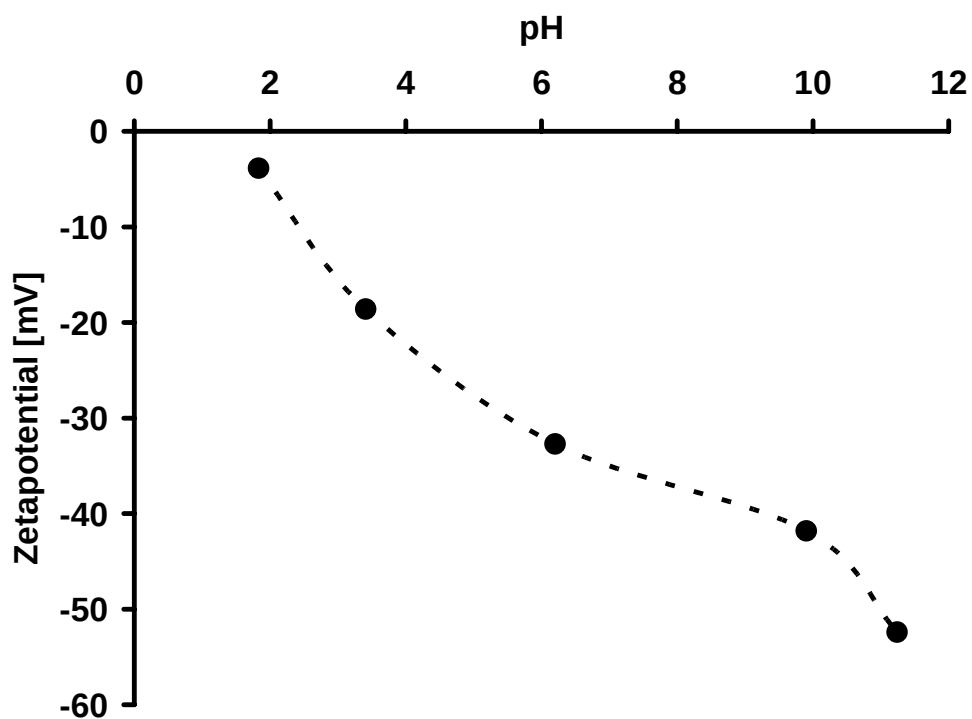


Figure 80: Experimentally determined variation of the zeta potential with respect to pH for the α -SiC/H₂O/LGG polar system

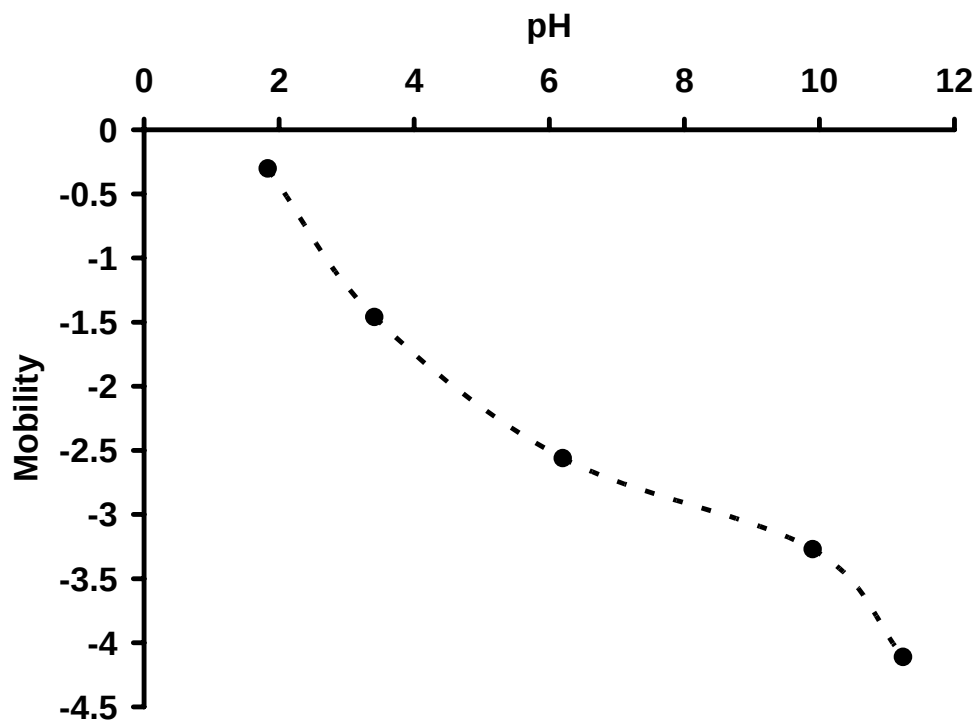


Figure 81: Experimentally determined variation of the mobility with respect to pH for the α -SiC/H₂O/LGG polar system

Figure (82) and figure (83) show the variation of the zeta potential of the suspension with respect to the amount of pH and the variation of the mobility of the particles with respect to the pH for the α -SiC/H₂O/LGG based polar dispersions system for the case with the addition of PAA-B. In this case the mechanism for the dispersion is due to the repulsion between the electrical double layers (electro-steric) of the α -SiC and LGG particles and the steric hindrance created in the system due to the addition of PAA-B. The pH at the IEP for the α -SiC/H₂O/LGG based polar dispersions system for the case with the addition of PAA-B is determined to be 1.9 from figure (82).

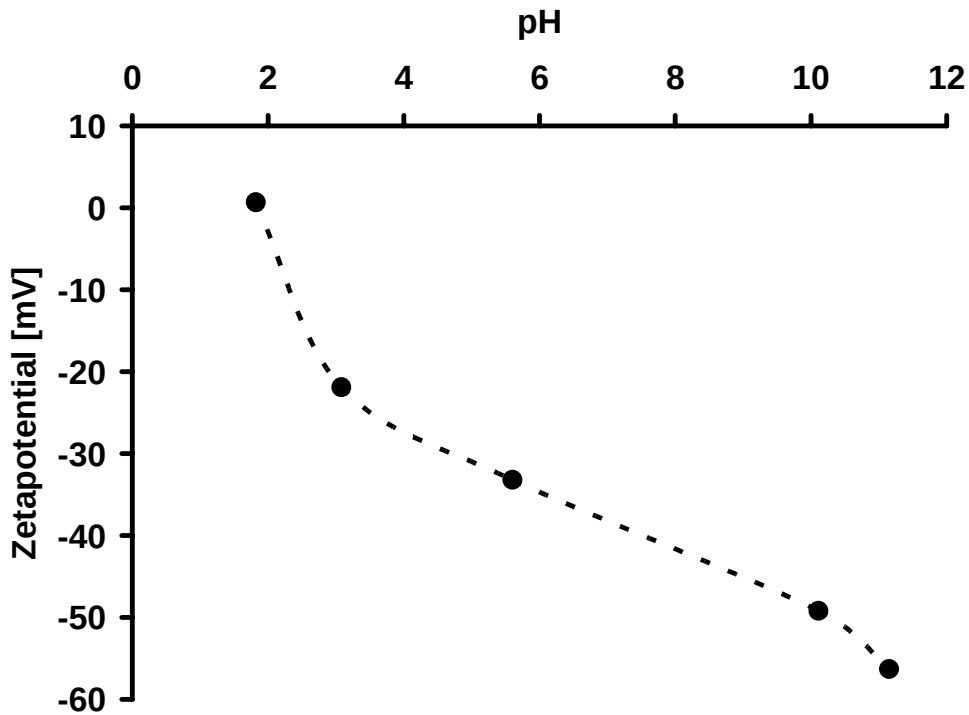


Figure 82: Experimentally determined variation of the zeta potential with respect to pH for the α -SiC/H₂O/LGG polar system with PAA-B

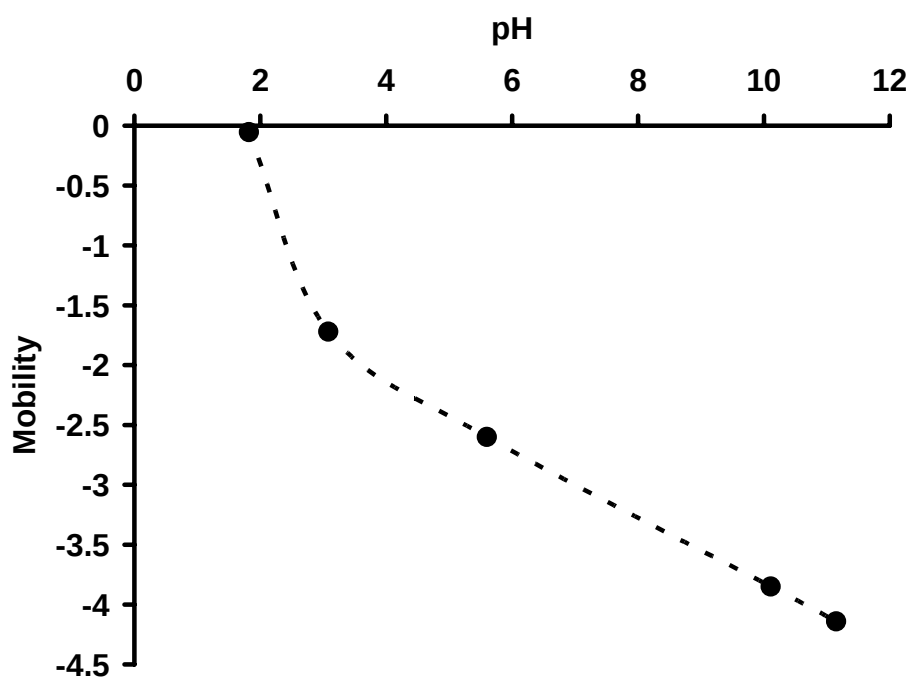


Figure 83: Experimentally determined variation of the mobility with respect to pH for the α -SiC/H₂O/LGG polar system with PAA-B

4.2.2.3 Comparison of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

The analysis for the zeta potential variations with respect to the pH and the variations of the mobility of the particles in suspension with respect to the pH for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions are presented and discussed in this section. From figure (84) and figure (85) it can be seen that for the case of the α -SiC/H₂O/ α -SiC polar based dispersion system with the addition of the dispersant PAA-A, at the pH value at the IEP for the case with α -SiC/H₂O/ α -SiC without the addition of PAA-A, the zeta potential value is – 22 mV. This value is in concurrence with the mathematical analysis discussed in the previous sections. This result signifies that at the pH of 3.6 for the α -SiC/H₂O/ α -SiC polar based dispersion system, the PAA-A steric hindrance is significant enough to create the necessary repulsion in order to have a well dispersed suspension. A

similar result is obtained for the case of the α -SiC/H₂O/LGG polar based dispersion system with the addition of the dispersant PAA-B, at the pH value at the IEP for the case with α -SiC/H₂O/LGG without the addition of PAA-B, the zeta potential value is +10 mV. This value is also in agreement with the mathematical analysis discussed in the previous sections. The result signifies that at the pH of 1.4 for the α -SiC/H₂O/LGG polar based dispersion system, the PAA-B steric hindrance is significant enough to create the necessary repulsion in order to have a well dispersed suspension. From the results obtained it is also seen that there is a charge difference for the cases with α -SiC/H₂O/ α -SiC and without α -SiC/H₂O/LGG in order to prepare stable suspensions. It is also seen that in the case of the α -SiC/H₂O/LGG systems since the system is more repulsive than the α -SiC/H₂O/ α -SiC polar based system, a lower zeta potential value is sufficient to create the required stable suspension.

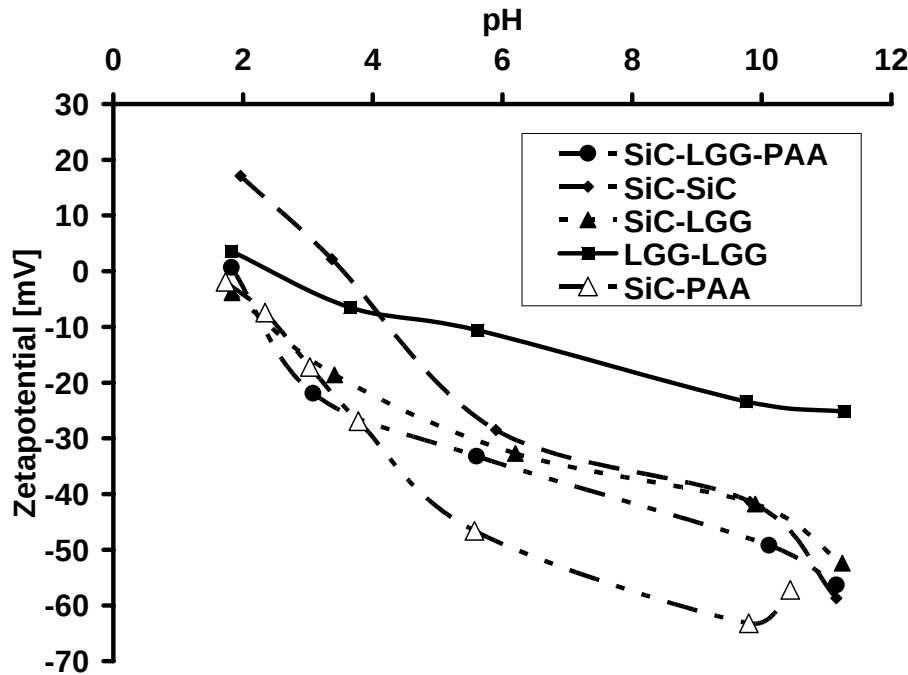


Figure 84 (a): Experimentally determined variation of the zeta potential with respect to pH for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar based systems with and without PAA

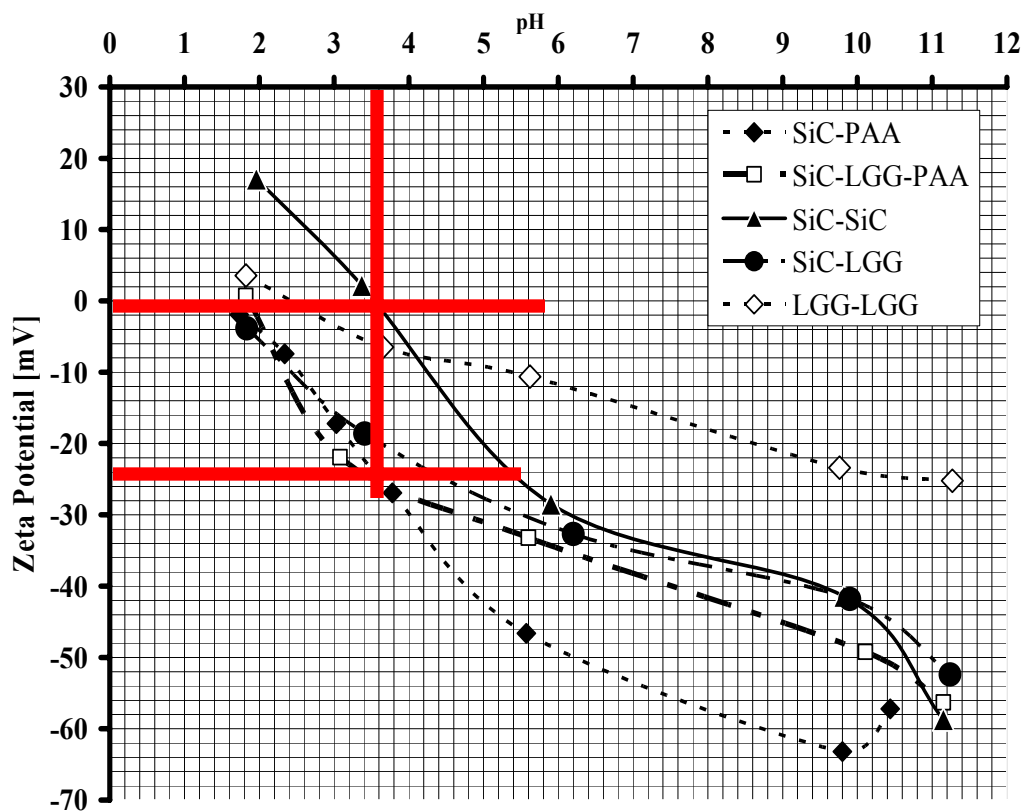


Figure 84 (b): Detailed view of figure 84 (a)

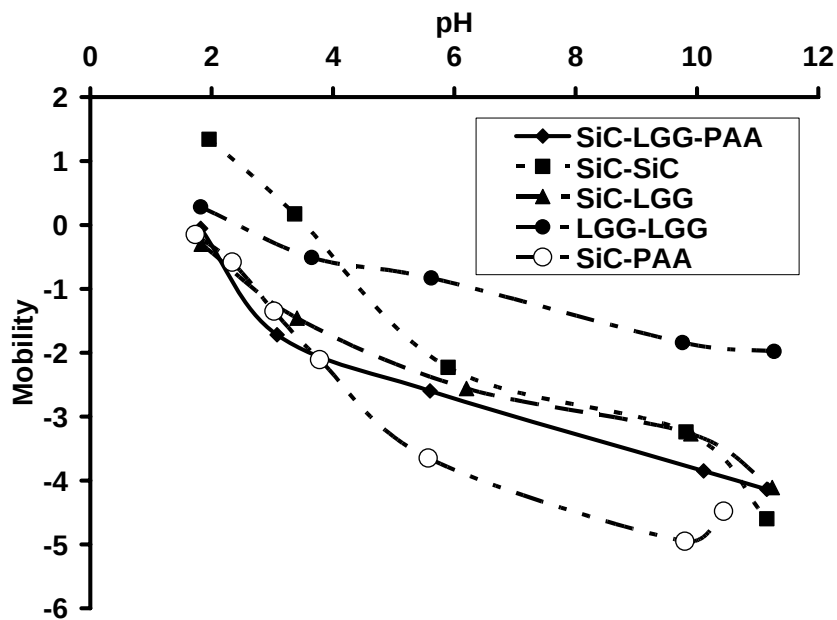


Figure 85: Experimentally determined variation of the mobility with respect to pH for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG polar based systems with and without PAA

4.2.3 Determination of the Optimum Amount of Duramax B-1020 for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

Measured amounts of H₂O and PAA-A (in the case of α -SiC/H₂O/ α -SiC suspensions) and PAA-B (in the case of α -SiC/H₂O/LGG suspensions) are taken in a beaker and placed on a hot stirrer till the polymer dissolves in the solvent. This is followed by the addition of the measured amounts of Duramax B-1020. This is followed by the addition of the α -SiC nanoparticles and the slurry is placed on a rotating mill for 24 hours at an rpm of 60 with alumina milling media. For one set of samples, LGG is added after this period. The samples are placed once again on the rotating mill for another 24 hours with an rpm of 60. For the samples with LGG no milling media are added in the process. This is followed by placing the samples on the Cole-Parmer ultrasonic bath for 6 hours and followed by the Branson ultrasonic bath for 30 minutes. The required suspension is thus prepared and the viscosity measurements are carried out. For the viscosity measurements the temperature for the shear flow measurements is set to 298 K. The slurry is pre-sheared at 800 s⁻¹ and allowed to rest for 60 seconds before the rheological analysis is recorded. The measurements are carried out from a shear rate of 0.001 to 1000 s⁻¹. The relative viscosity of the slurry is calculated as the ratio of the slurry viscosity to that of the solvent (in this case H₂O) at the same temperature. The viscosity of water is calculated using the equation (69). Duramax B-1020 was used as the binder as it is soluble in the polar solvent used.

4.2.3.1 α -SiC/H₂O/ α -SiC Based Polar Dispersions

For the α -SiC/H₂O/ α -SiC based polar dispersions the rheological data obtained with respect to the Duramax B-1020 addition is presented in this section. Figure (86) is the variation of the viscosity of the α -SiC/H₂O/ α -SiC based polar dispersions with respect to the amount of Duramax B-1020 added to the system at different shear rates. The addition of the Duramax B-1020 in small concentrations provides bridges between the particles which help with providing strength to the green body. [38] From figure (86) the optimum range of Duramax B-1020 is selected for the experimentation which is the one in which the suspension viscosity is the lowest and is found to be at a binder weight percent of 0.25 for the α -SiC/H₂O/ α -SiC based polar dispersions.

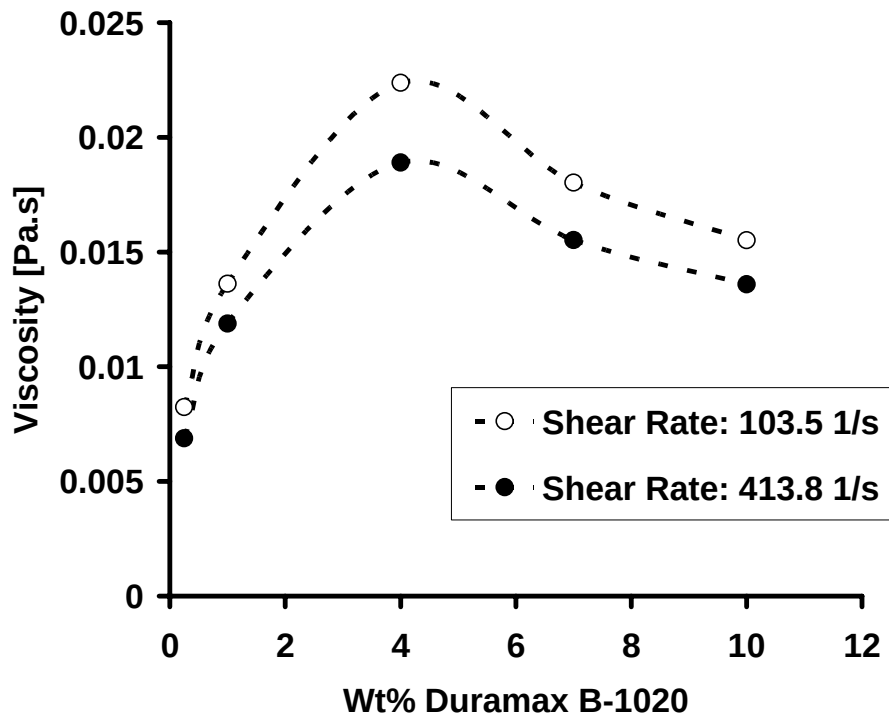


Figure 86: Experimentally determined variation of the viscosity with respect to the wt% Duramax B-1020 for the α -SiC/H₂O/ α -SiC based polar dispersion system at different shear rates

Figure (87) and figure (88) are the variation of the viscosity with respect to shear rate and the variation of shear stress with respect to shear rate at different amounts of Duramax B-1020 added for the α -SiC/H₂O/ α -SiC based polar dispersions. The addition of the Duramax B-1020 is seen to first increase the suspension viscosity and then with further additions of the binder the α -SiC/H₂O/ α -SiC based polar dispersions viscosity is reduced. From figure (87) and figure (88) it is seen that the α -SiC/H₂O/ α -SiC based polar dispersions have a shear thinning behavior.

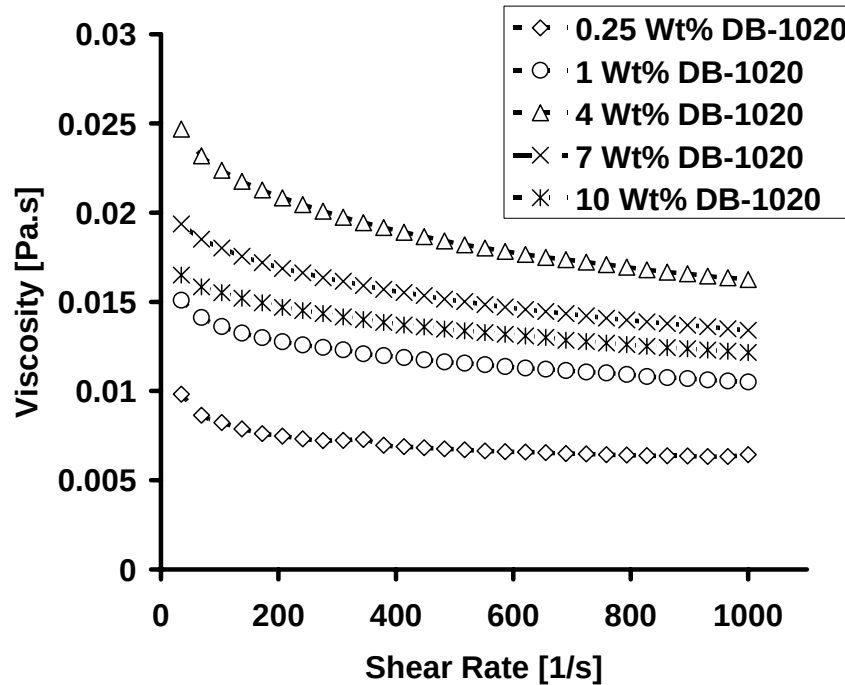


Figure 87: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system for different wt% Duramax B-1020

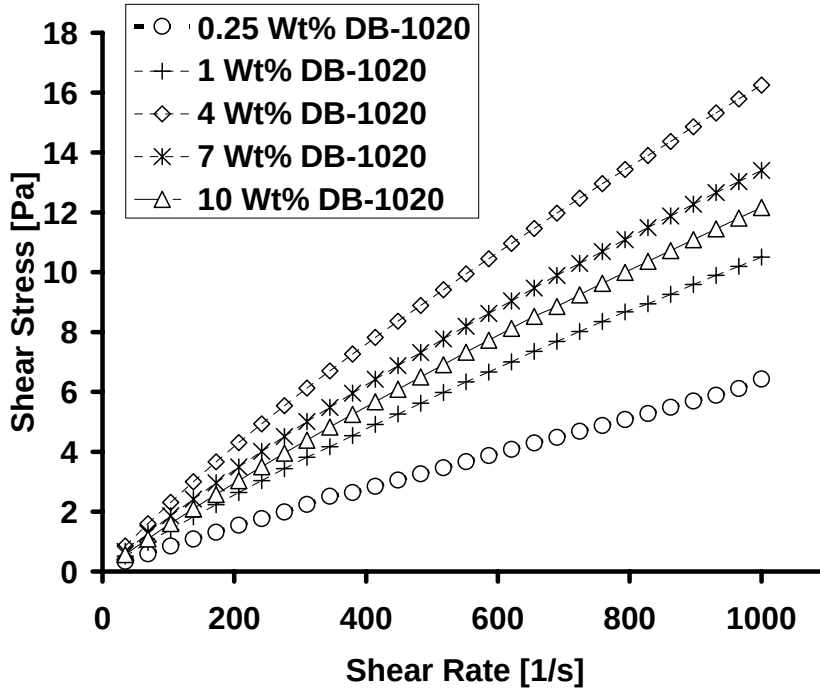


Figure 88: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system for different wt% Duramax B-1020

4.2.3.2 α -SiC/H₂O/LGG Based Polar Dispersions

The rheological data obtained with respect to the Duramax B-1020 addition for the α -SiC/H₂O/LGG based polar dispersions is presented in this section. The variation of the viscosity of the α -SiC/H₂O/LGG based polar dispersions with respect to the amount of Duramax B-1020 added to the system at different shear rates of 103.5 s⁻¹, 206.9 s⁻¹ and 413.8 s⁻¹ is seen in figure (89). The optimum range of Duramax B-1020 is selected for the experimentation data seen as in figure (89) is the one in which the suspension viscosity is the lowest and is found to be at a binder weight percent of 0.25 for the α -SiC/H₂O/LGG based polar dispersions.

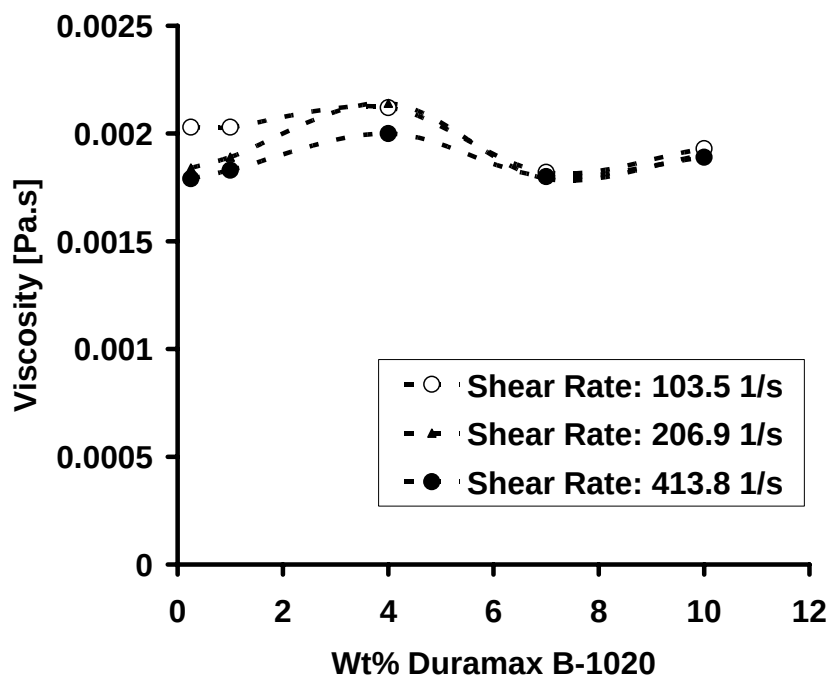


Figure 89: Experimentally determined variation of the viscosity with respect to the wt% Duramax B-1020 for the α -SiC/H₂O/LGG based polar dispersion system at different shear rates

The variation of the viscosity with respect to shear rate and the variation of shear stress with respect to shear rate at different amounts of Duramax B-1020 added for the α -

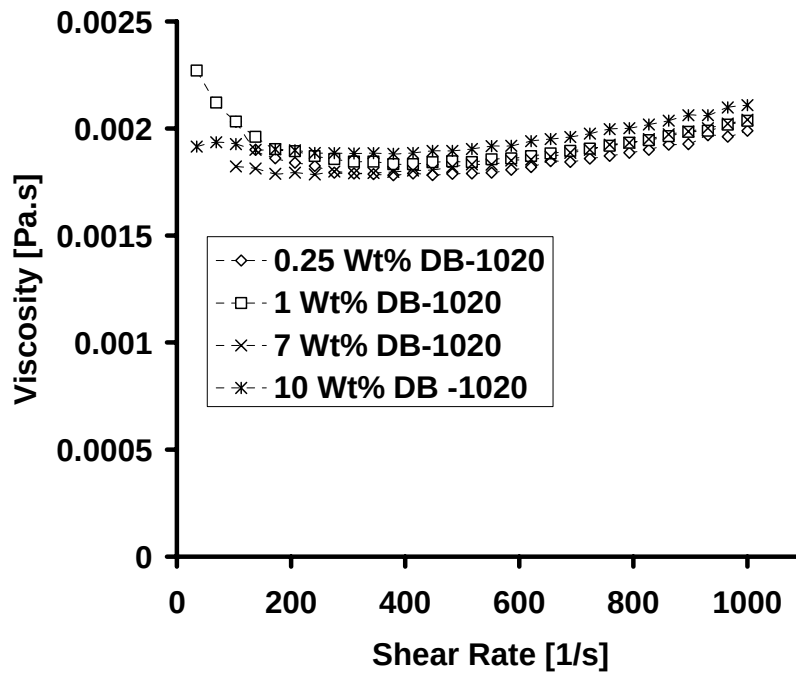


Figure 90: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/LGG based polar dispersion system for different wt% Duramax B-1020

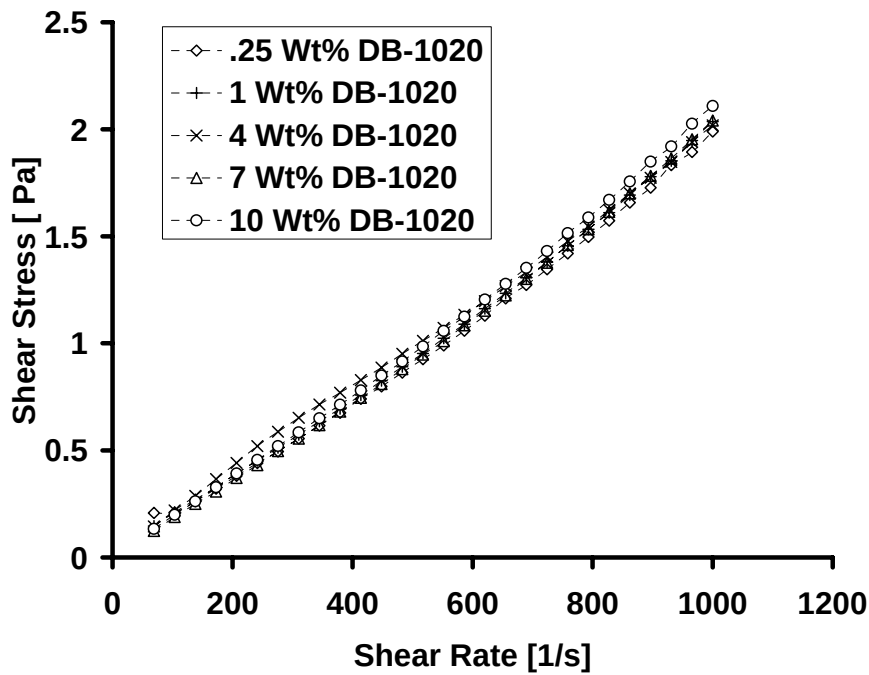


Figure 91: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/LGG based polar dispersion system for different wt% Duramax B-1020

SiC/H₂O/LGG based polar dispersions are seen in figure (90) and figure (91). From the figures it is also seen that the α -SiC/H₂O/LGG based polar dispersions thin with the application of shear.

4.2.3.3 Comparison of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

For the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions the rheological data obtained with respect to the Duramax B-1020 addition is presented in this section. Figure (92) and figure (93) show the variation of the viscosity of the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar system with respect to the amount of Duramax B-1020 added to the systems at different shear rates of 103.5 s⁻¹ and 206.9 s⁻¹. From the figures it can be seen that the viscosity variation for the α -SiC/H₂O/ α -SiC based polar dispersions is very large compared to the α -SiC/H₂O/LGG based polar dispersions. It is also seen that there is not too much variation in the viscosity value for the α -SiC/H₂O/LGG based polar dispersions.

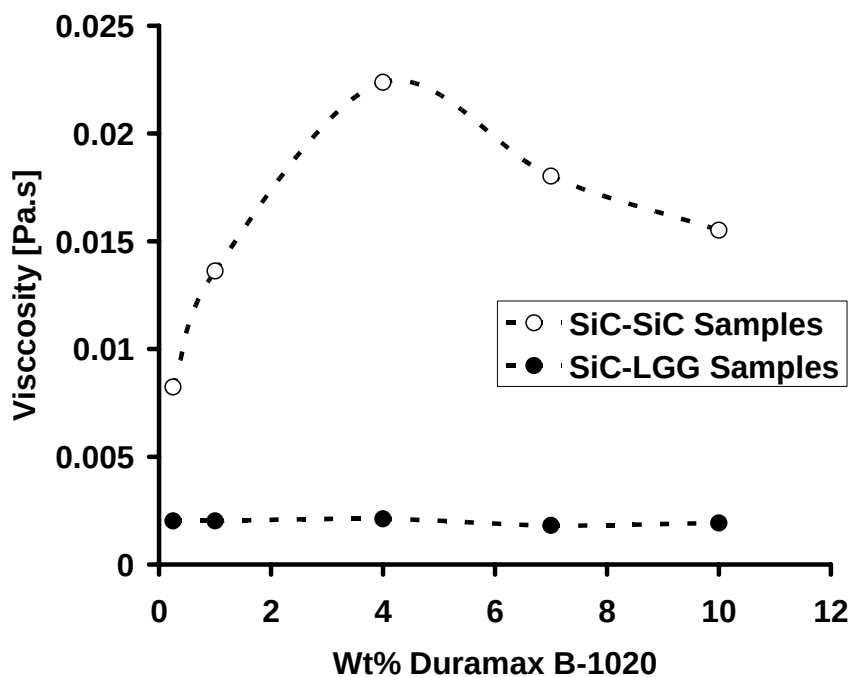


Figure 92: Experimentally determined variation of the viscosity with respect to the wt% Duramax B-1020 for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion system at a shear rate of 103.5 s⁻¹

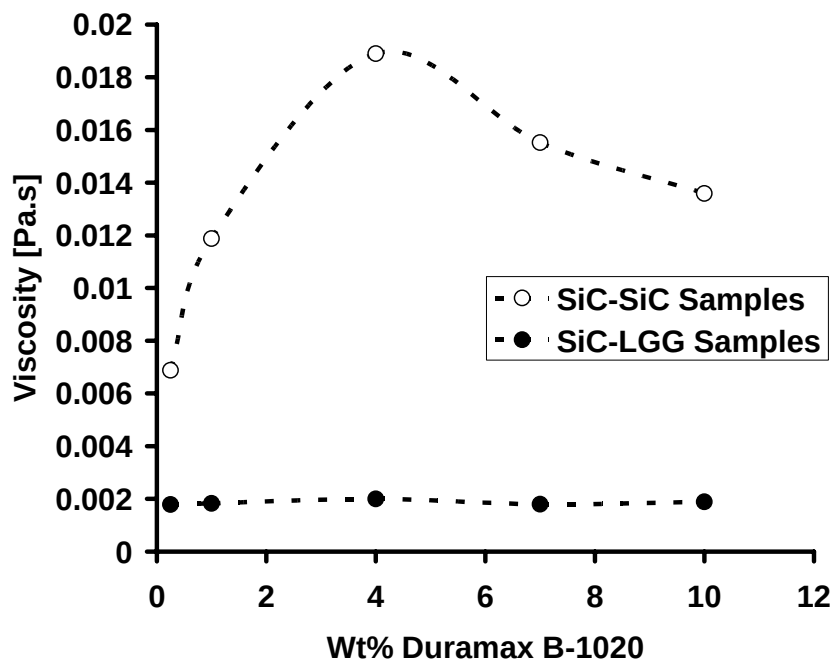


Figure 93: Experimentally determined variation of the viscosity with respect to the wt% Duramax B-1020 for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion system at a shear rate of 206.9 s⁻¹

4.2.4 Determination of the Optimum Amount of Poly Ethylene Glycol (PEG) for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

The calculated and measured amounts of H₂O and PAA-A (in the case of α -SiC/H₂O/ α -SiC suspensions) and PAA-B (in the case of α -SiC/H₂O/LGG suspensions) are taken in a beaker and kept on a hot stirrer until the polymer dissolves in the solvent. This is followed by the addition of the optimum amounts of Duramax-B1020 and measured amounts of PEG. The set is then once again placed on the stirrer until the plasticizer dissolves in the solvent. This is followed by the addition of the α -SiC nanoparticles and the slurry is placed on a rotating mill for 24 hours at an rpm of 60 with alumina milling media. For one set of samples, LGG is added after this period. The samples are placed once again on the rotating mill for another 24 hours with an rpm of 60. For the samples with LGG no milling media are added in the process. This is followed by placing the samples on the Cole-Parmer ultrasonic bath for 6 hours and followed by the Branson ultrasonic bath for 30 minutes. The required suspension is thus prepared and the viscosity measurements are carried out. For the viscosity measurements, the temperature for the shear flow measurements is set to 298 K. The slurry is pre-sheared at 800 s⁻¹ and allowed to rest for 60 seconds before the rheological analysis is recorded. The measurements are carried out from a shear rate of 0.001 to 1000 s⁻¹. The relative viscosity of the slurry is calculated as the ratio of the slurry viscosity to that of the solvent (in this case H₂O) at the same temperature. The viscosity of water is calculated using the equation (69).

4.2.4.1 α -SiC/H₂O/ α -SiC Based Polar Dispersions

For the α -SiC/H₂O/ α -SiC based polar dispersions the rheological data obtained with respect to the PEG addition is presented in this section. Figure (94) is the variation of the viscosity of the α -SiC/H₂O/ α -SiC based polar dispersions with respect to the amount of PEG added to the system at different shear rates. The addition of the PEG softens the binder which helps with increasing the flexibility of the green body fabricated. [38] From figure (94) the optimum range of PEG is selected for the experimentation which is the one in which the suspension viscosity is the lowest and is found to be at a plasticizer weight percent of 0.25 for the α -SiC/H₂O/ α -SiC based polar dispersions.

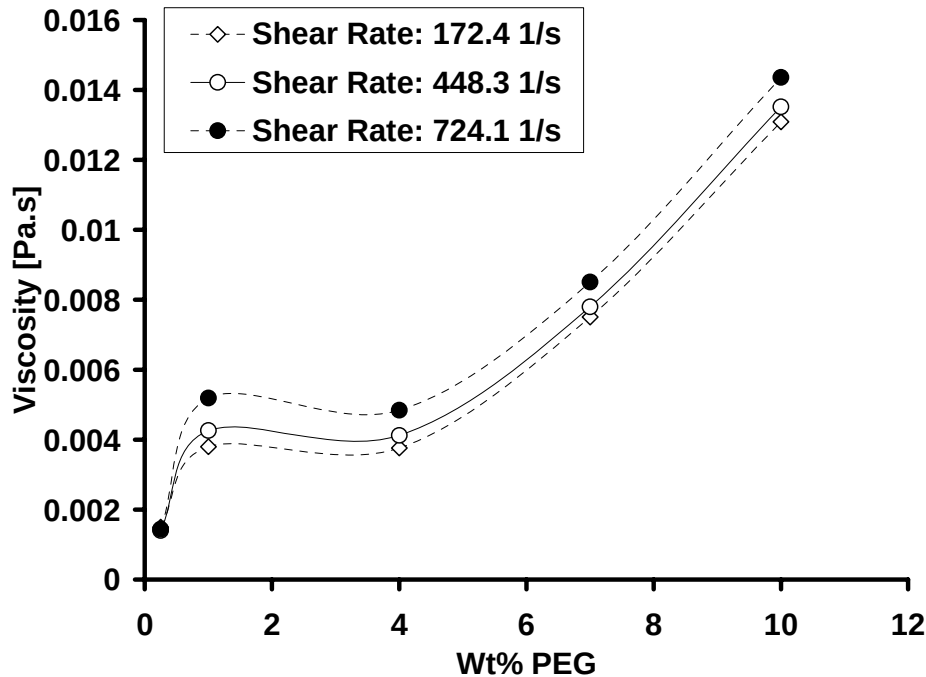


Figure 94: Experimentally determined variation of the viscosity with respect to the wt% PEG for the α -SiC/H₂O/ α -SiC based polar dispersion system at different shear rates

Figure (95) and figure (96) show the variation of viscosity with respect to shear rate and the variation of shear stress with respect to shear rate at different amounts of PEG added

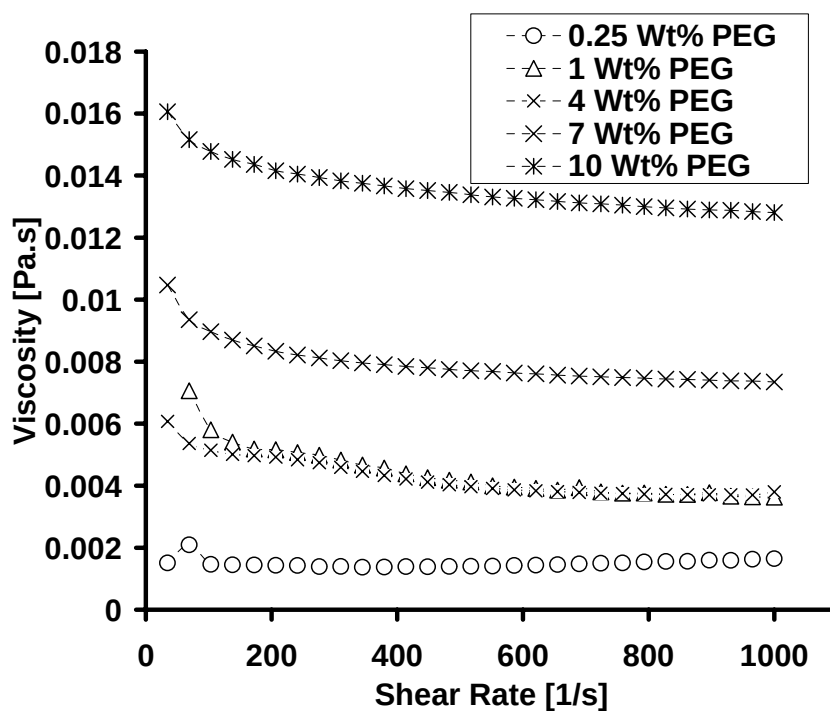


Figure 95: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system at different wt% PEG

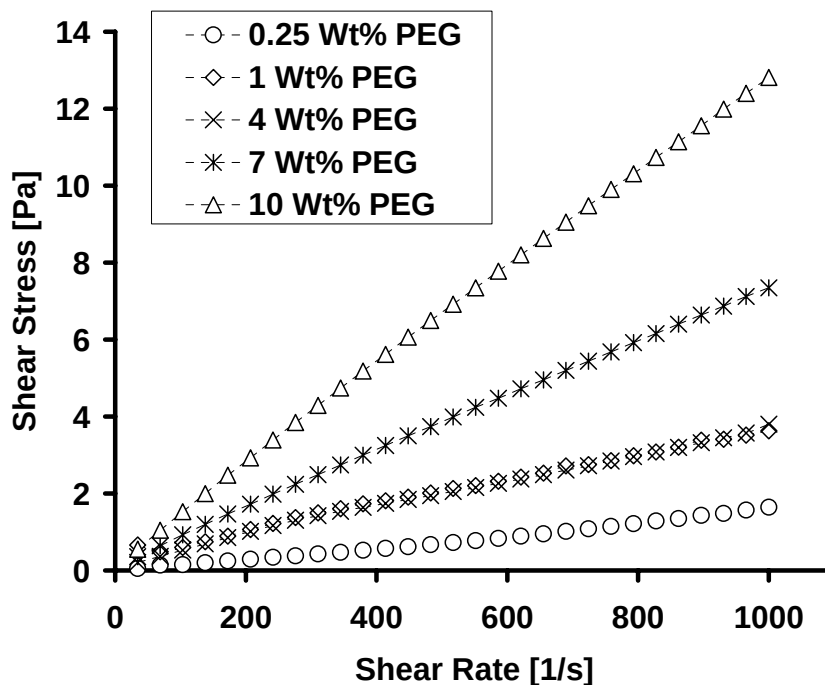


Figure 96: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system at different wt% PEG

for the α -SiC/H₂O/ α -SiC based polar dispersions. The addition of the PEG increases the suspension viscosity for the α -SiC/H₂O/ α -SiC based polar dispersions. From figure (95) and figure (96) it is seen that the α -SiC/H₂O/ α -SiC based polar dispersions have a shear thinning behavior

4.2.4.2 α -SiC/H₂O/LGG Based Polar Dispersions

The rheological data obtained with respect to the PEG addition for the α -SiC/H₂O/LGG based polar dispersions is presented in this section. The variation of the viscosity of the α -SiC/H₂O/LGG based polar dispersions with respect to the amount of PEG added to the system at different shear rates of 172.4 s⁻¹, 448.3 s⁻¹ and 724.1 s⁻¹ is presented in figure (97). PEG addition softens the binder which helps with increasing the flexibility of the green body fabricated. [38] The optimum range of PEG selected for the experimentation is the one in which the suspension viscosity is the lowest and is found to be at a plasticizer weight percent of 0.25 for the α -SiC/H₂O/LGG based polar dispersions as seen in figure (97).

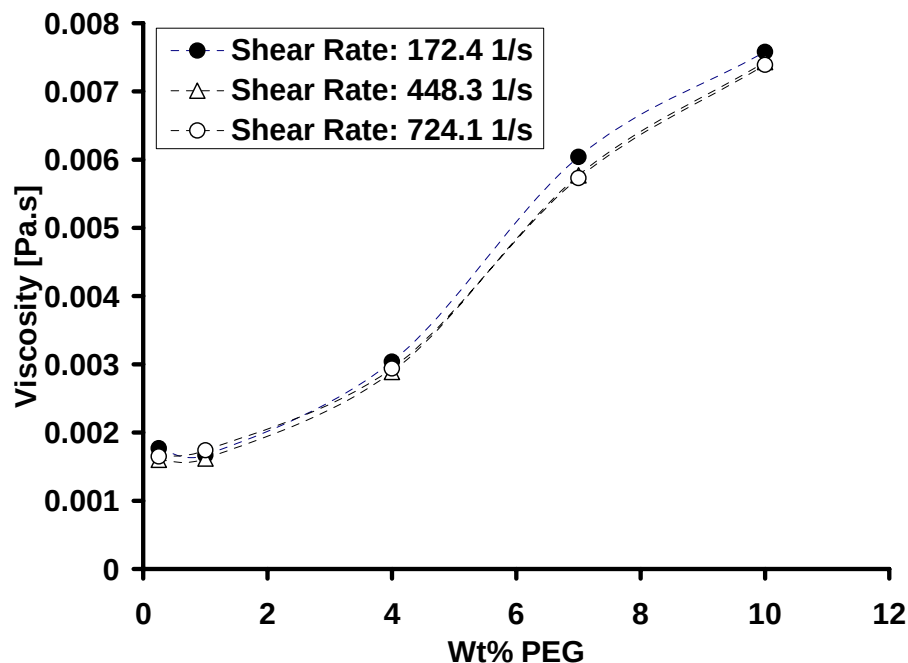


Figure 97: Experimentally determined variation of the viscosity with respect to the wt% PEG for the α -SiC/H₂O/LGG based polar dispersion system at different shear rates

The variation of viscosity with respect to shear rate and the variation of shear stress with respect to shear rate at different amounts of PEG added for the α -SiC/H₂O/LGG based polar dispersions are seen in figure (98) and figure (99). PEG addition increases the suspension viscosity for the α -SiC/H₂O/LGG based polar dispersions. From figure (98) and figure (99) it is seen that the α -SiC/H₂O/LGG based polar dispersions exhibit a shear thinning behavior.

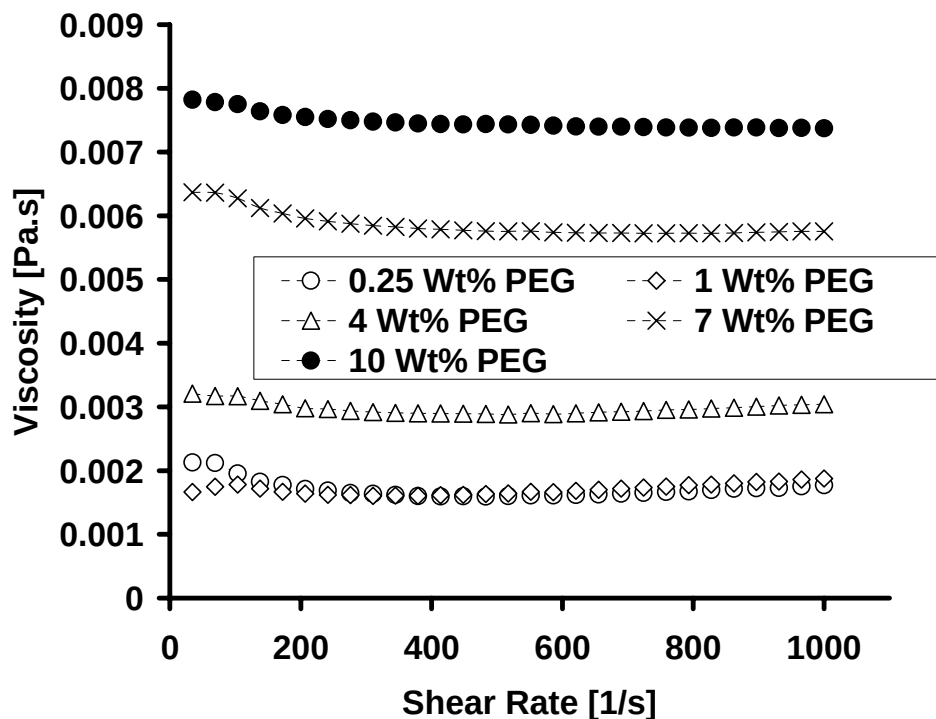


Figure 98: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/LGG based polar dispersion system at different wt% PEG

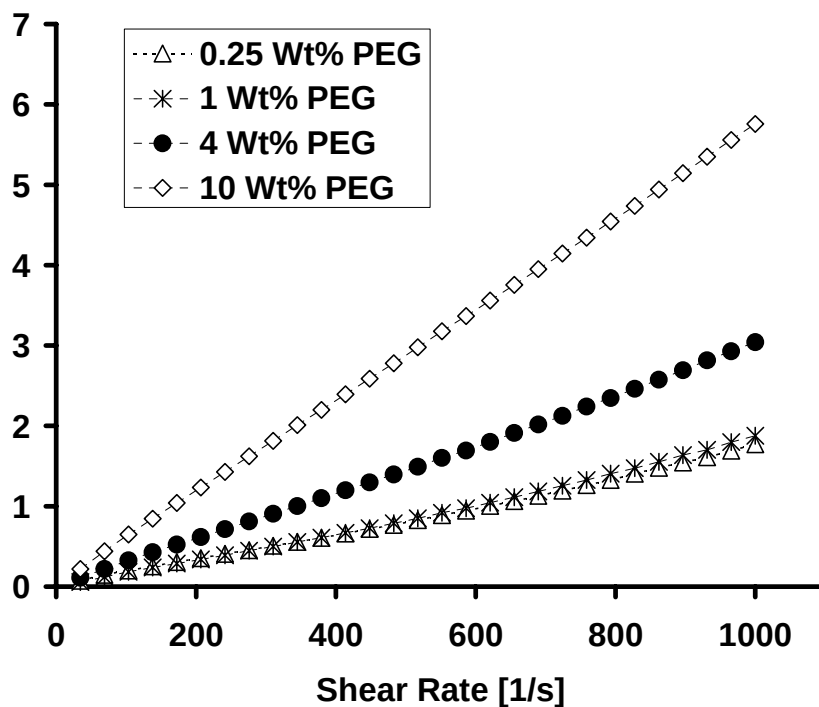


Figure 99: Experimentally determined variation of the shear stress with respect to the wt% PEG for the α -SiC/H₂O/LGG based polar dispersion system at different shear rates

4.2.4.3 Comparison of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

For the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions the rheological data obtained with respect to the PEG addition is presented in this section. Figure (100), (101) and (102) show the variation of the viscosity of the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions with respect to the amount of PEG added to the system at different shear rates of 172.4 s⁻¹, 448.3 s⁻¹ and 724.4 s⁻¹. From the figures it can be seen that the viscosity variation for the α -SiC/H₂O/ α -SiC based polar dispersions have higher viscosity values as compared to the α -SiC/H₂O/LGG based polar dispersions at the same weight percent of PEG.

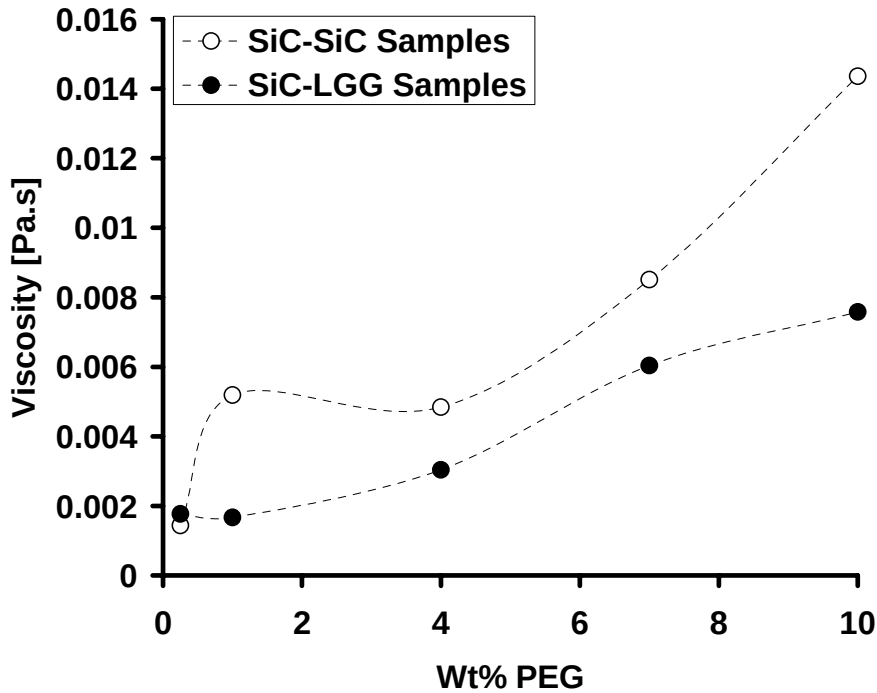


Figure 100: Experimentally determined variation of the viscosity with respect to the wt% PEG for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion systems at a shear rate of 172.4 s⁻¹

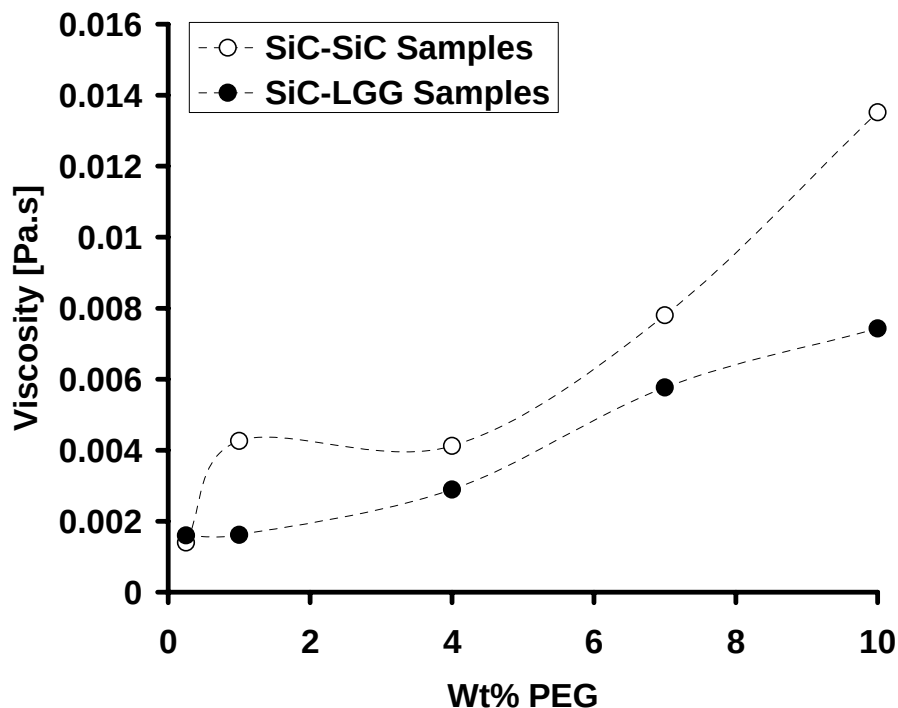


Figure 101: Experimentally determined variation of the viscosity with respect to the wt% PEG for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion systems at a shear rate of 448.3 s⁻¹

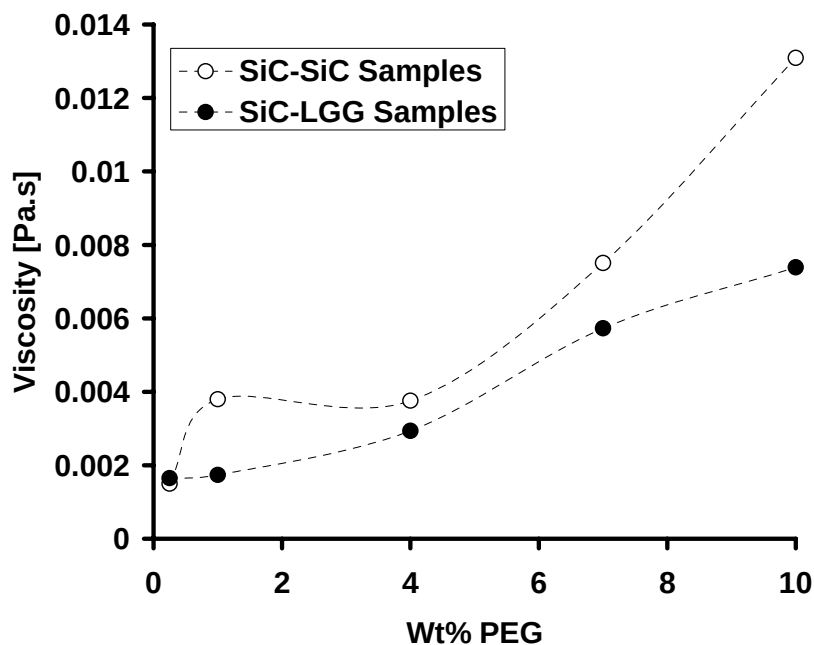


Figure 102: Experimentally determined variation of the viscosity with respect to the wt% PEG for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion systems at a shear rate of 724.1 s⁻¹

4.2.5 Determination of the Solids Loading for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

Measured amounts of H₂O and PAA-A (in the case of α -SiC/H₂O/ α -SiC suspensions) and PAA-B (in the case of α -SiC/H₂O/LGG suspensions) are taken in a beaker and placed on a hot stirrer till the polymer dissolves in the solvent. This is followed by the addition of measured amounts of Duramax B-1020 and PEG and the system is placed on a stirrer again until the binder and plasticizer dissolves in the solvent. This is followed by the addition of the α -SiC nanoparticles and the slurry is placed on a rotating mill for 24 hours at an rpm of 60 with alumina milling media. For one set of samples, LGG is added after this period. The samples are placed once again on the rotating mill for another 24 hours with an rpm of 60. For the samples with LGG no milling media are added in the process. This is followed by placing the samples on the Cole-Parmer ultrasonic bath for 6 hours and followed by the Branson ultrasonic bath for 30 minutes. The required suspension is thus prepared and the viscosity measurements are carried out. For the viscosity measurements the temperature for the shear flow measurements is set to 298 K. The slurry is pre-sheared at 800 s⁻¹ and allowed to rest for 60 seconds before the rheological analysis is recorded. The measurements are carried out from a shear rate of 0.001 to 1000 s⁻¹. The relative viscosity of the slurry is calculated as the ratio of the slurry viscosity to that of the solvent (in this case H₂O) at the same temperature. The viscosity of H₂O is calculated using the equation (69).

4.2.5.1 α -SiC/H₂O/ α -SiC Based Polar Dispersions

For the α -SiC/H₂O/ α -SiC based polar dispersions the rheological data obtained with respect to the solids loading of the system is presented in this section. Figure (103) is the variation of the viscosity of the α -SiC/H₂O/ α -SiC based polar dispersions with respect to the solids loading of the system at different shear rates. It is seen that with an increase in the solids loading initially there is a small increment in the viscosity but after a while the viscosity increases exponentially with small changes in the solids loading. The solids loading value when the viscosity values reach infinity is the one in which the α -SiC/H₂O/ α -SiC based polar dispersions has the maximum solids loading at a minimum viscosity value. The calculations for the maximum solids loading for the α -SiC/H₂O/ α -SiC based polar dispersions are presented in the later sections of the dissertation.

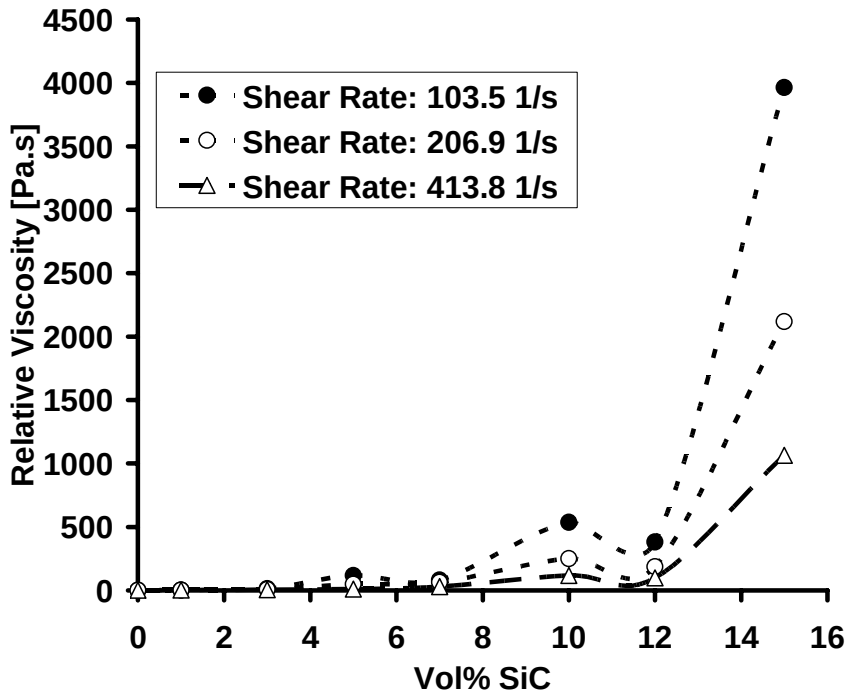


Figure 103: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion system at different shear rates

Figure (104) and figure (105) show the variation of viscosity with respect to shear rate and the variation of shear stress with respect to shear rate at different solids loading amounts added for the α -SiC/H₂O/ α -SiC based polar dispersions. It can also be seen that with an increase in the solids loading there is also an increase in the viscosity values in the α -SiC/H₂O/ α -SiC based polar dispersions. From figure (104) and figure (105) it is seen that the α -SiC/H₂O/ α -SiC based polar dispersions have a shear thinning behavior

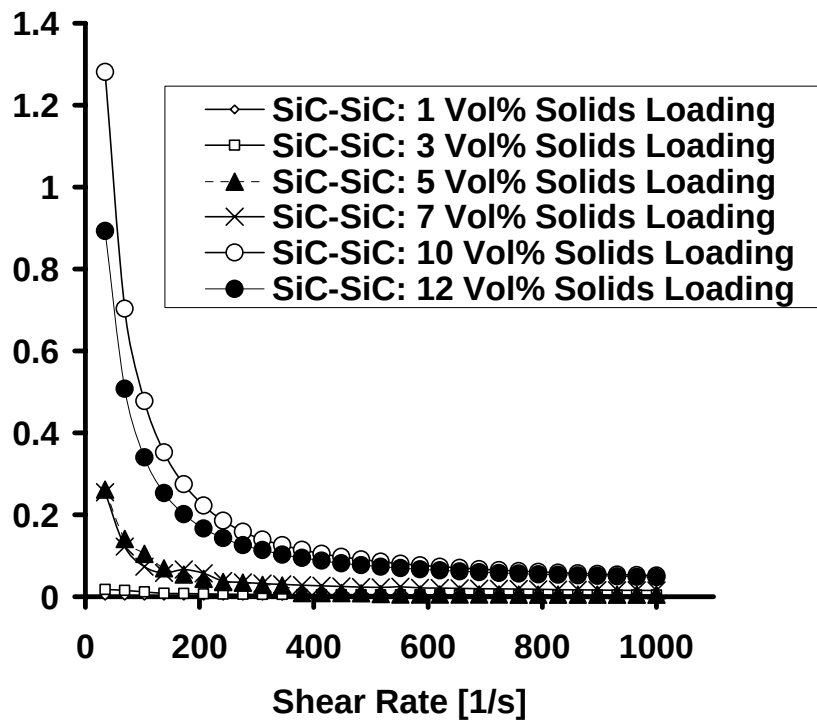


Figure 104: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system at different solids loading

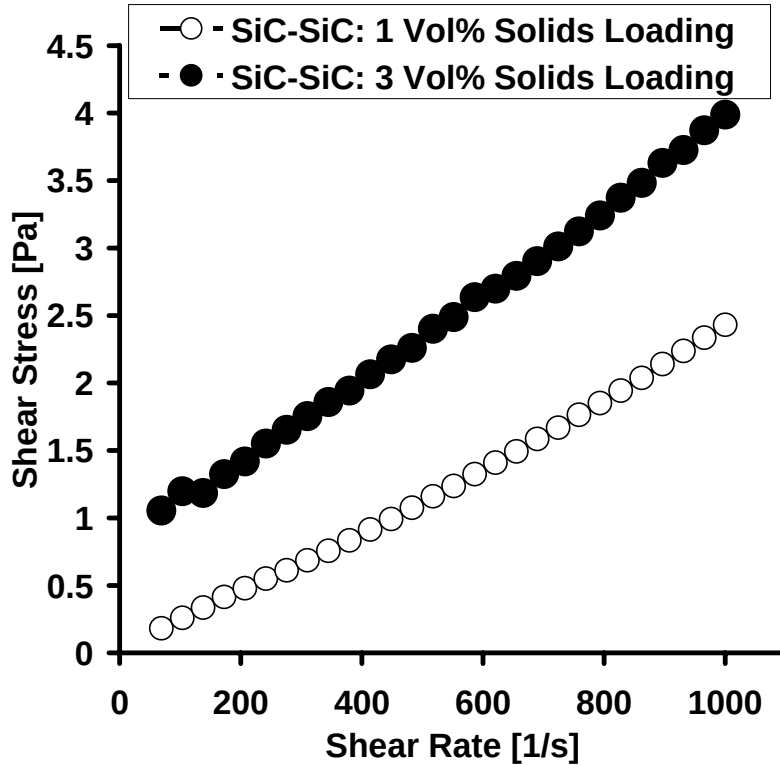


Figure 105: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system at different solids loading

4.2.5.2 α -SiC/H₂O/LGG Based Polar Dispersions

The rheological data obtained with respect to the solids loading for the α -SiC/H₂O/LGG based polar dispersions is presented in this section. The variation of the viscosity of the α -SiC/H₂O/LGG based polar dispersions with respect to the solids loading of the system at different shear rates is seen in figure (106). At first an increment of viscosity with an increase in the solids loading is minimal but after certain solids loading the viscosity increases exponentially with small changes in the solids loading. The solids loading value where the viscosity values reach infinity is the one in which the α -SiC/H₂O/LGG based polar dispersions has the maximum solids loading at a minimum viscosity value. The mathematical calculations and equation fitting curves for the maximum solids loading for

the α -SiC/H₂O/LGG based polar dispersions are presented in the later sections of the dissertation.

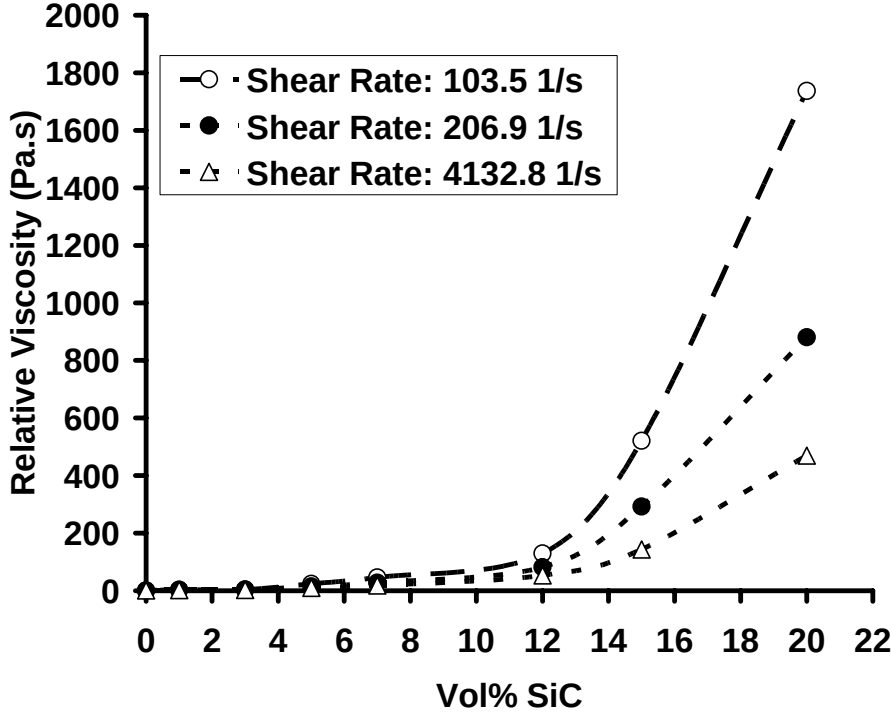


Figure 106: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/LGG based polar dispersion system at different shear rates

The variation of viscosity with respect to shear rate and the variation of shear stress with respect to shear rate at different solids loading amounts added for the α -SiC/H₂O/LGG based polar dispersions are seen in figure (107) and figure (108). As expected with an increase in the solids loading there is also an increase in the viscosity values in the α -SiC/H₂O/LGG based polar dispersions. The α -SiC/H₂O/ α -SiC based polar dispersions also tend to thin under applied shear as seen in figure (107) and figure (108).

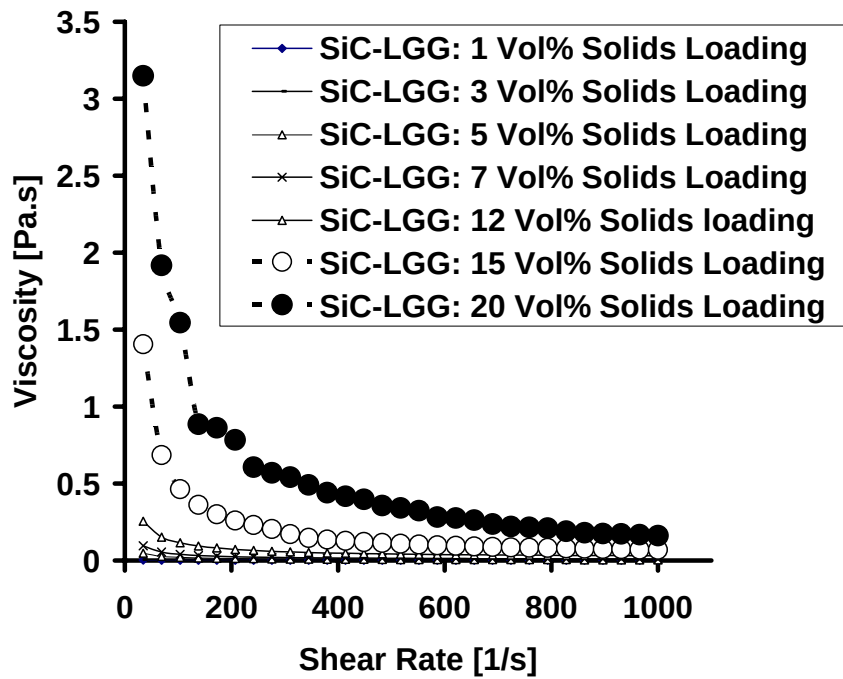


Figure 107: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/LGG based polar dispersion system at different solids loading

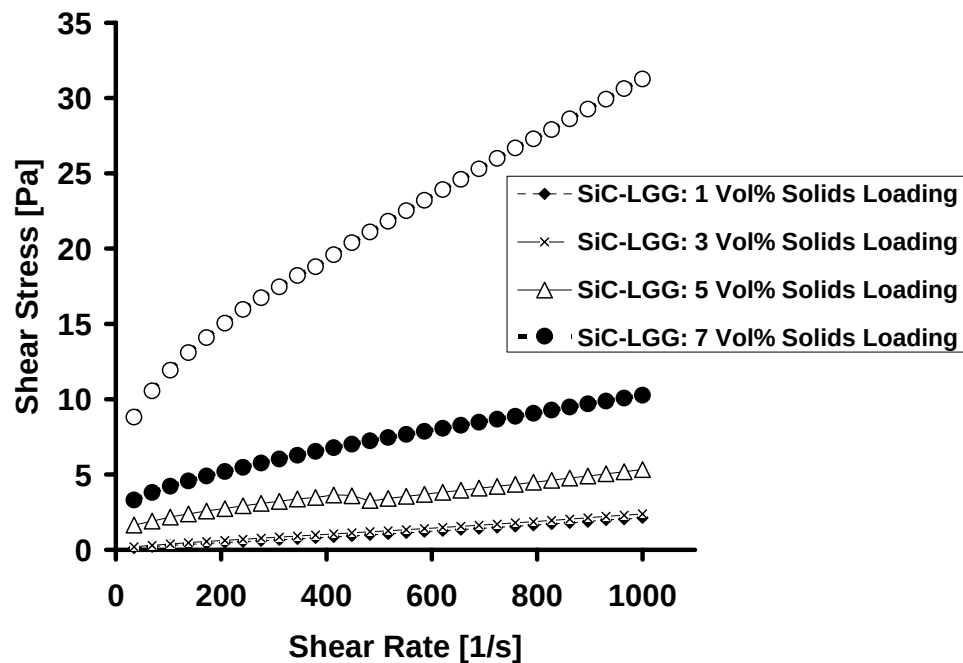


Figure 108: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/LGG based polar dispersion system at different solids loading

In this section the focus is on the α -SiC/H₂O/ α -SiC (control) based polar dispersions. The rheological data obtained with respect to the solids loading of the system is presented in this section as well. Figure (109) is the variation of the viscosity of the α -SiC/H₂O/ α -SiC (control) based polar dispersions with respect to the solids loading of the system at different shear rates. The viscosity is initially seen to have small increases with increasing solids loading. However after a certain point large increments in the viscosity are seen for small changes in the solids loading. The solids loading value where the suspension viscosity becomes infinity is the one in which the α -SiC/H₂O/ α -SiC (control) based polar dispersions has the maximum solids loading at a minimum viscosity value. The calculations for the maximum solids loading for the α -SiC/H₂O/ α -SiC (control) based polar dispersions are presented in the following sections.

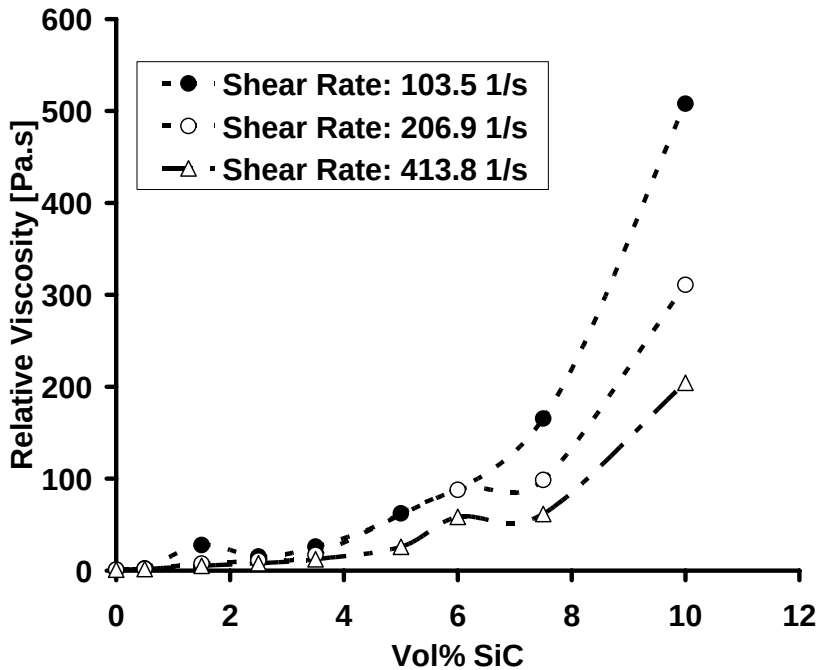


Figure 109: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion system (control) at different shear rates

Figure (110) and figure (111) show the variation of viscosity with respect to shear rate and the variation of shear stress with respect to shear rate at different solids loading amounts added for the α -SiC/H₂O/ α -SiC (control) based polar dispersions. There is an increase in the viscosity of the samples with solids loading in the α -SiC/H₂O/ α -SiC (control) based polar dispersions. From figure (110) and figure (111) it is seen that the α -SiC/H₂O/ α -SiC (control) based polar dispersions have a shear thinning behavior.

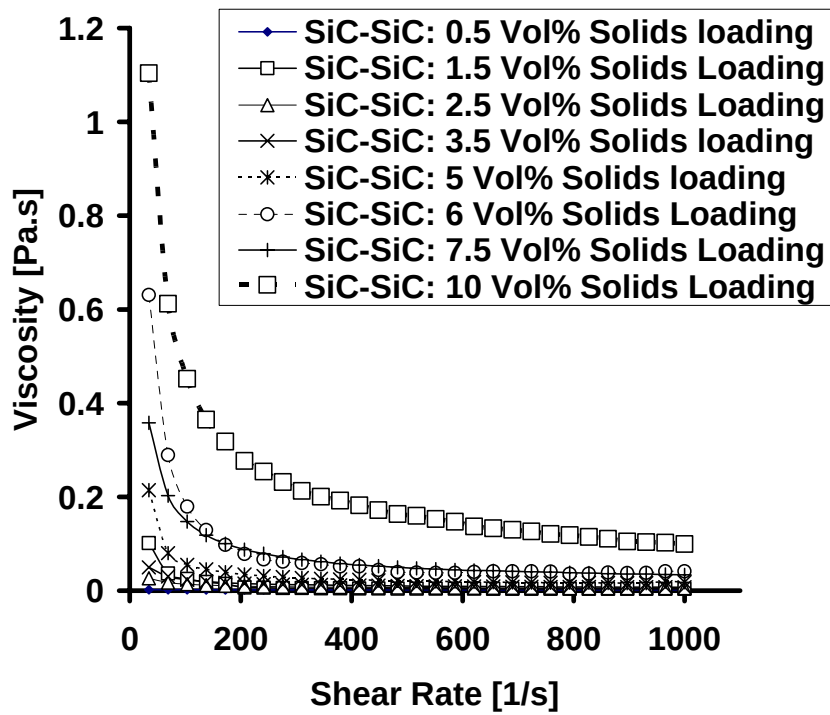


Figure 110: Experimentally determined variation of the viscosity with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system (control) at different solids loading

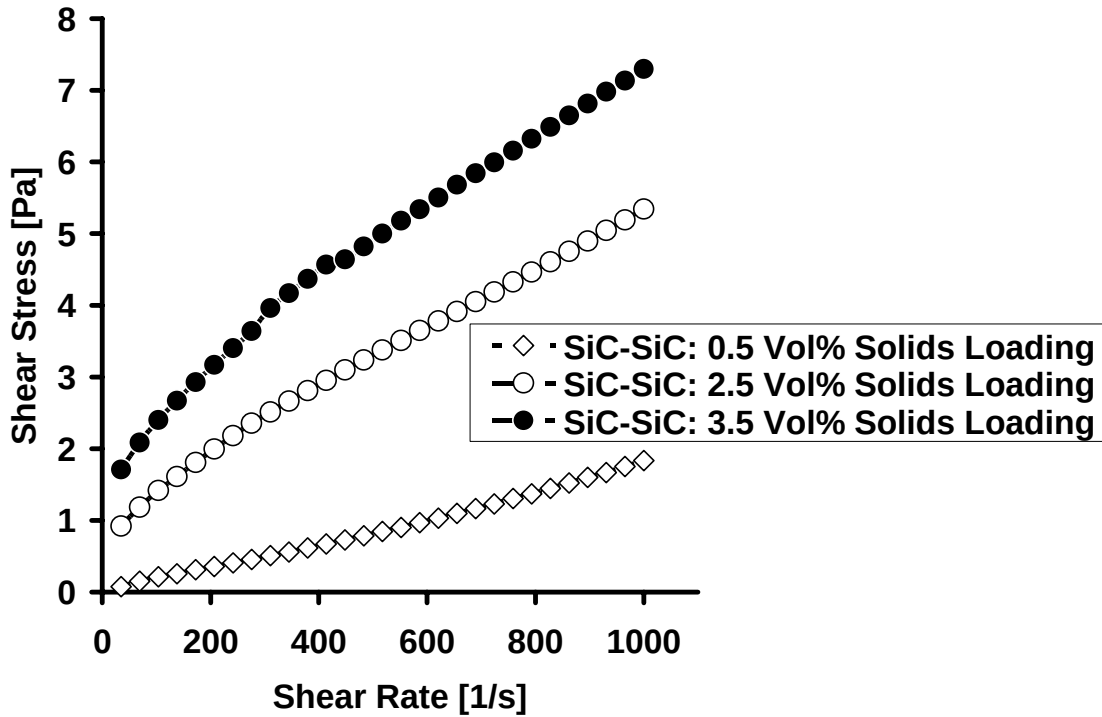


Figure 111: Experimentally determined variation of the shear stress with respect to the shear rate for the α -SiC/H₂O/ α -SiC based polar dispersion system (control) at different solids loading

4.2.5.3 Comparison of α -SiC/ H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

For the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions the rheological data obtained with respect to the variations in the solids loading of the system is presented in this section. Figure (112), (113) and (114) show the variation of the viscosity of the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based polar dispersions with respect to the solids loading of the system at different shear rates of 103.5 s^{-1} , 206.9 s^{-1} and 413.8 s^{-1} . From the figures it can be seen that the viscosity variation for the α -SiC/H₂O/ α -SiC based polar dispersions have higher viscosity values as

compared to the α -SiC/H₂O/LGG based polar dispersions at the same solids loading value.

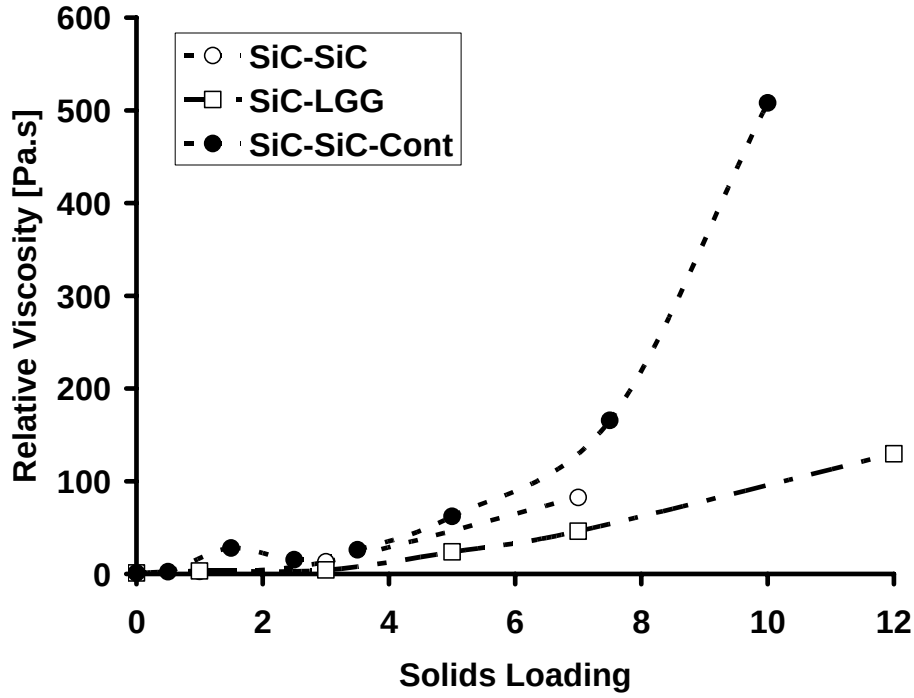


Figure 112: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion systems at a shear rate of 103.5 s^{-1}

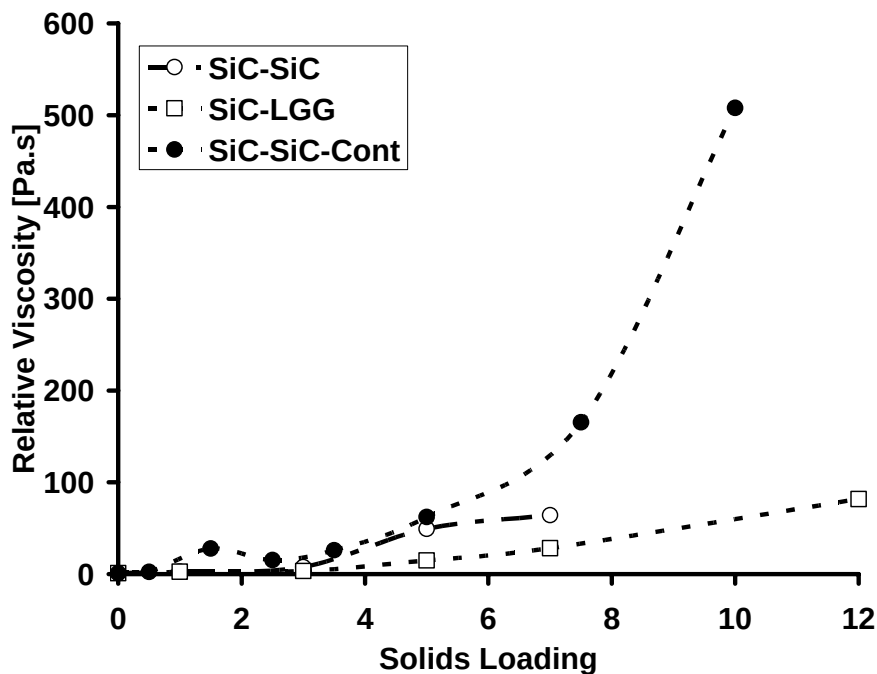


Figure 113: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion systems at a shear rate of 206.9 s⁻¹

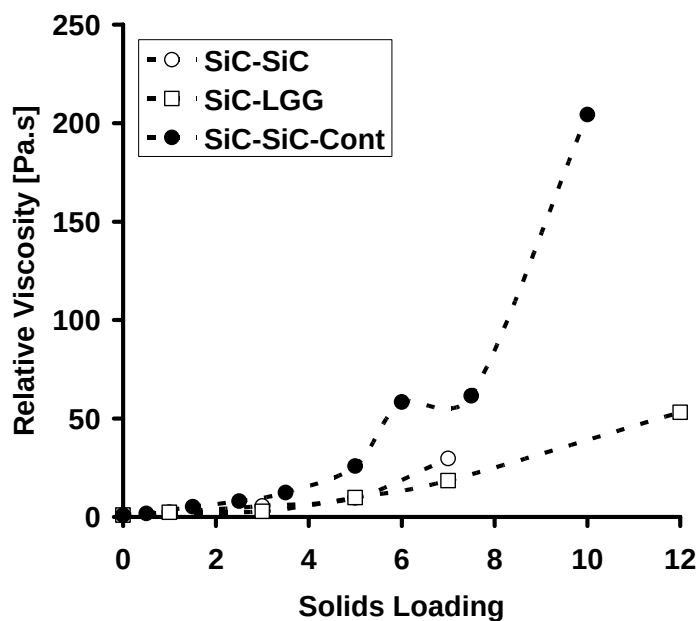


Figure 114: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion systems at a shear rate of 413.8 s⁻¹

4.2.6 Determination of the Maximum Solids Loading for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

For the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions the viscosity of the dispersions depends on the solids loading and the viscosity value reaches infinity at a maximum solids loading value denoted by ' ϕ_m '. The maximum packing for the system or its solids loading depend on the particle shape and size constituting the packing. In the case when the maximum solids loading situation is arrived at, the α -SiC nanoparticles in the α -SiC/H₂O/ α -SiC and the α -SiC and LGG particles in the α -SiC/H₂O/LGG based polar dispersions are so close to each other that we can consider the separation distance between the particles to be negligible. [4] The Krieger-Dougherty equation for determination of the maximum solids loading for a suspension is given by equation (70).

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \quad (70)$$

where, ' ϕ ' is the maximum solids loading and ' $[\eta]$ ' is the intrinsic viscosity.

However, Dabak et al proposed another model which is given by equation (71). [126]

$$\eta_r = \left(1 + \frac{[\eta]\phi_m\phi}{n(\phi_m - \phi)}\right)^n \quad (71)$$

where, ' n ' is the suspension dependent parameter and ' $[\eta]$ ' is the intrinsic viscosity.

It is seen that considering the various equations relating the viscosity of the suspension to its concentration a basic form of the equations can be arrived at as given by equation (72).

$$1 - \eta_r^{-1/2} = f(\phi) \quad (72)$$

where, ‘ n ’ is equal to two for most high-shear applications.

On further investigation it is found that this is a linear plot and hence the term on the right hand side of equation (72) can be modified to the form as seen in equation (73). [126]

$$1 - \eta_r^{-1/2} = m\phi + C \quad (73)$$

where, ‘ m ’ is the slope of the line and ‘ C ’ is a constant.

In the case for the maximum solids loading, the relative viscosity of the dispersion becomes infinity and hence equation (73) becomes equation (74).

$$m\phi_m + C = 1 \quad (74)$$

On solving equation (74), we can calculate the maximum solids loading as given by equation (75).

$$\phi_m = \frac{1-C}{m} \quad (75)$$

In the following sections the rheological data obtained from the experimentation are fit to these equations (termed as the ‘Liu’ model) in order to calculate the maximum solids loading.

4.2.6.1 α -SiC/H₂O/ α -SiC Based Polar Dispersions

The determination of the maximum solids loading based on the rheological data obtained for the α -SiC/H₂O/ α -SiC based polar dispersions system is presented in this section. It is observed that with an increase in the solids loading initially there is a small increment in the viscosity but after a while the viscosity increases exponentially with small changes in the solids loading. The Kreiger-Dougherty fit as seen in equation (70) was tried to be plotted for the samples, however the fitting did not seem to be correct and hence they were not used for the maximum solids loading calculations. Figures (115), (116) and (117) are the best fit curves for the variation of the viscosity of the α -SiC/H₂O/ α -SiC based polar dispersions with respect to the solids loading of the system at shear rates of 103.6 s⁻¹, 206.9 s⁻¹ and 413.8 s⁻¹ respectively. From the best fitting curves the maximum solids loading for the α -SiC/H₂O/ α -SiC based polar dispersions at the various shear rates were obtained to be 16.7 vol% solids loading.

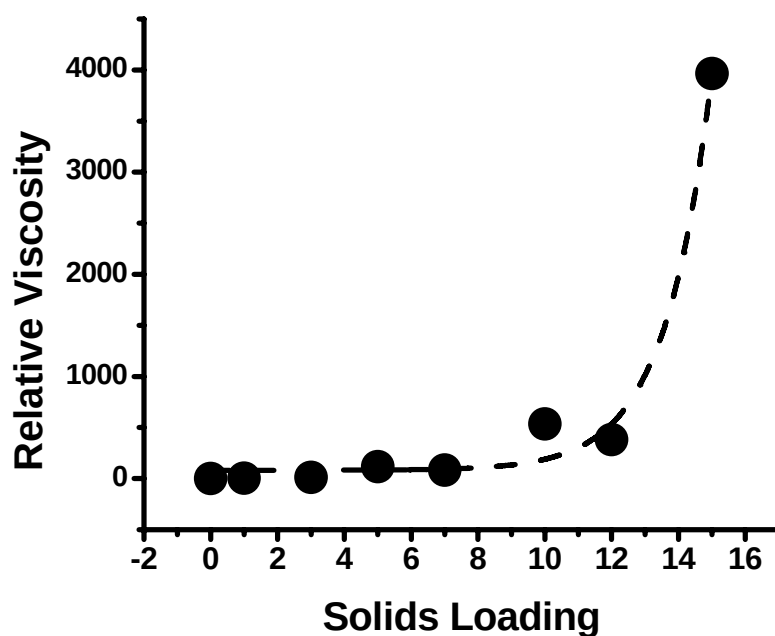


Figure 115: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion system at a shear rate of 103.6 s^{-1}

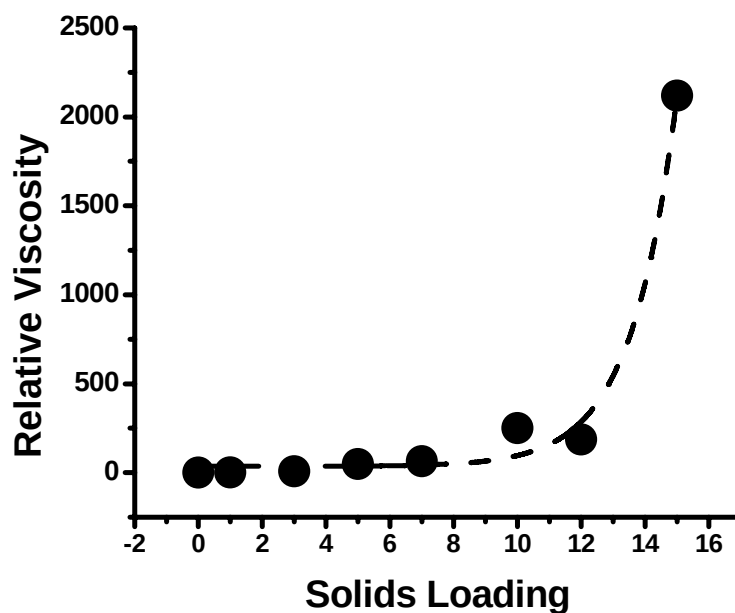


Figure 116: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion system at a shear rate of 206.9 s^{-1}

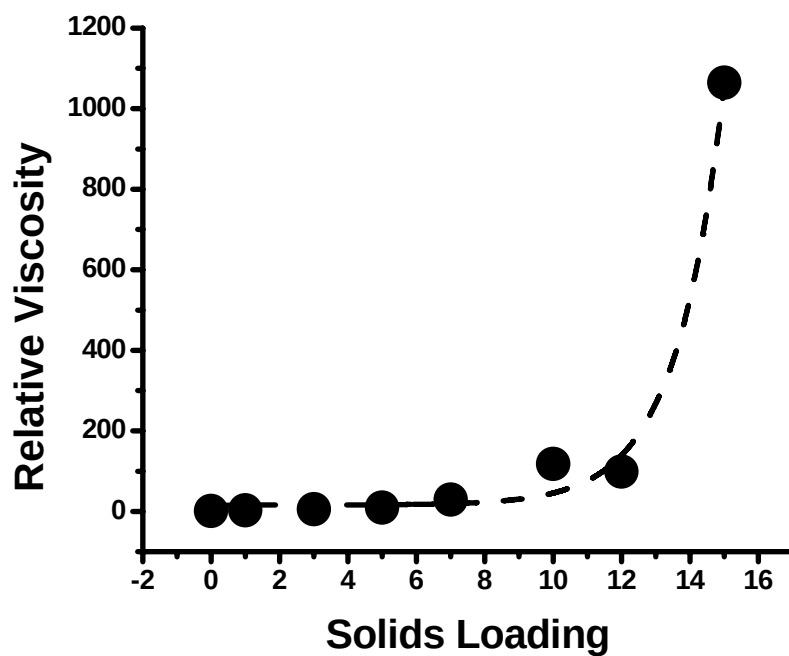


Figure 117: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion system at a shear rate of 413.8 s^{-1}

However, the plots made using equation (73) for the α -SiC/H₂O/ α -SiC based polar dispersions is shown in figure (118). An expanded version of figure (118) is seen in figure (119). From the data using the best fitting curve it is seen that the maximum solids loading for the α -SiC/H₂O/ α -SiC based polar dispersions is at 17 vol% solids loading.

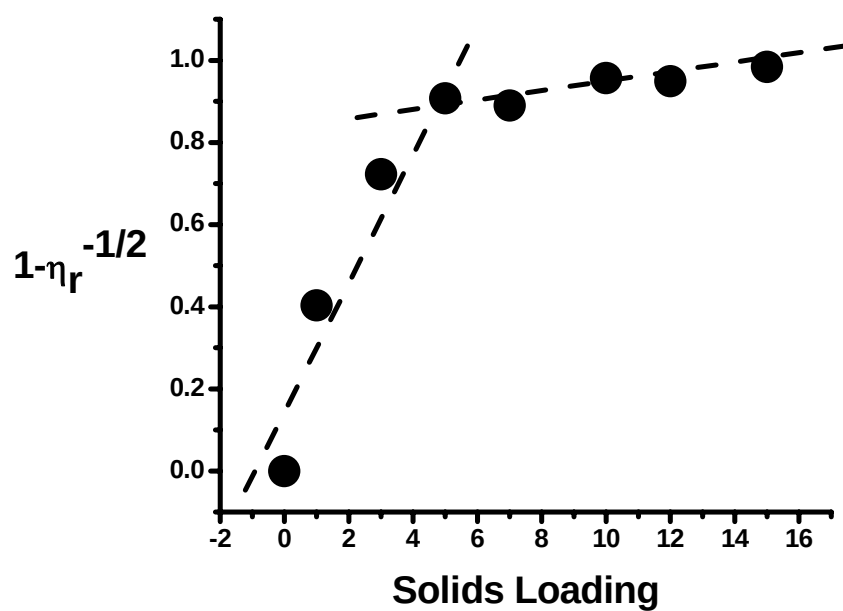


Figure 118: Calculation of the maximum solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion systems at a shear rate of 103.6 s⁻¹ using equation (73)

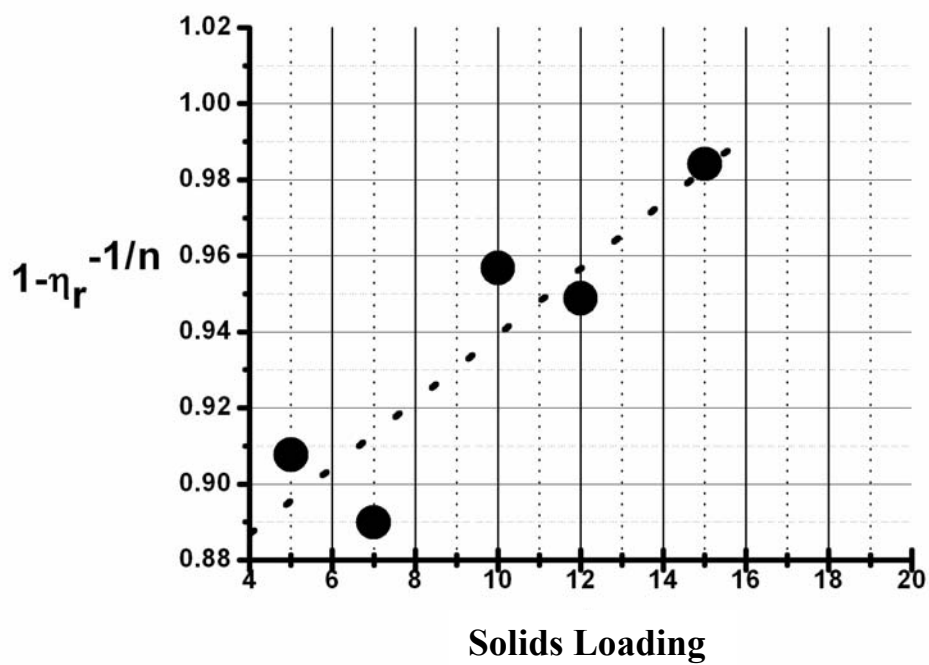


Figure 119: Expanded version of figure (118)

4.2.6.2 α -SiC/H₂O/LGG Based Polar Dispersions

For the α -SiC/H₂O/LGG based polar dispersions the determination of the maximum solids loading based on the rheological data obtained for the system is presented in this section. Initially there is a small increment in the viscosity but after a while the viscosity increases significantly with small changes in the solids loading. The Krieger-Dougherty fit as seen in equation (70) could not be plotted for the samples, since the fitting did not seem to be correct and hence they were not used for the maximum solids loading calculations. It is also understood that the Krieger-Dougherty fit works well only for the mono-sized spheres calculations. Figures (120), (121) and (122) are the best fit curves for the variation of the viscosity of the α -SiC/H₂O/LGG based polar dispersions with respect to the solids loading of the system at shear rates of 103.6 s⁻¹, 206.9 s⁻¹ and 413.8 s⁻¹ respectively. From the fitting curves the maximum solids loading for the α -SiC/H₂O/LGG based polar dispersions at the various shear rates were obtained to be 22.1 vol% solids loading.

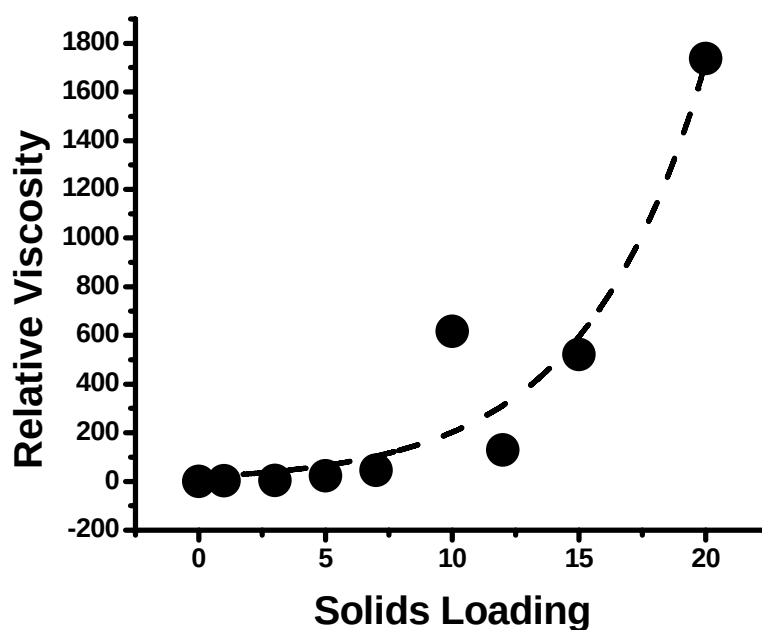


Figure 120: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/LGG based polar dispersion system at a shear rate of 103.6 s^{-1}

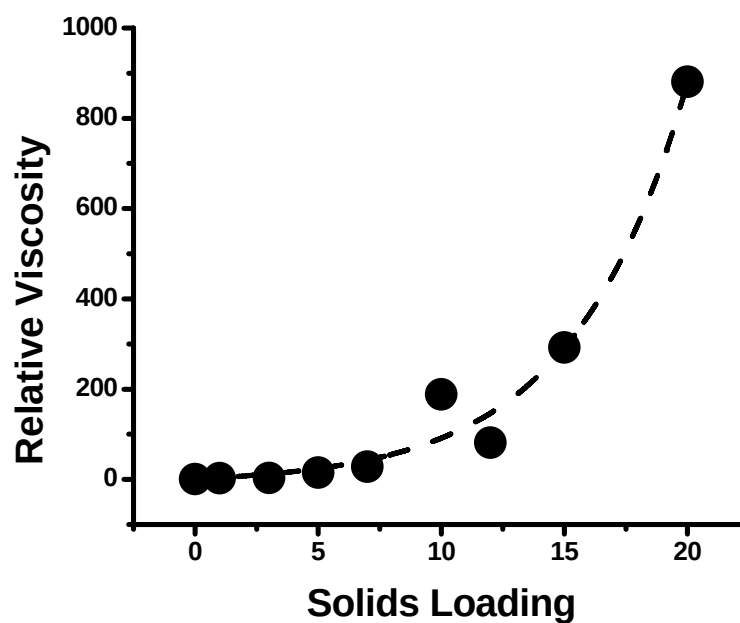


Figure 121: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/LGG based polar dispersion system at a shear rate of 206.9 s^{-1}

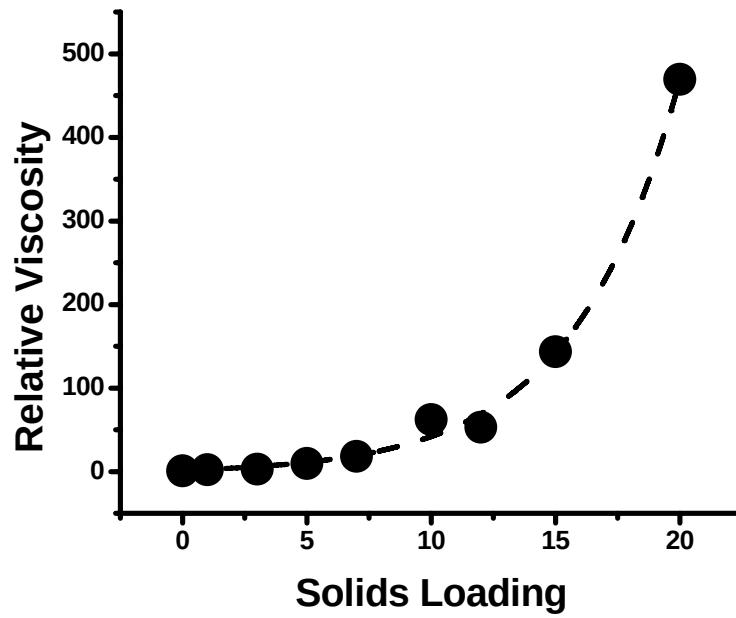


Figure 122: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/LGG based polar dispersion system at a shear rate of 413.8 s⁻¹

Also, the graphs made using equation (73) for the α -SiC/H₂O/LGG based polar dispersions is shown in figure (123). An expanded version of figure (123) is seen in figure (124). From the data it is seen that the maximum solids loading for the α -SiC/H₂O/LGG based polar dispersions is at 20 vol% solids loading.

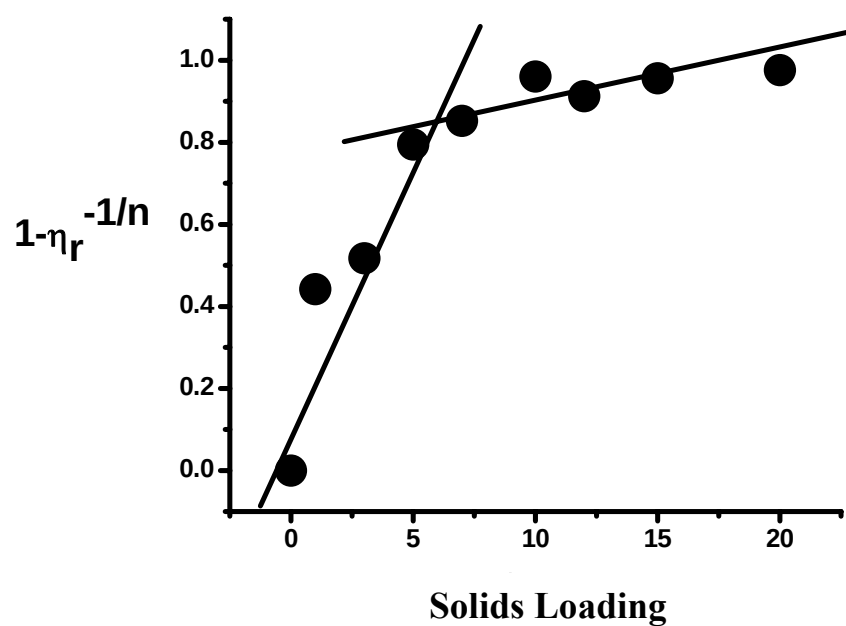


Figure 123: Calculation of the maximum solids loading for the α -SiC/H₂O/LGG based polar dispersion systems at a shear rate of 103.9 s⁻¹ using equation (73)

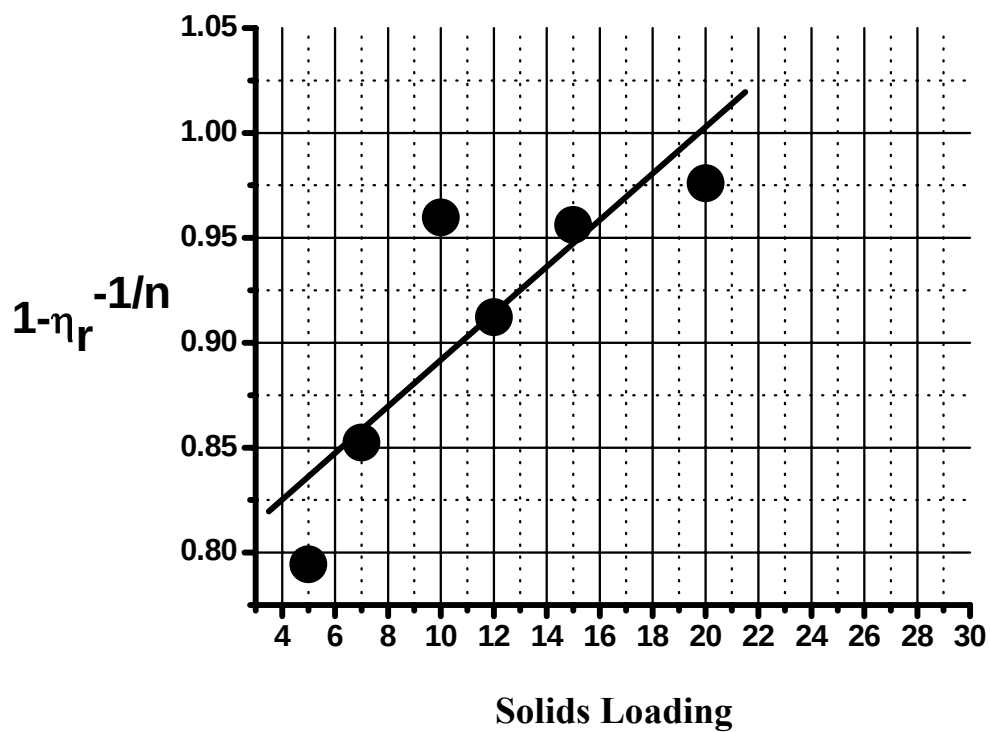


Figure 124: Expanded version of figure (123)

In this section the focus is on the α -SiC/H₂O/ α -SiC (control) based polar dispersions used for the determination of the maximum solids loading based on the rheological data obtained for the system. For these systems too it is seen that initially for an increase in the solids loading there is a small increment in the viscosity but after a while the viscosity increases exponentially with small changes in the solids loading. The Krieger-Dougherty fit as seen in equation (70) was tried to be plotted for the samples, however the fitting did not seem to be correct and hence it was not used for the maximum solids loading calculations. Figures (125), (126) and (127) are the best fit curves for the variation of the viscosity of the α -SiC/H₂O/ α -SiC (control) based polar dispersions with respect to the solids loading of the system at shear rates of 103.6 s⁻¹, 206.9 s⁻¹ and 413.8 s⁻¹ respectively. From the fitting curves the maximum solids loading for the α -SiC/H₂O/ α -SiC (control) based polar dispersions at the various shear rates were obtained to be 11.3 vol% solids loading.

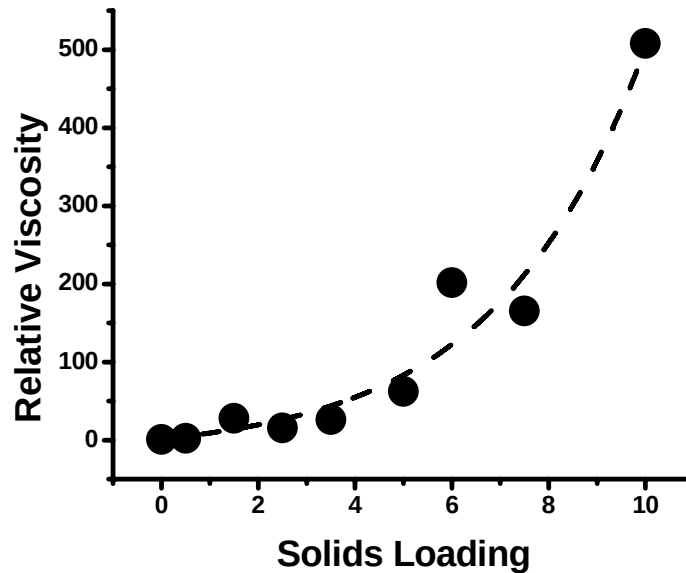


Figure 125: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion system (control) at a shear rate of 103.9 s⁻¹

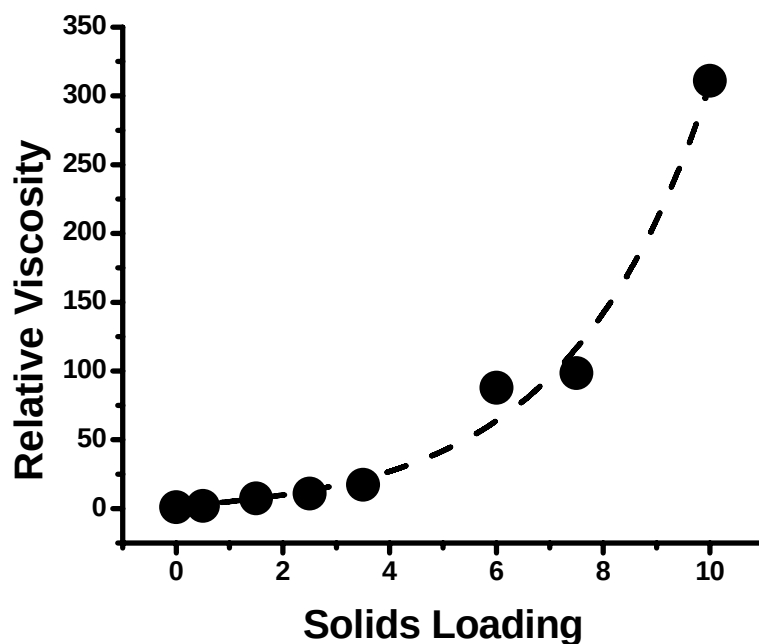


Figure 126: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion system (control) at a shear rate of 206.8 s⁻¹

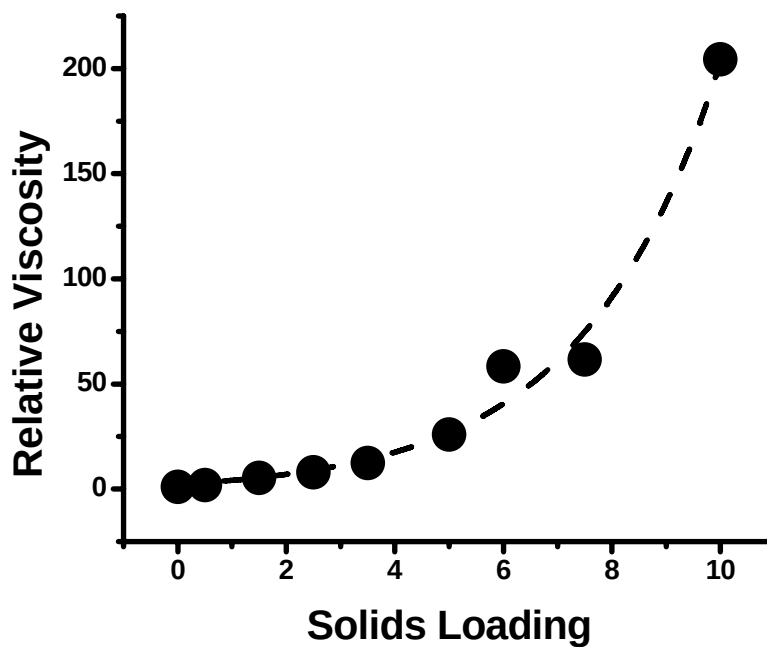


Figure 127: Experimentally determined variation of the viscosity with respect to the solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion system (control) at a shear rate of 413.8 s⁻¹

However, the plot made using equation (73) for the α -SiC/H₂O/ α -SiC (control) based polar dispersion is shown in figure (128). An expanded version of figure (128) is seen in figure (129). From the data it is seen that the maximum solids loading for the α -SiC/H₂O/ α -SiC (control) based polar dispersions is at 11 vol% solids loading.

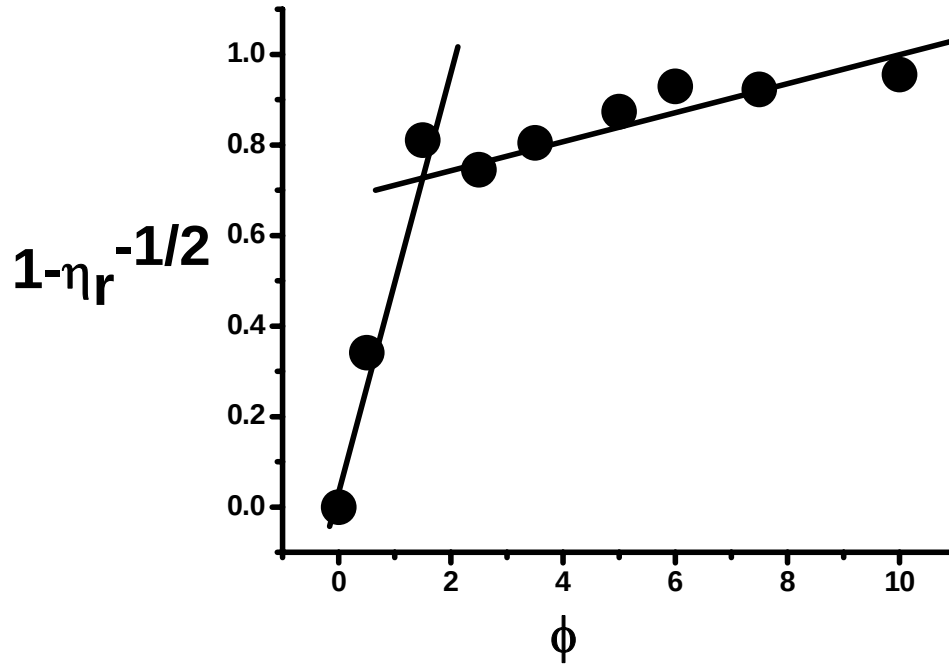


Figure 128: Calculation of the maximum solids loading for the α -SiC/H₂O/ α -SiC based polar dispersion systems (control) at a shear rate of 103.6 s⁻¹ using equation (73)

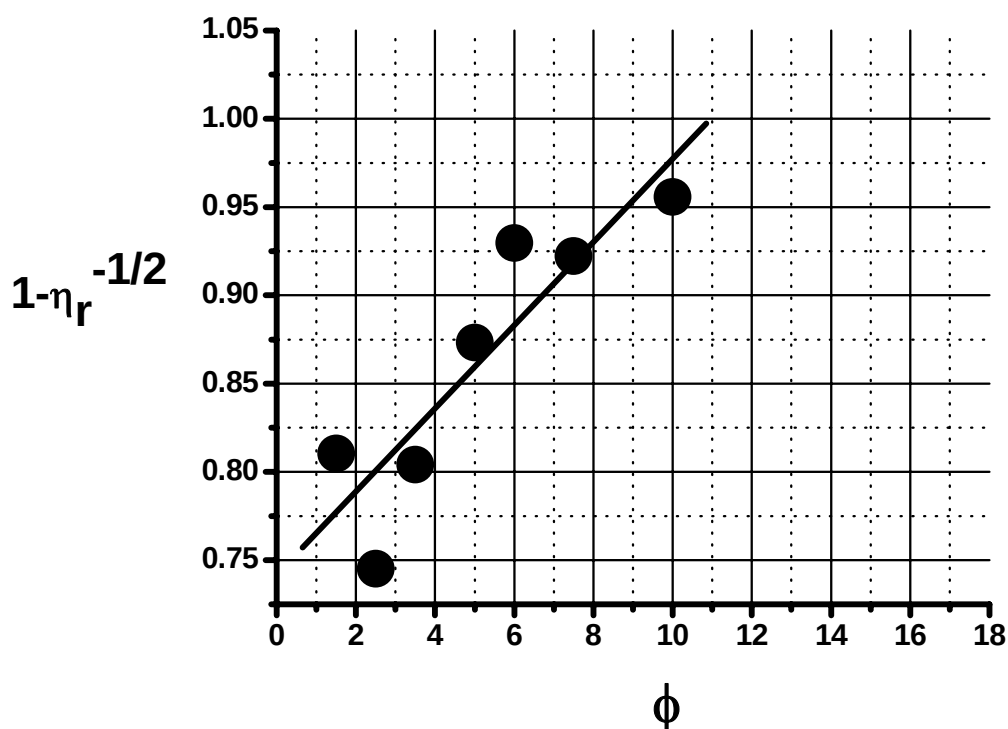


Figure 129: Expanded version of figure (128)

4.2.6.3 Comparison of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

From the solids loading data calculated for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions it is seen that there is a difference in the maximum solids loading values for the different polar solvent based systems. The maximum solids loading values for the best fit model for the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based polar dispersions were calculated to be 16.7 vol%, 22.1 vol% and 11.3 vol% respectively. The maximum solids loading values for the Liu model for the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based polar dispersions were calculated to be 17 vol%, 20 vol% and 11 vol% respectively. The Kreiger-

Dougherty model for the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based polar dispersions were found to be not suitable for these nano dispersion systems.

4.3 Casting and Fabrication of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based

Polar Dispersions

The dispersed samples of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersion prepared were cast and characterized in order to determine their green and sintered properties.

4.3.1 Determination of the Optimum Solids Loading to Cast α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

The optimum solids loading for the dispersed samples of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions was determined to be 17 vol% and 20 vol% respectively. However, depending on the final application for the dispersions, various solids loadings of the system maybe utilized as will be discussed in the later sections. In order to test the maximum solids loading that can be used for a practical experimental system, a test similar to the ASTM standard C 860-00 (2005) is carried out and the results discussed in the following section. [127]

4.3.1.1 α -SiC/H₂O/ α -SiC Based Polar Dispersions

Figure (130) shows the results of the modified test similar to the ASTM standard test with different solids loading for samples of α -SiC/H₂O/ α -SiC based polar dispersions. Depending on the final application for the dispersion the appropriate solids loading value maybe selected. It is seen that at low solids loading values the samples have low viscosity and hence can be easily cast. However, at higher solids loading values, the suspension viscosity increases and casting becomes difficult.

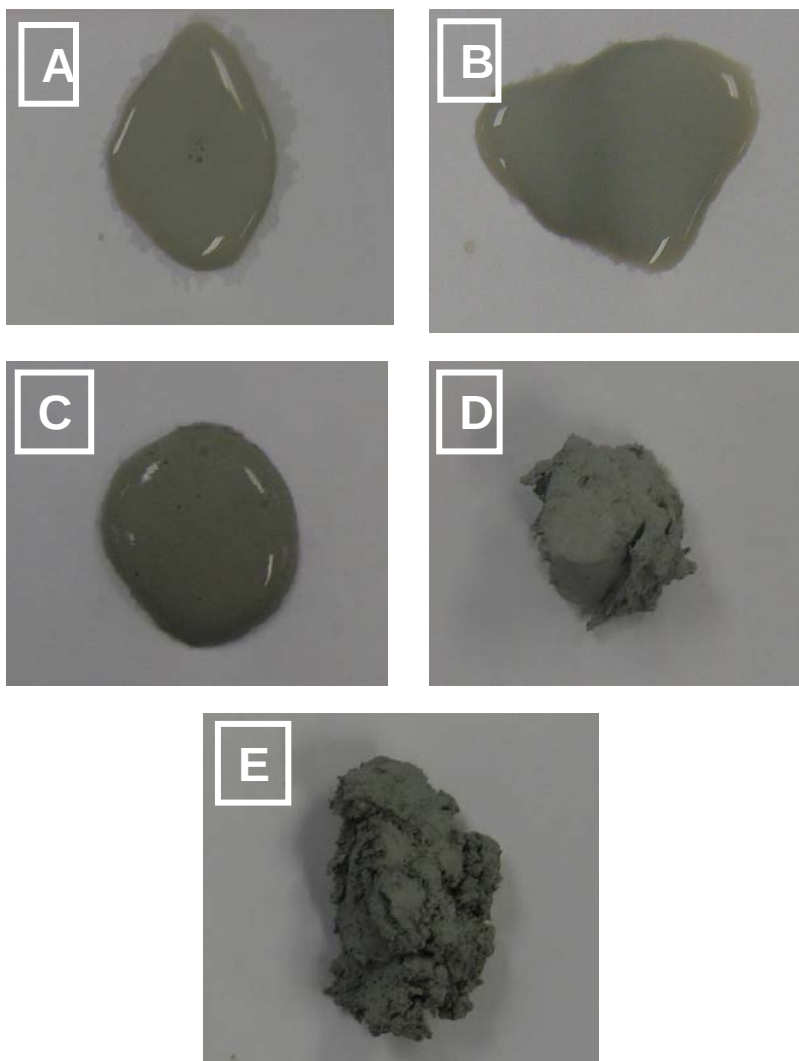


Figure 130: Samples prepared with different solids loading for casting the α -SiC/H₂O/ α -SiC based polar dispersions. (a) 1 vol% (b) 5 vol% (c) 10 vol% (d) 15 vol% and (e) 20 vol% solids loading

4.3.1.2 α -SiC/H₂O/LGG Based Polar Dispersions

The results of the modified test similar to the ASTM standard test mentioned earlier with different solids loading for the dispersed samples of α -SiC/H₂O/LGG based polar dispersions is presented in figure (131). The final application for the dispersion determines the appropriate solids loading value that needs to be selected. From the figure it is seen that at low solids loading values the samples have low viscosity. However, at

higher solids loading values, the suspension viscosity increases. An appropriate balance of the solids loading is necessary to cast samples so that they have a high solids loading but a low enough viscosity so that can be easily cast.

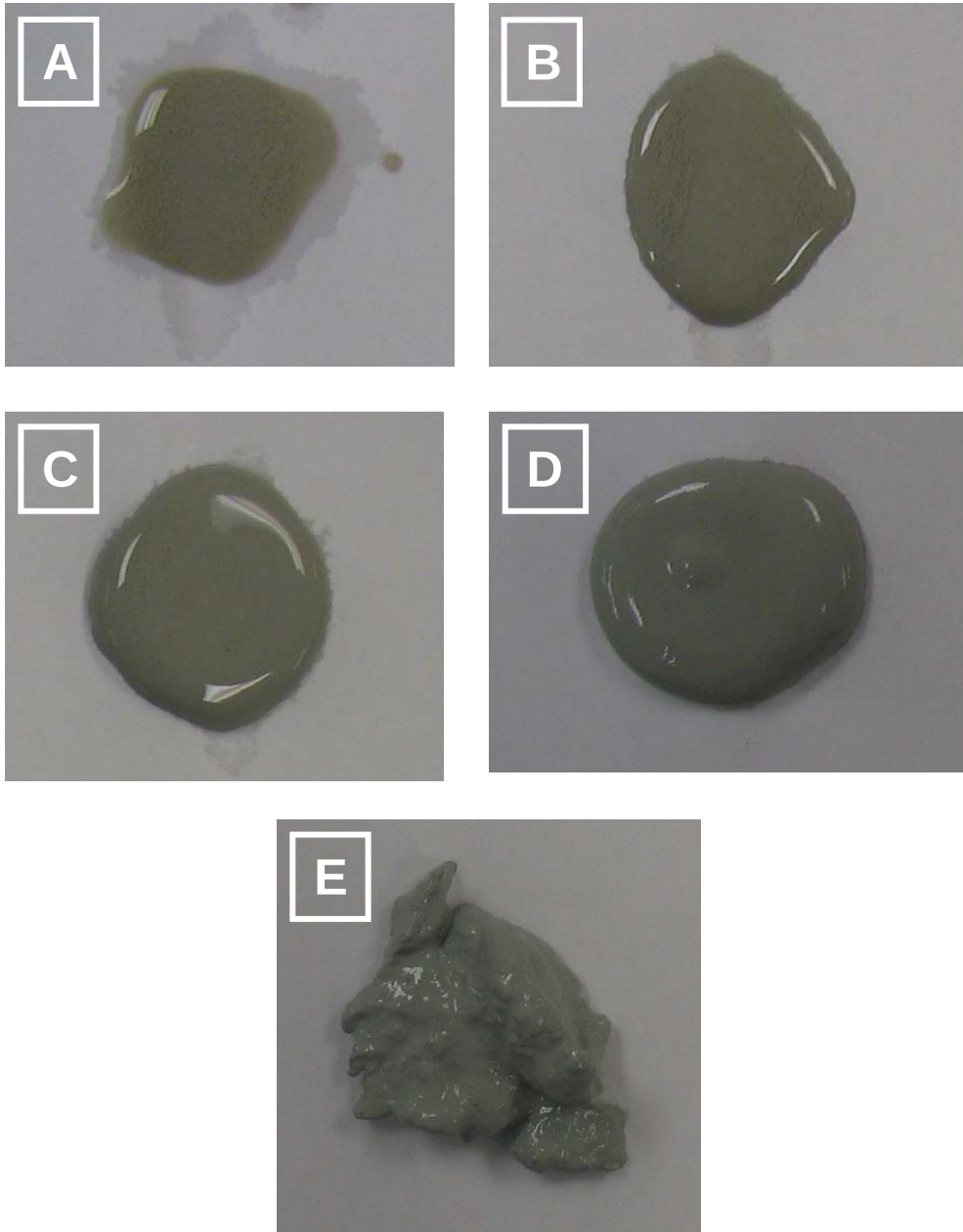


Figure 131: Samples prepared with different solids loading for casting the α -SiC/H₂O/LGG based polar dispersions. (a) 1 vol% (b) 5 vol% (c) 10 vol% (d) 15 vol% and (e) 20 vol% solids loading

The results for the modified test similar to the ASTM standard test with different solids loading for the dispersed samples of α -SiC/H₂O/ α -SiC (control) based polar dispersions are presented in figure (132). Here too depending on the final application for the

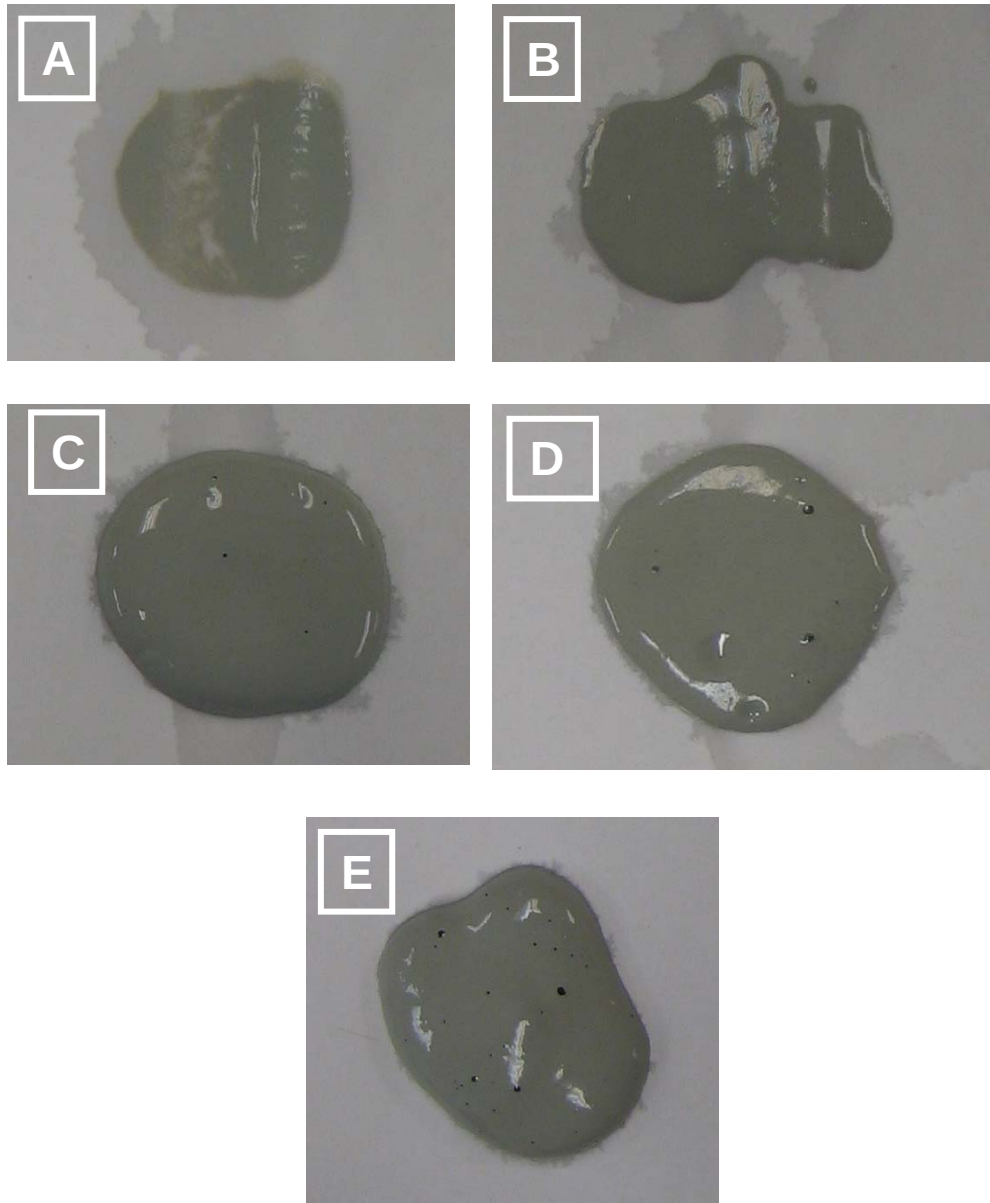


Figure 132: Samples prepared with different solids loading for casting the α -SiC/H₂O/ α -SiC (control) based polar dispersions. (a) 1 vol% (b) 5 vol% (c) 10 vol% (d) 15 vol% and (e) 20 vol% solids loading

dispersion the appropriate solids loading value is selected. It is seen that at low solids loading values the samples have low viscosity and hence can be easily cast. However, at higher solids loading values, the suspension viscosity increases and casting becomes difficult. It is seen that these samples have a much lower viscosity than the previous sample sets, which could be attributed to the fact that the solids content in these systems are lower.

4.3.1.3 Comparison of α -SiC/ H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

Depending on the solids loading of the dispersion, the viscosity of the system varies and hence, as mentioned earlier, depending on the final application of the dispersion, the appropriate solids loading can be selected. For processes that require casting a part, it is essential to have the maximum solids loading possible so that the part when fabricated will have the least shrinkage and the maximum density. However, for this the slurry characteristics must be such that it has the maximum solids loading or packing with a sufficiently low viscosity so the slurry can easily flow into the mould cavity. For other applications including targeted drug delivery (Appendix C) a thin slurry (very low viscosity) are essential. Thus, depending on the final application the appropriate solids loading value can be selected.

4.3.2 Application of α -SiC/H₂O/LGG Dispersions: Novel Porous Material

Fabrication Methodology

Here, we discuss a novel method for fabricating porous materials different from the traditional methods for fabricating porous materials as mentioned in chapter 3. This method is based on the degeneration of the biological agent leaving behind a pore in the material. Thus, the pore size produced will be of the size of the biological agent used. The biological agents chosen to generate the pore can include yeast, bacteria, protozoans, viruses and cells. This procedure can be used for different kinds of materials including metals, polymers, ceramics and nanoparticles. The preliminary results from these experimentations are presented and discussed in Appendix 2.

4.3.2.1 Concept

The novel biologically derived methodology towards fabricating porous materials is based on dispersing nanoparticles and biological agents such that the particles surround the biological agent and later subjecting the material to elevated temperatures as seen in figure (133). In this method, the pore formation is by the removal of the biological agent at elevated temperatures. The biological agent has a chemical structure containing carbon, hydrogen and oxygen atoms which gets decomposed at high temperatures producing a material with porosity. The amount of porosity will depend on the amount and size of the biological agent used. By careful control of a nanoparticle suspension the nanoparticles can be well dispersed. This can be achieved by the addition of appropriate

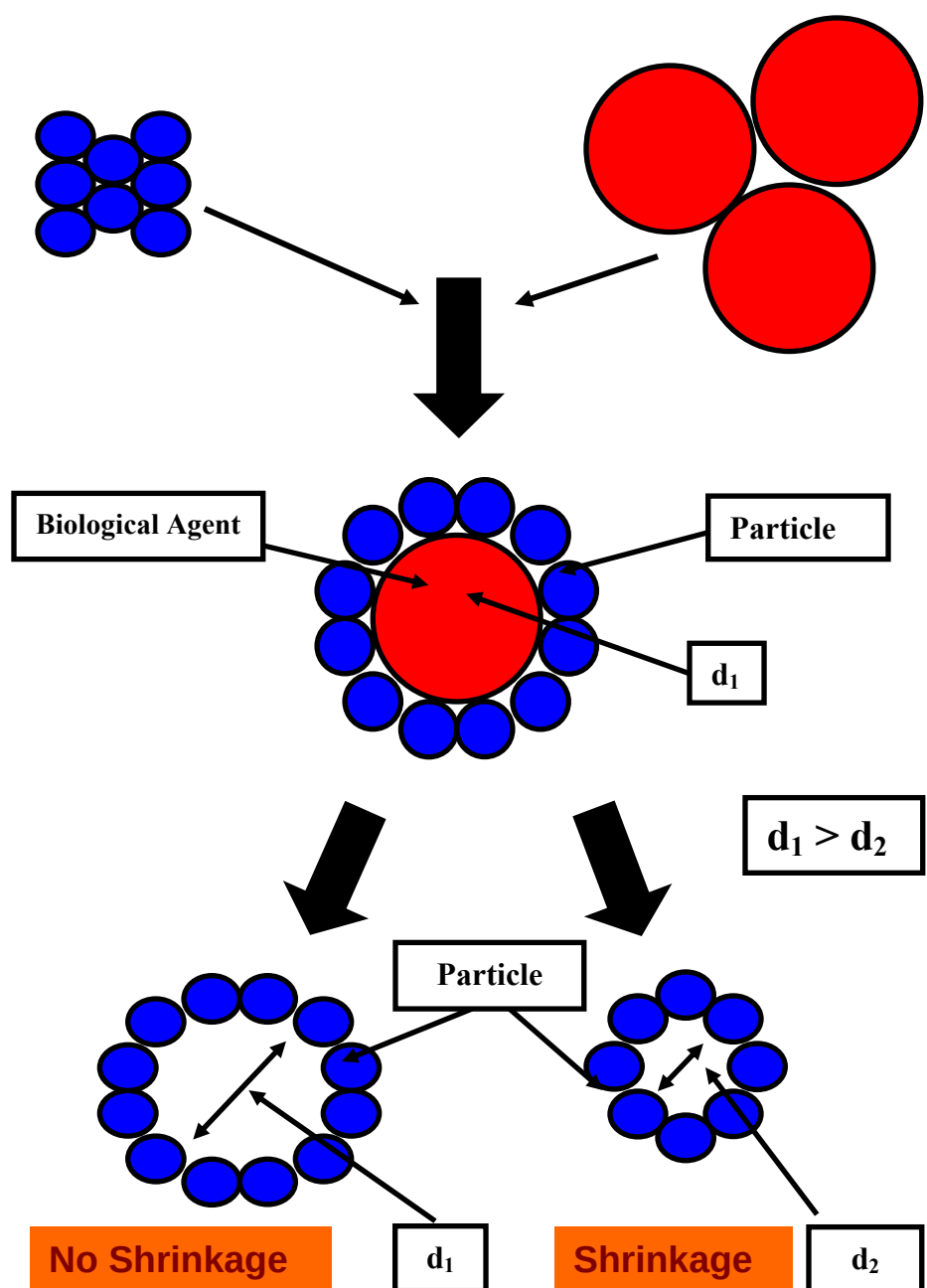


Figure 133: Schematic of novel porous material production method

dispersants and surfactants to the nanoparticle suspension in the appropriate amounts by controlling the rheology of the system. If we add the biological agent into the suspension and control the parameters appropriately we can have the nanoparticles arranged around

the biological agent. By subjecting this structure to elevated temperatures, the biological agent may be dried or vaporized producing a mixture of gases containing carbon, hydrogen and oxygen species. This leaves a pore in the material which is related to the size of the biological agent that was used. Air drying can also be done to make the porous structural material using this technique, but the only constrain with this method would be that it would take more time.

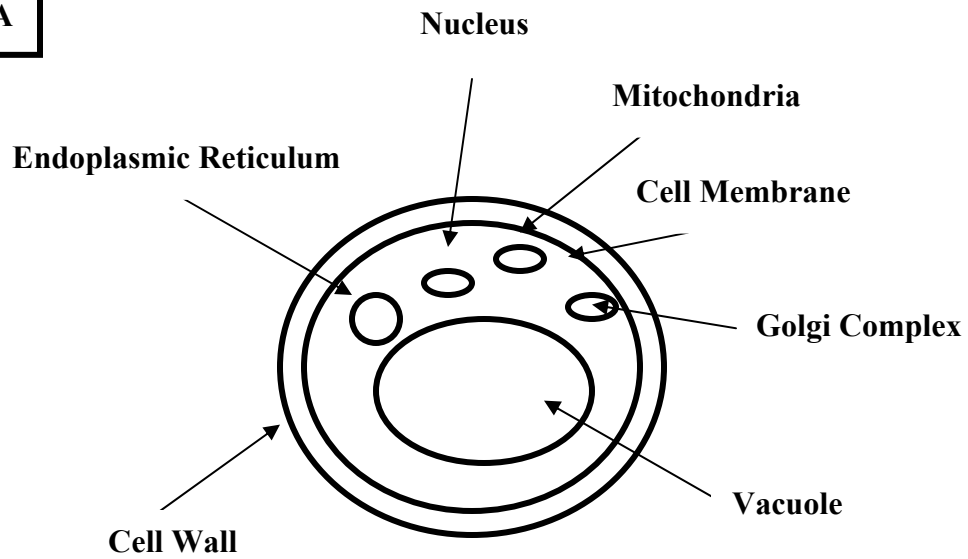
Figure (134), is a schematic of the biological agents (a) single celled fungi and (b) bacteria.

Figure (135), is a schematic showing the various shapes of the bacteria. We can take advantage of this property by choosing the right kind of bacteria needed for the specific application (depending on the shape of the porosity required in the final material).

4.3.2.2 Potential Advantages

This method of production of porous materials using biological agents may help reduce the manufacturing process complications and may reduce costs. We can save on the cost of storage and procurement of the fugitive material as the biological agent once purchased can be cultured in a agar or broth form and can be used as and when needed. The biological agents [cells, fungi, bacteria, virus protozoans] are of different size ranges. This can help control the size of the pores in the material by choosing the right combination of the biological agent and the particle size [nano or micron] of the material chosen [polymer, ceramic or metal]. The amount of porosity in the material

A



B

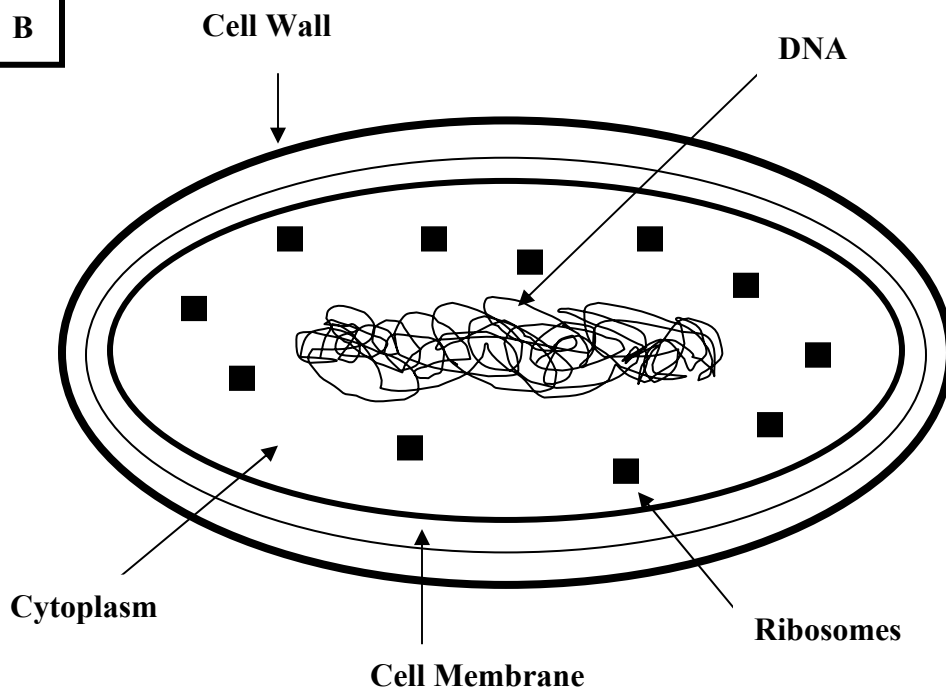


Figure 134: Schematic of (a) single celled fungi and (b) bacteria (Figures not to scale)

can be controlled by controlling the growth of the biological agent and the amount of the nutrient media and its composition. Whenever the required porosity is achieved the growth of the biological agent can be inhibited, thus leaving us with the required porosity

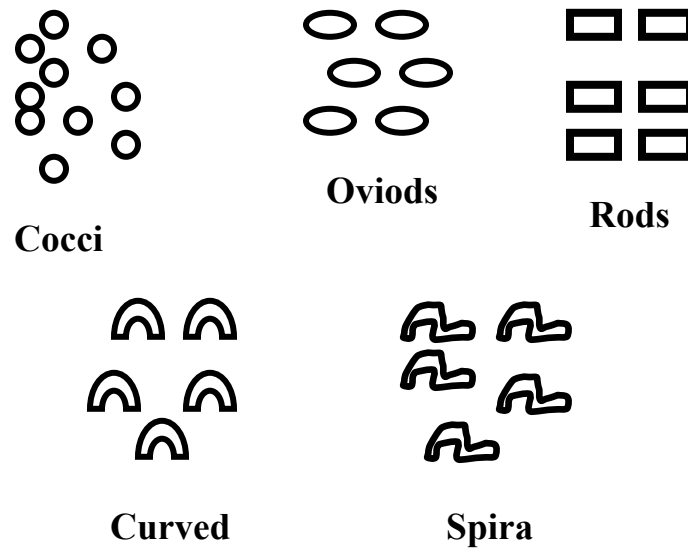


Figure 135: Schematic showing the different shapes that different bacteria possess

in the material. A random arrangement of pores in the structural material can be produced by using a mixture of different biological agents and different sized material. Nano sized pores can also be produced by this technique. Another advantage of this process is that it lowers the amount of volatile organics produced.

4.3.2.3 Porous Material Fabrication

Since preliminary results using this novel technology was successful as seen in Appendix B, the samples prepared as mentioned in the discussions earlier are tested for this concept

as well. Using the dispersed samples of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions this novel porous material fabrication technique can be utilized to fabricate micro and nano porous materials.

4.3.3 Digital Images of Slip Casting of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

In the slip casting process the dispersions are poured into the Plaster of Paris moulds of the desired shape. Due to shrinkage of the part due to the drained casting technique, the part can be removed once dried. Twelve volume percent solids loading samples of the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based polar dispersions were used for the slip casting process. The digital images for the green and sintered α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based slip cast dispersion samples are presented and discussed in this section.

From figure (136) it can be seen that near net shape samples can be prepared using this technique.



Figure 136: Digital image of the α -SiC/H₂O/ α -SiC based slip cast sample at 1000°C (left) and a quarter (right)

Figures (137), (138) and (139) are digital images of the green α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based slip cast dispersion samples.

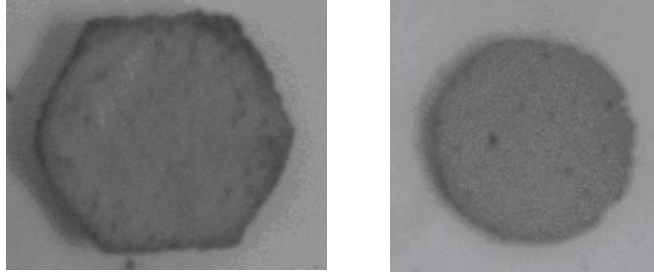


Figure 137: Digital images of the α -SiC/H₂O/ α -SiC based slip cast samples at 25 °C

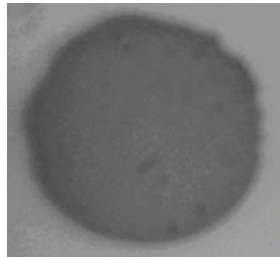


Figure 138: Digital images of the α -SiC/H₂O/LGG based slip cast sample at 25 °C

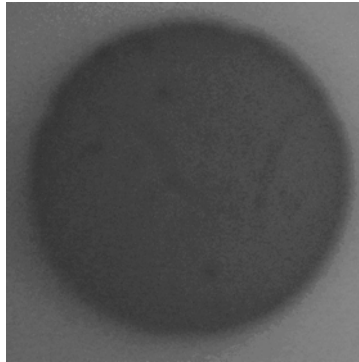


Figure 139: Digital image of the α -SiC/H₂O/ α -SiC based slip cast sample (control) at 25 °C

4.3.4 Digital Images of Freeze Casting of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Dispersions

In the freeze casting process, first a mould is made using the poly (dimethylsiloxane) epoxy (RTV 664 A 01P, GE) of the shape desired and allowed to cure for 20 hours. The α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based polar dispersions are then poured into the silicone mould. The sample set is first air dried for 60 minutes and then cooled in the freeze dryer to -35 °C and held for two hours to ensure thorough freezing. The samples are then subjected to a pressure of 10 Pa and the temperature was held at -35 °C for 46 hours so that the frozen water can sublime and hence forms the green compact. Twelve volume percent solids loading samples of the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H α -SiC (control) based polar dispersions were used for the freeze casting process. The digital images for the green α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based freeze cast dispersion samples are shown in figures (140), (141), (142) and (143). From figure (140) it is seen that near net shape samples can be prepared using this technique.



Figure 140: Digital image of the α -SiC/H₂O/LGG based freeze cast sample at 25 °C (left) and a quarter (right)

Figures (141), (142) and (143) are digital images of the green α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based freeze cast dispersion samples.



Figure 141: Digital image of the α -SiC/H₂O/ α -SiC based freeze cast sample at 25 °C

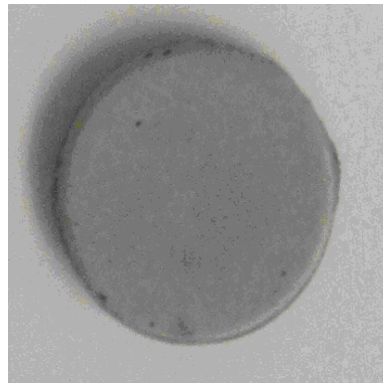


Figure 142: Digital image of the α -SiC/H₂O/LGG based freeze cast sample at 25 °C

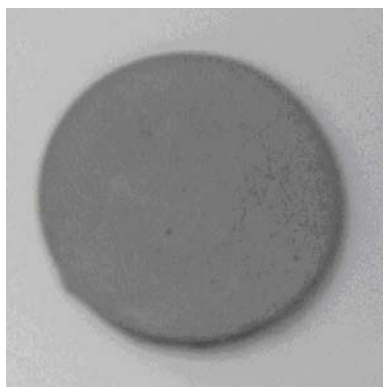


Figure 143: Digital image of the α -SiC/H₂O/ α -SiC based freeze cast sample (control) at 25 °C

4.4 Green and Sintered Density Characterization of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Slip Cast Dispersions

The green and the sintered density sample characterization were done using the ASTM standard C-914-95. [128] The samples tested were the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar slip cast dispersions. This technique is based on the Archimedes principle wherein the sample volume is measured by a liquid (water) displacement technique.

The green and sintered samples prepared from slip casting were first dried in a furnace at 105 °C for 6 hours so as to remove the entrapped moisture present in the samples. The samples were then weighed in air and the sample weight recorded as ' α '. The samples were then coated with melted paraffin wax. Paraffin wax was used as they have a known constant density (0.89 g/cm³) that does not change with repeated cooling and melting cycles. The paraffin wax coating would also help with preventing water entering the sample pores while the samples are immersed in water and altering the amount of water displaced for the volume measurement. Care was also taken to prevent any entrapment of air bubbles during the coating process. Once coated, the samples were weighed in air and their weight recorded as ' τ '. The samples were then suspended in water using a wire suspension and their suspended weight measured as ' γ '. The density of the samples are determined by the volume difference in the suspended and the dry samples.

The volume of the sample including the wax (V_a) was calculated using equation (76).

$$V_a = \frac{\tau - \gamma}{\rho_{sol}} \quad (76)$$

where, ' ρ_{sol} ' is the density of the solvent (in this case H₂O, which is 0.998 g/cm³ at 25°C)

The volume of the wax coating on the test sample (V_w) was calculated using equation (77).

$$V_w = \frac{\tau - \alpha}{\rho_w} \quad (77)$$

where, ' ρ_w ' is the density of the paraffin wax which is 0.89 g/cm³.

The bulk density of the samples is given by the quotient of the initial weight of the sample divided by the volume of the test specimen from which the volume of paraffin wax has been excluded. Hence, the bulk density of the sample is calculated using the equation (78).

$$\rho_{gn} = \frac{\alpha}{V_a - V_w} \quad (78)$$

where, ' ρ_{gn} ' is the bulk density of the sample.

The density data in this research is presented as a percent relative density to the theoretical density of the α -SiC, which is calculated using the equation (79).

$$D\% = \frac{\rho_{gn}}{\rho_t} * 100 \quad (79)$$

where, ' ρ_t ' is the bulk density of α -SiC (which is taken to be 3.1 g/cm³) and ' $D\%$ ' is the relative percentage density of the sample. [129]

The results of the bulk density measurements for the samples are presented in tables (15), (16) and (17). Table (15) shows the density values for α -SiC/H₂O/ α -SiC samples

Table 15: Variation of the α -SiC/H₂O/ α -SiC samples bulk density

HEAT TREATMENT TEMPERATURE IN AIR [°C]	BULK DENSITY [g/cm ³]	RELATIVE BULK DENSITY [D%]
25	2	60
150	2	76
500	2	74

Tables (16) and (17) shows the density values for α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) samples

Table 16: Variation of the α -SiC/H₂O/LGG samples bulk density

HEAT TREATMENT TEMPERATURE IN AIR [°C]	BULK DENSITY [g/cm ³]	RELATIVE BULK DENSITY [D%]
25	1	49
150	1	46
500	1	54

1000	1	50
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Table 17: Variation of the α -SiC/H₂O/ α -SiC samples (control) bulk density

HEAT TREATMENT TEMPERATURE IN AIR [°C]	BULK DENSITY [g/cm ³]	RELATIVE BULK DENSITY [D%]
25	1	55
150	1	67
500	2	79
1000	3	87

From the data in tables (15), (16) and (17) it is seen that for the case with the α -SiC/H₂O/ α -SiC samples the bulk density values are higher than that for the α -SiC/H₂O/LGG samples and so is the case with the relative bulk density values. It is also seen that for the α -SiC/H₂O/ α -SiC samples in general, with an increase in temperature there is an increase in the density values. It should be also noted that the method gives an estimate for the density values. However, it is a good method to get an initial approximation for the density of the samples fabricated.

4.5 Green and Sintered Porosity Characterization of α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Slip Cast Dispersions

The porosity characterization for the green and sintered sample characterization were done using the ASTM standard C-20-00 [130] and ASTM standard C-830-00 [131]. The samples tested were the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar slip cast

dispersions. This technique is based on the Archimedes principle wherein the sample volume is measured by a liquid (water) displacement technique.

The green and the sintered samples were initially heated in a furnace to 105 °C for six hours in order to remove any moisture present on the samples. The green and sintered samples are then weighed and their dry weight recorded as 'δ'. The samples were then placed in boiling water for two hours. The samples when placed in the boiling water are suspended in the liquid medium so that the samples are entirely covered with water. The samples were then allowed to cool and kept immersed in water for twelve hours. The samples are then weighed while being suspended in water and their weights are recorded as 'ε'. The green and sintered samples are then taken out from the water and their saturated weigh measured as 'ω'.

The percent apparent porosity for the samples gives the relationship of the volume of the open porosity in the sample to the sample's exterior volume and is calculated using equation (80).

$$\%P_a = \frac{\omega - \delta}{\omega - \varepsilon} * 100 \quad (80)$$

where, '%P_a' is the percent apparent porosity for the sample.

The percent water absorption which gives the relationship of the amount of water absorbed by the sample to the weight of dry sample and is calculated using equation (81).

$$\%A = \frac{\omega - \delta}{\delta} * 100 \quad (81)$$

where, ‘% A’ is the percent water absorption for the sample.

The percent closed porosity for the samples are calculated using equation (82).

$$\%P_c = \frac{V_{cp}}{V_b} * 100 \quad (82)$$

where, ‘%P_c’ is the percent closed porosity for the sample.

The total porosity of the samples are calculated using equation (83).

$$\%P_t = \frac{(V_{op} + V_{cp})}{V_b} * 100 \quad (83)$$

where, ‘% P_t’ is the percent total porosity for the sample.

The volume of closed porosity in the samples is calculated using equation (84).

$$V_{cp} = V_a - V_t \quad (84)$$

where, ‘V_{cp}’ is the percent closed porosity for the sample.

The volume of apparent porosity in the samples is calculated using equation (85).

$$V_a = \frac{\delta - \varepsilon}{\rho_{sol}} \quad (85)$$

where, ' V_a ' is the apparent porosity for the sample and ' ρ_{sol} ' is the density of the solvent (in this case H₂O which is 0.98 g/cc).

The volume of total porosity in the samples is calculated using equation (86).

$$V_t = \frac{\delta}{\rho_{ms}} \quad (86)$$

where, ' V_t ' is the total porosity for the sample and ' ρ_{ms} ' is the density of the sample material (in this case α -SiC which is 3.1 g/cc).

The volume of the bulk porosity in the samples is calculated using equation (87).

$$V_b = \frac{\omega - \varepsilon}{\rho_{sol}} \quad (87)$$

where, ' V_b ' is the bulk porosity for the sample and ' ρ_{sol} ' is the density of the solvent (in this case H₂O which is 0.98 g/cc).

The volume of open porosity in the samples is calculated using equation (88).

$$V_{op} = \frac{\omega - \delta}{\rho_s} \quad (88)$$

where, ' V_{op} ' is the open porosity for the sample and ' ρ_s ' is the density of the solvent (in this case H₂O which is 0.98 g/cc).

The results of the porosity measurements for the samples are presented in table (18), (19) and (20). Table (18) shows the density values for α -SiC/H₂O/ α -SiC samples

Table 18: Variation of the α -SiC/H₂O/ α -SiC samples percent apparent porosity (% P_a), percent water absorption (% A), percent closed porosity (% P_c) and percent total porosity (% P_t) with temperature

HEAT TREATMENT TEMPERATURE IN AIR[°C]	% P _a	% A	% P _c	% P _t
25	18	7	5	23
100	23	11	10	32
500	24	10	1	24
1000	20	9	7	27

Table (19) and (20) shows the density values for α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) samples

Table 19: Variation of the α -SiC/H₂O/LGG samples percent apparent porosity (% P_a), percent water absorption (% A), percent closed porosity (% P_c) and percent total porosity (% P_t) with temperature

HEAT TREATMENT TEMPERATURE IN AIR [°C]	% P _a	% A	% P _c	% P _t
25	16	13	45	62
100	44	29	-	53
500	36	29	23	60
1000	33	25	25	59

Table 20: Variation of the α -SiC/H₂O/ α -SiC samples (control) percent apparent porosity (% P_a), percent water absorption (% A), percent closed porosity (% P_c) and percent total porosity (% P_t) with temperature

HEAT TREATMENT TEMPERATURE [°C]	% P _a	% A	% P _c	% P _t
25	9	3	8	17
100	12	4	3	15
500	14	6	5	19
1000	11	4	5	16

It can be seen from the data in tables (18), (19) and (20) that for the case with the α -SiC/H₂O/ α -SiC samples, the total porosity values are lower than that for the α -SiC/H₂O/LGG samples and so is the case with the apparent porosity values. In general, it is seen that for the α -SiC/H₂O/ α -SiC samples with a decrease in temperature, there is an increase in the porosity values. It should be also noted that the method gives an estimate for the density values. However, it is a good method to get an initial approximation for the porosity of the samples fabricated.

4.6 Electron Microscopy Images of Green and Sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Slip Cast Dispersions

The electron microscopy images for the green and sintered α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based slip cast dispersion samples are presented and discussed in this section.

It is seen from the figures (144) through (156) that there is a significant increase in the amount of porosity in the SiC/H₂O/LGG based slip cast dispersion samples and that there

are also regions in the sample where the nanoparticles seem to have surrounded the bacteria leading to porosity sizes in the size range of LGG. Figures (144), (145) and (146) are of the green α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based slip cast dispersion samples at 25 °C.

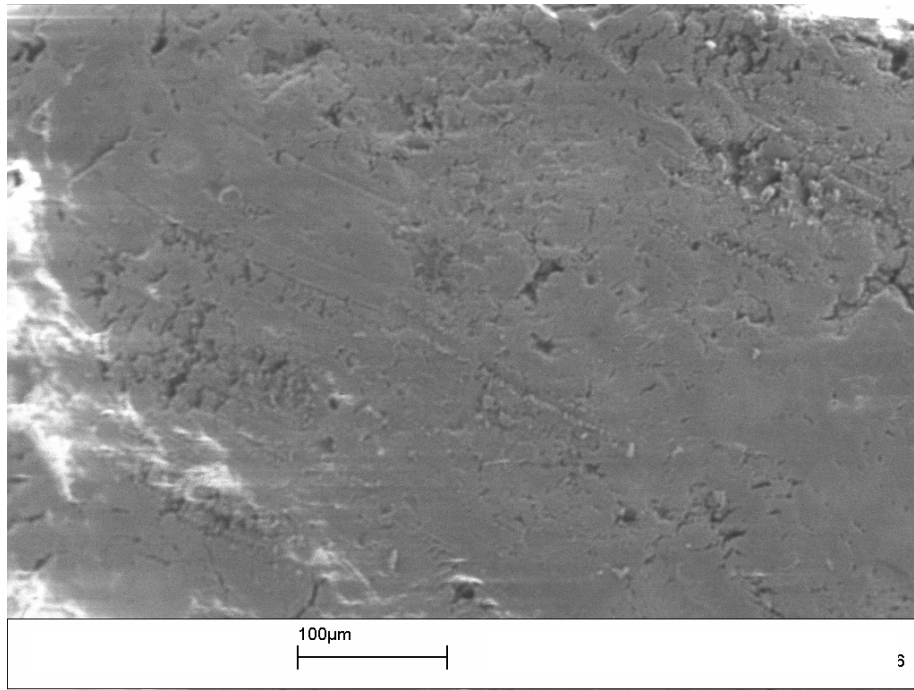


Figure 144: SEM image of the surface of the α -SiC/H₂O/ α -SiC based slip cast sample at 25 °C

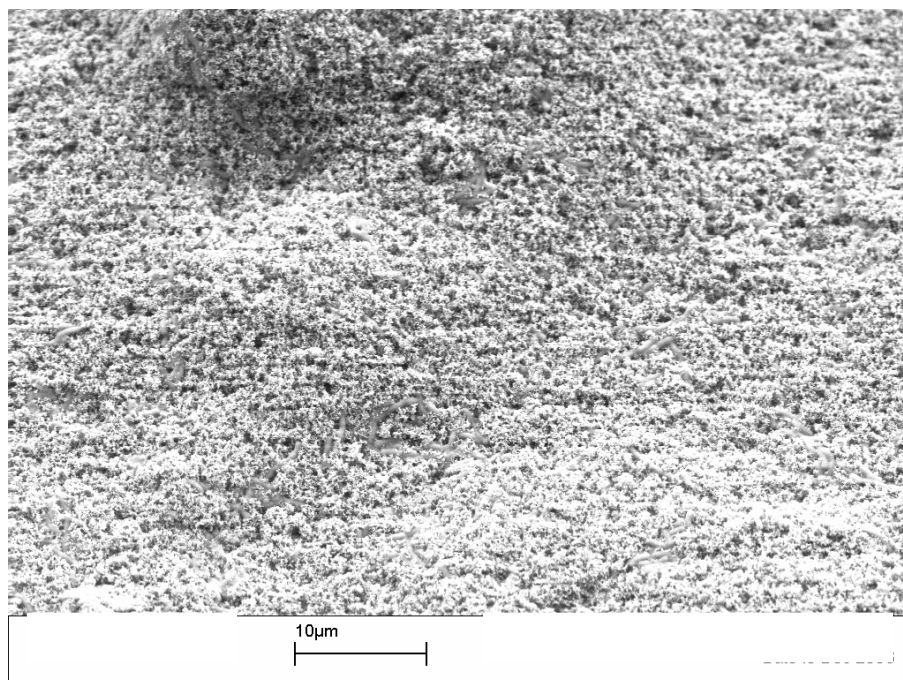


Figure 145: SEM image of the α -SiC/H₂O/LGG based slip cast sample at 25 °C

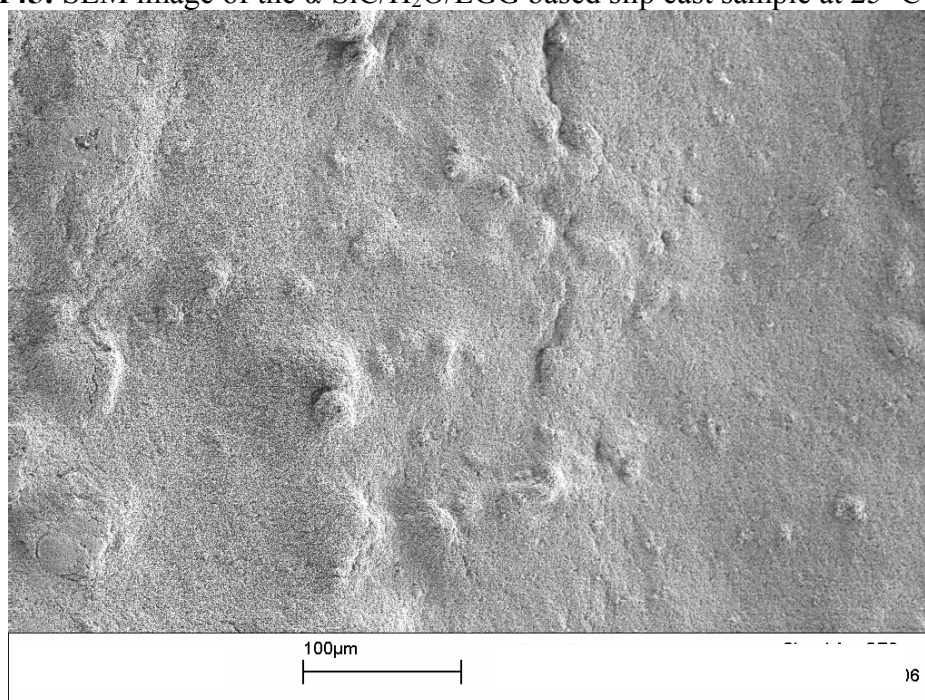


Figure 146: SEM image of the α -SiC/H₂O/ α -SiC based slip cast sample (control) at 25 °C

Figures (147), (148) and (149) are of the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based slip cast dispersion samples at 150 °C. The binders burn out at this temperature leading to the formation of the porosity in the material.

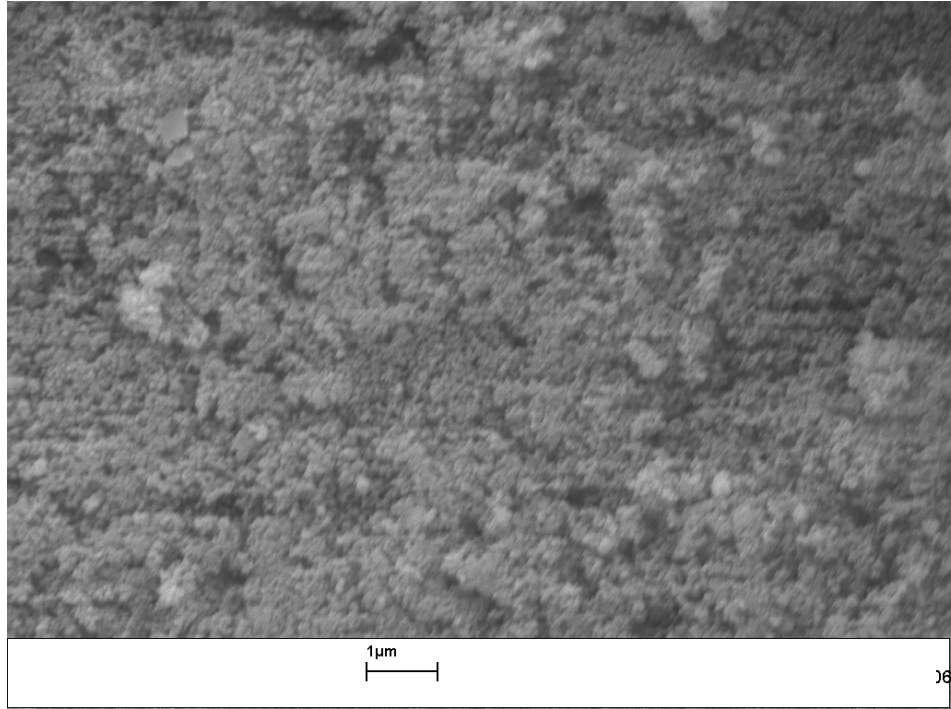


Figure 147: SEM image of the α -SiC/H₂O/ α -SiC based slip cast sample at 150°C

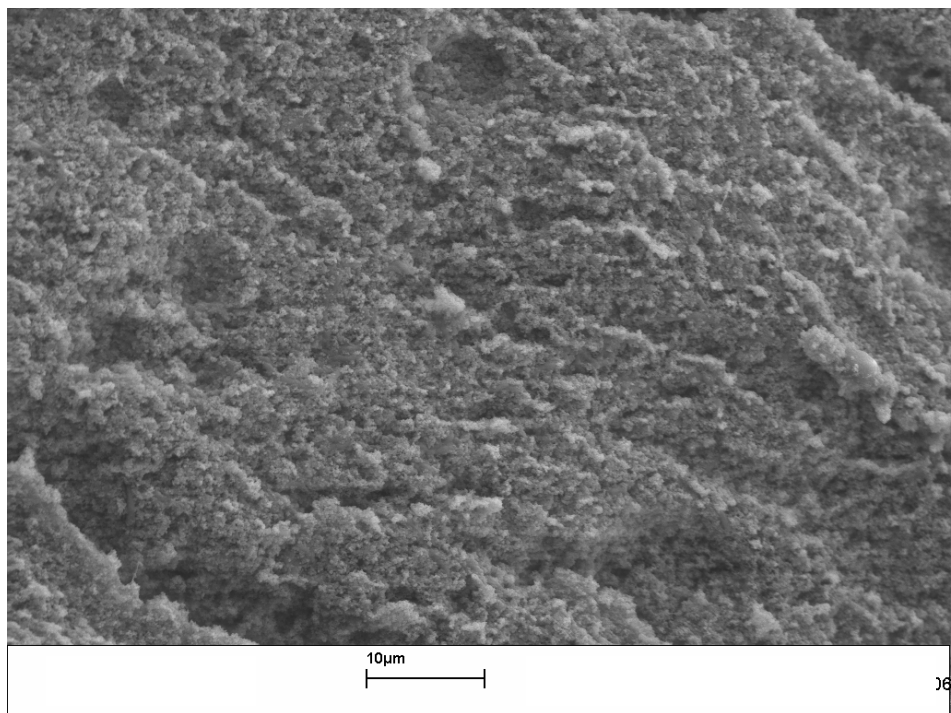


Figure 148: SEM image of the α -SiC/H₂O/LGG based slip cast sample at 150°C

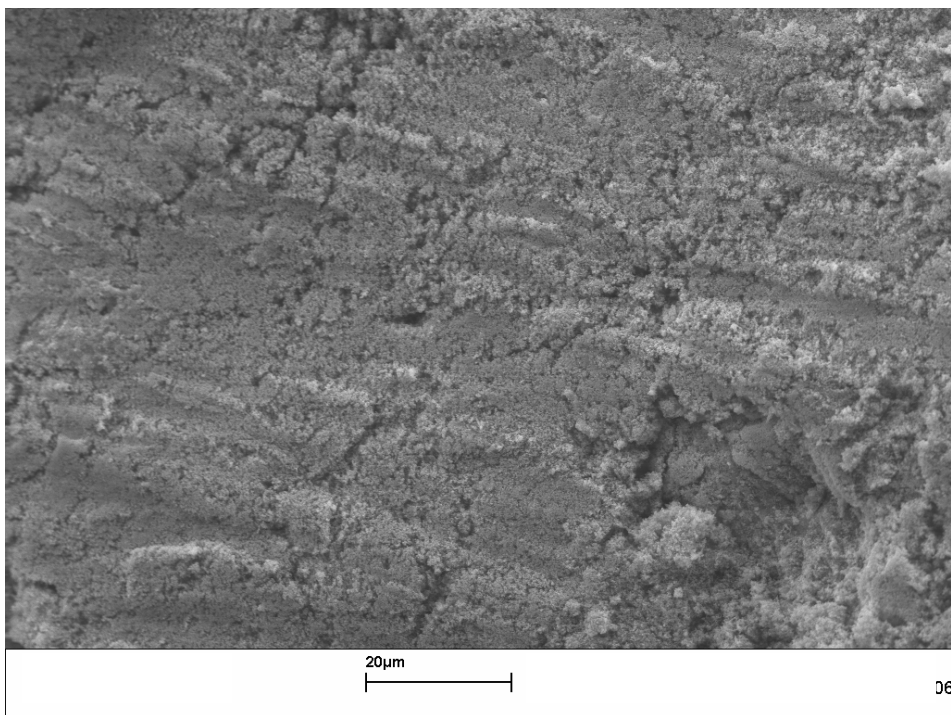


Figure 149: SEM image of the α -SiC/H₂O/ α -SiC based slip cast sample (control) at 150°C

Figures (150), (151) and (152) are of the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based slip cast dispersion samples at 500 °C. The binder burn out has already occurred by this temperature leading to the sintering (agglomeration of fines) of the particles thus increasing the density of the sample.

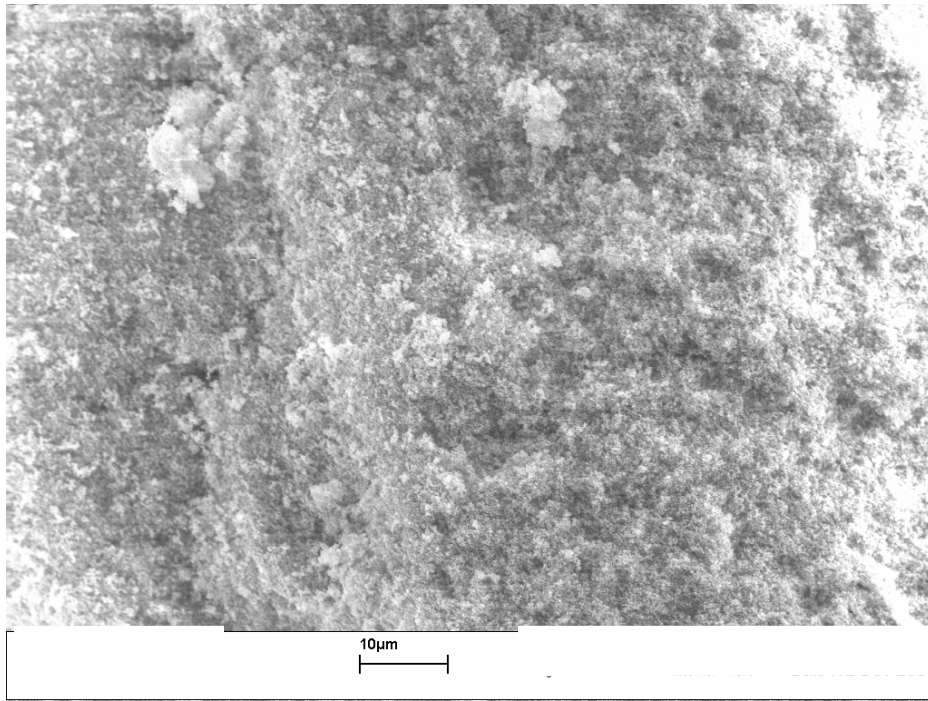


Figure 150: SEM image of the α -SiC/H₂O/ α -SiC based slip cast sample at 500°C

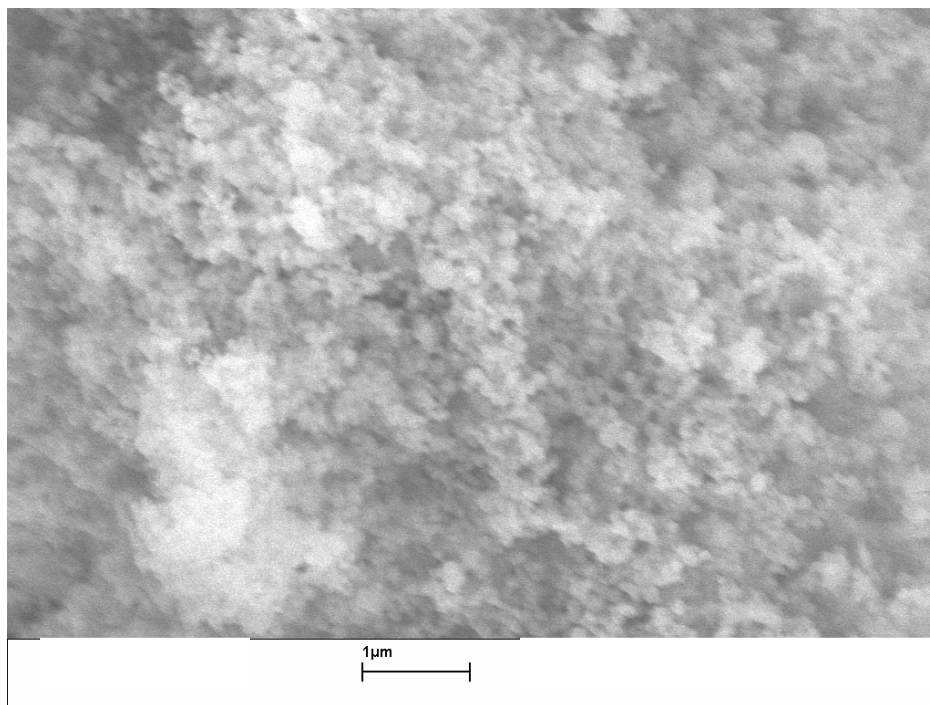


Figure 151: SEM image of the α -SiC/H₂O/LGG based slip cast sample at 500°C

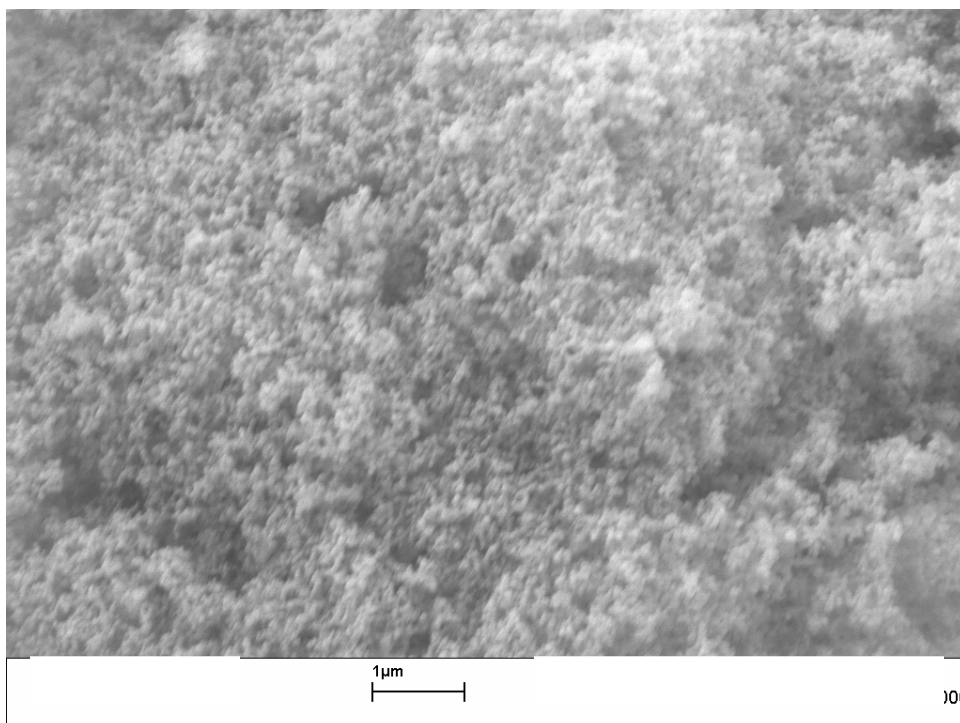


Figure 152: SEM image of the α -SiC/H₂O/ α -SiC based slip cast sample (control) at 500°C

Figures (153), (154) and (155) are of the α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based slip cast dispersion samples at 1000 °C. The sintering of the particles occurs thus increasing the density of the sample. The porosity in the α -SiC/H₂O/LGG based slip cast dispersion samples of the size of the LGG used; can also be seen at selected regions in the micrographs.

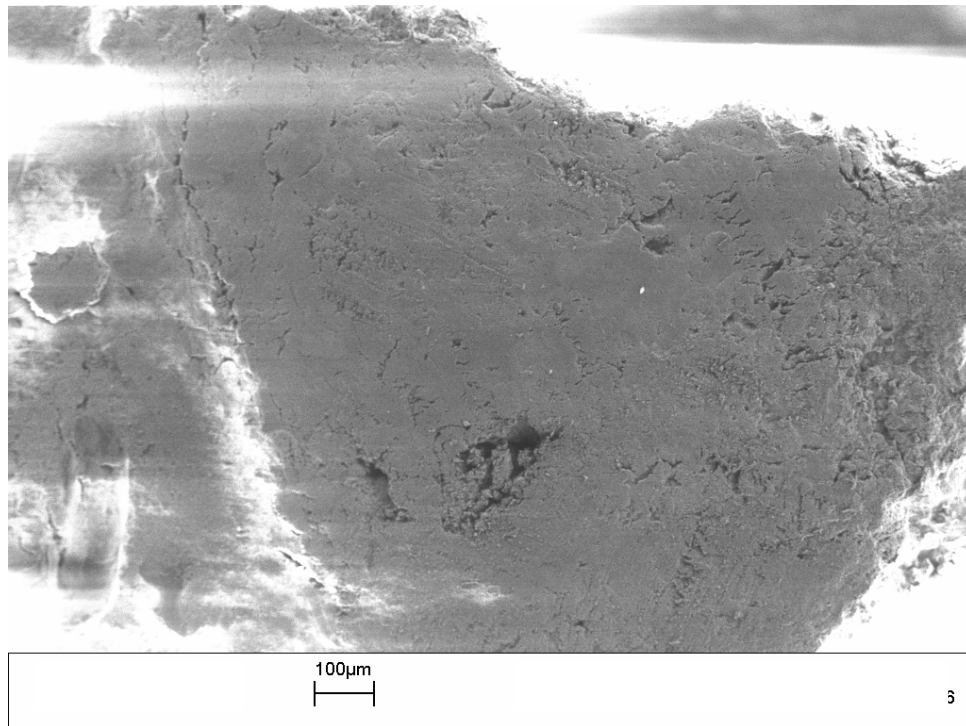


Figure 153: SEM image of the α -SiC/H₂O/ α -SiC based slip cast sample at 1000°C

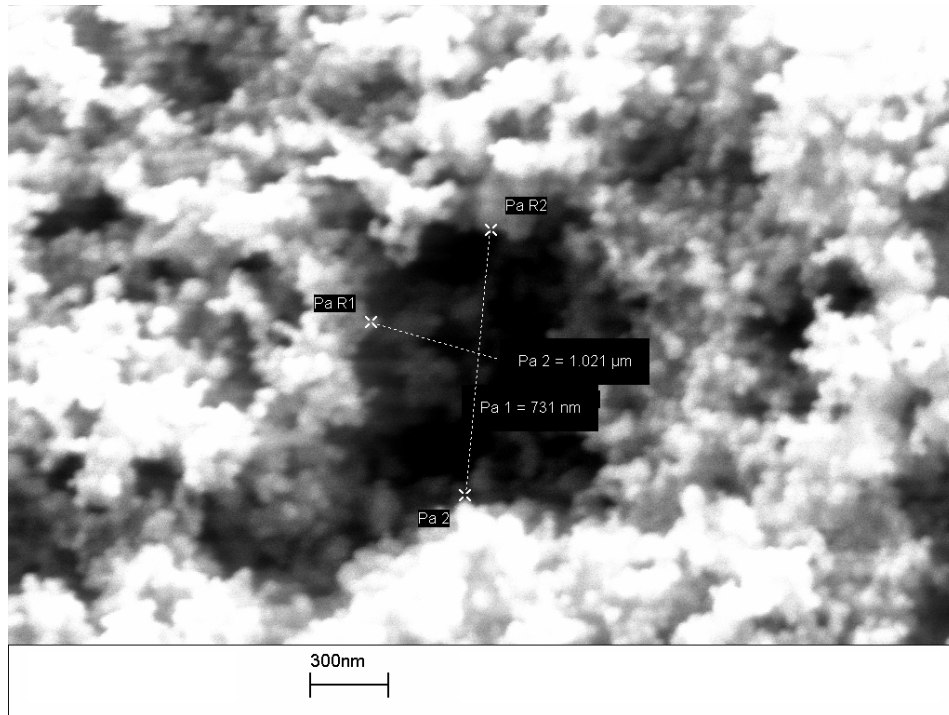


Figure 154: SEM image of the α -SiC/H₂O/LGG based slip cast sample at 1000°C showing single pore formation

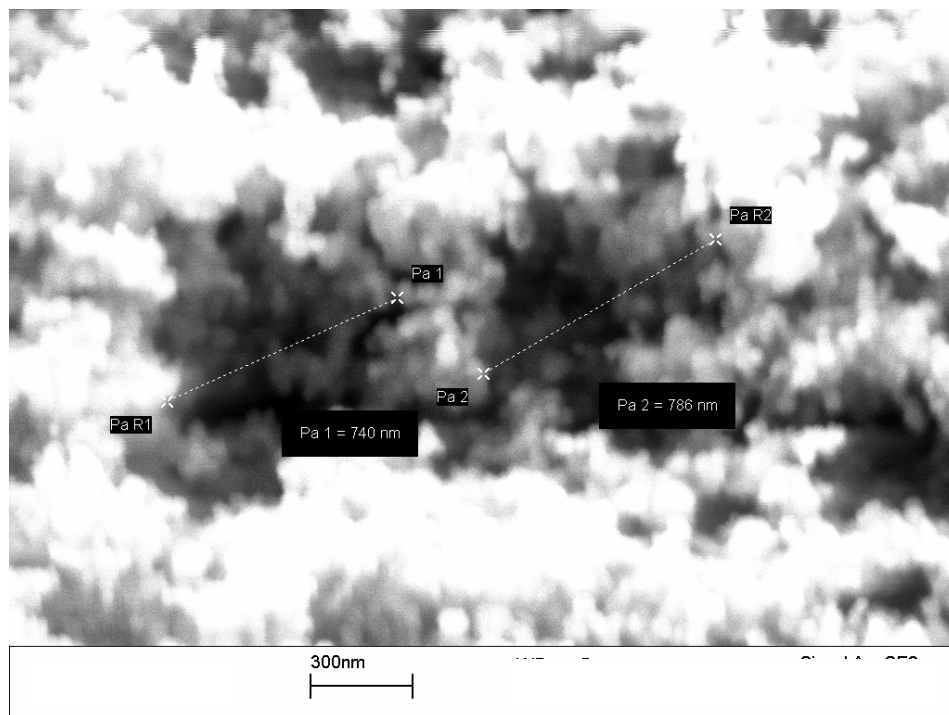


Figure 155: SEM image of the α -SiC/H₂O/LGG based slip cast sample at 1000°C showing porosity

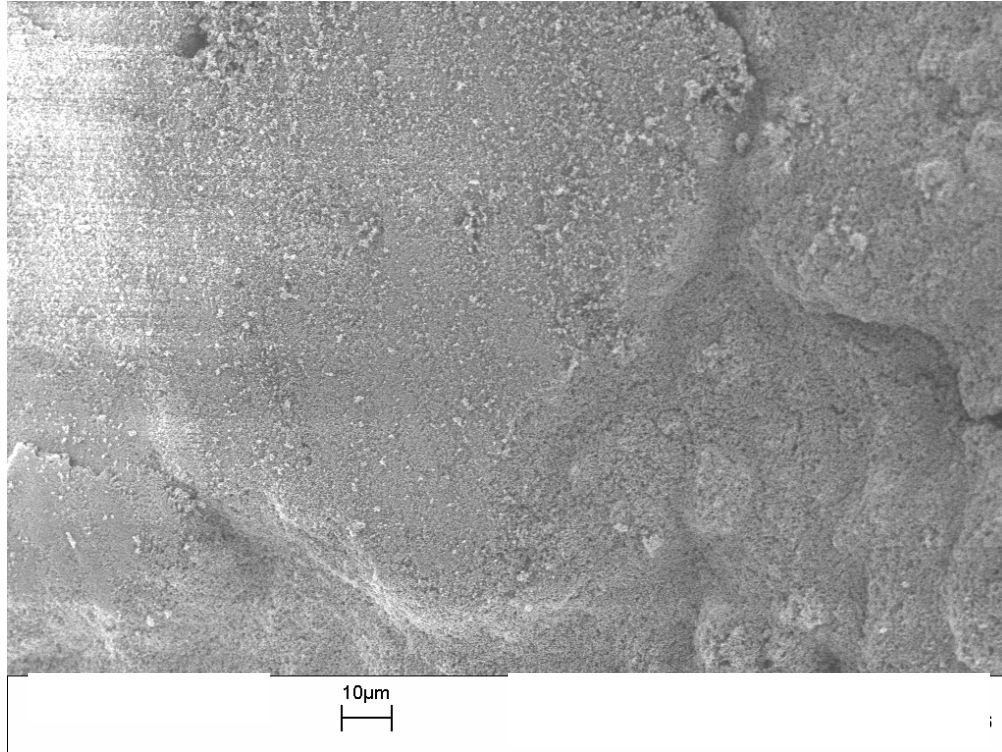


Figure 156: SEM image of α -SiC/H₂O/ α -SiC based slip cast sample (control) at 1000°C

4.7 Electron Microscopy Images of Green and Sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Freeze Cast Dispersions

The electron microscopy images for the green and sintered α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based freeze cast dispersion samples are shown in figures (157), (158) and (159). It can be seen from the figures that there is a significant increase in the amount of porosity in the samples containing LGG and that the porosity in the freeze cast samples are much higher than the samples cast using the slip casting technique.

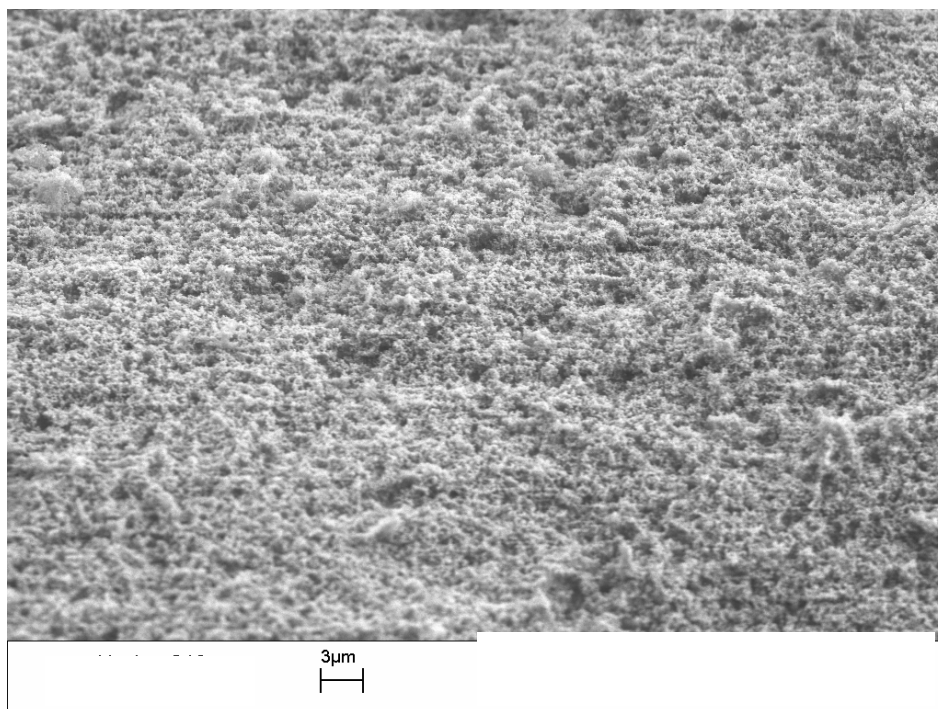


Figure 157: SEM image of the α -SiC/H₂O/ α -SiC based freeze cast sample at 25 °C

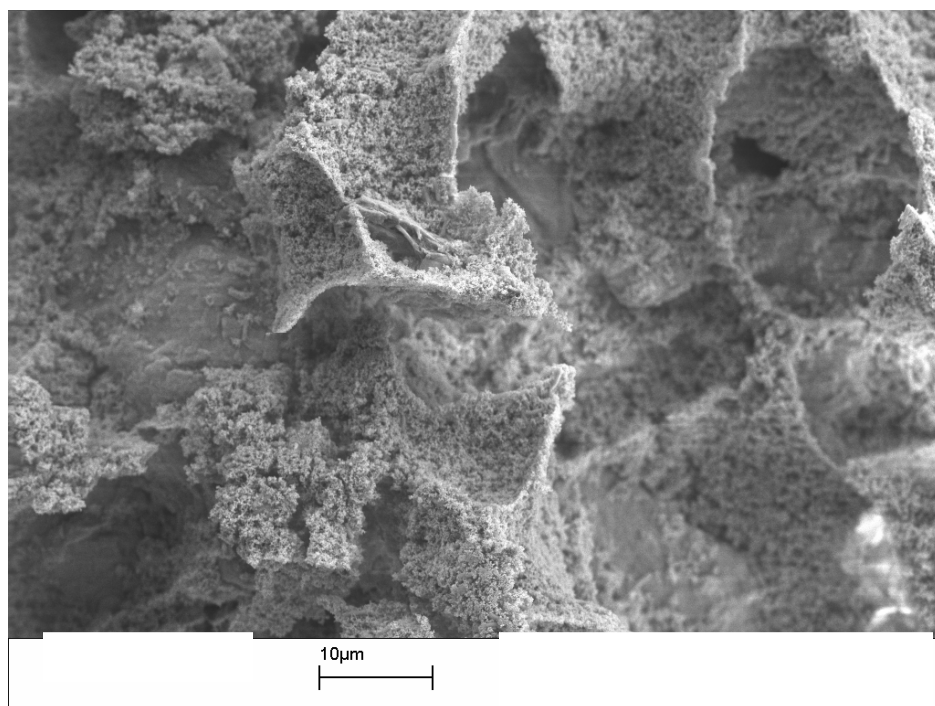


Figure 158: SEM image of the α -SiC/H₂O/LGG based freeze cast sample at 25 °C

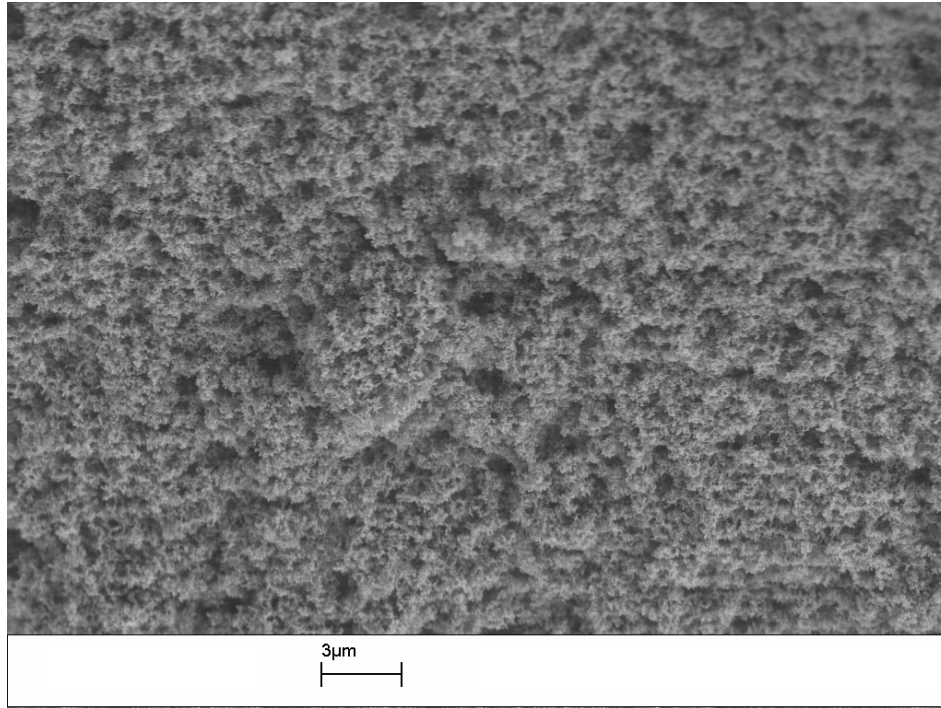


Figure 159: SEM image of α -SiC/H₂O/ α -SiC based freeze cast sample (control) at 25 °C

4.8 Diametric Compression Testing for Green and Sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG Based Polar Slip Cast Dispersions

One of the tests commonly used to measure the strength for ceramics is the diametric compression test or the splitting tensile test. The slip cast green and sintered samples are subjected to the diametric compression testing and the procedure as seen in ASTM standard D-3967-05 is used. [132] The diametric compression test is understood to be a good test to measure the strength of the materials as it gives an indication of the sample microstructure and uniformity as it is sensitive to the flaws present in the sample. [133-138] The diametric compression testing for the green and sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar slip cast dispersions were performed using the Instron 4204

compression testing machine with a 1 kN load cell attachment with a loading rate of 0.5 mm/minute.

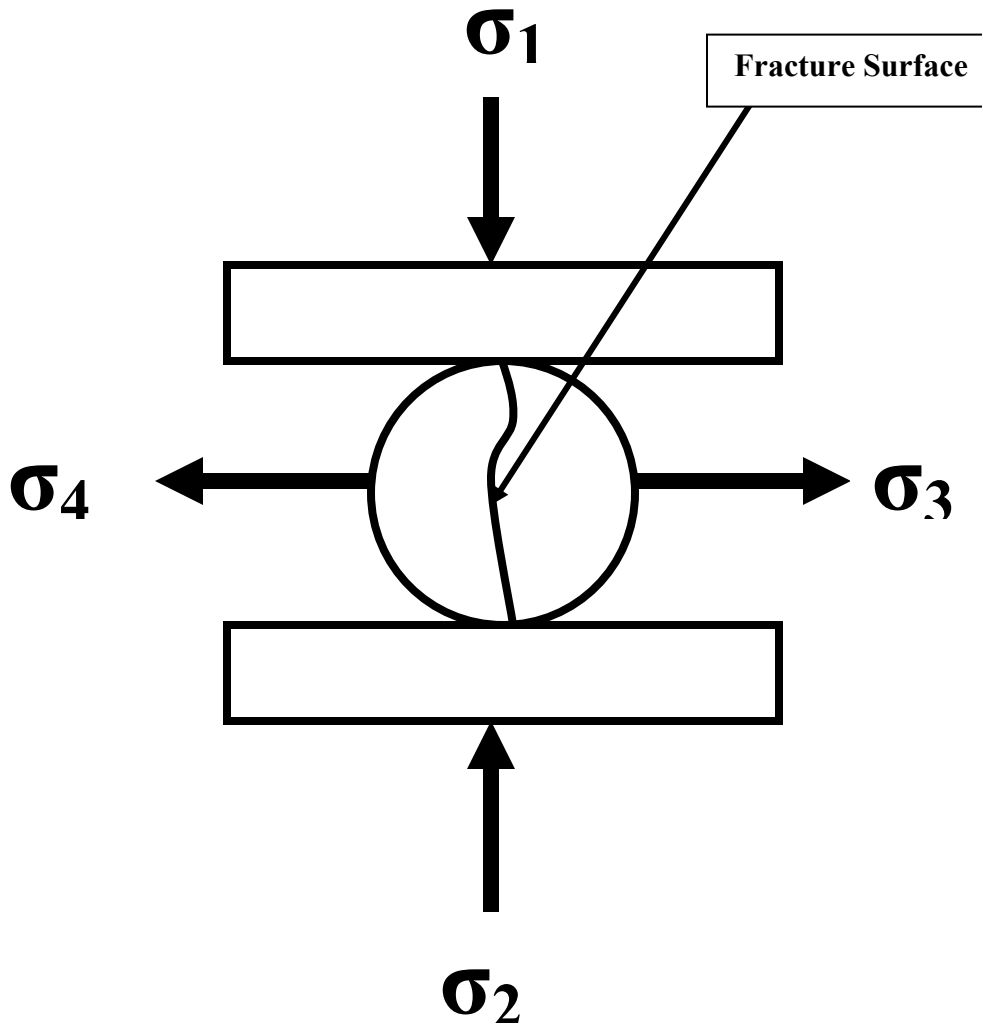


Figure 160: Schematic showing the force balance on a sample subjected to compression loading. ' σ_1 ' and ' σ_2 ' being the compressive stress being applied on the sample and ' σ_3 ' and ' σ_4 ' are the tensile stresses. The fracture surface is also seen in the schematic

When the compressive forces are applied on the sample, the sample will break along the sample diameter as shown in figure (161). The reason for this is that the tensile stresses pull along the loading diameter of the sample.

The splitting tensile strength for the samples is calculated using the equation (89).

$$\sigma_t = \frac{2P}{\pi LD} \quad (89)$$

where, ' σ_t ' is the splitting tensile strength, ' P ' is the maximum applied load indicated by the testing machine, ' L ' is the length of the cylindrical sample and ' D ' is the diameter of the sample.

A digital picture of the experimental setup is shown in figure (161).

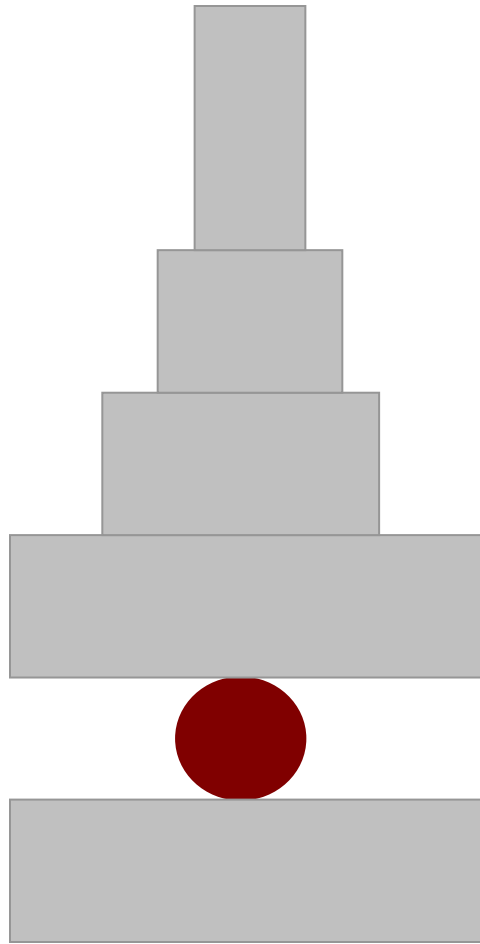


Figure 161: The experimental arrangement for the diametric compression test

The results of the diametric compression testing measurements for testing the green α -SiC/H₂O/ α -SiC, α -SiC/H₂O/LGG and α -SiC/H₂O/ α -SiC (control) based polar slip cast dispersions are presented in figure (162). A variation in the splitting tensile strength values for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG samples is observed. It is seen that the green α -SiC/H₂O/ α -SiC based polar slip cast dispersions have a higher splitting tensile strength values than the α -SiC/H₂O/LGG based polar slip cast dispersions. This could be due to the higher density and better packing of the particles for the α -SiC/H₂O/ α -SiC samples compared to the α -SiC/H₂O/LGG based polar slip cast dispersions samples. The fracture surface of one of the samples is also seen in figure (163).

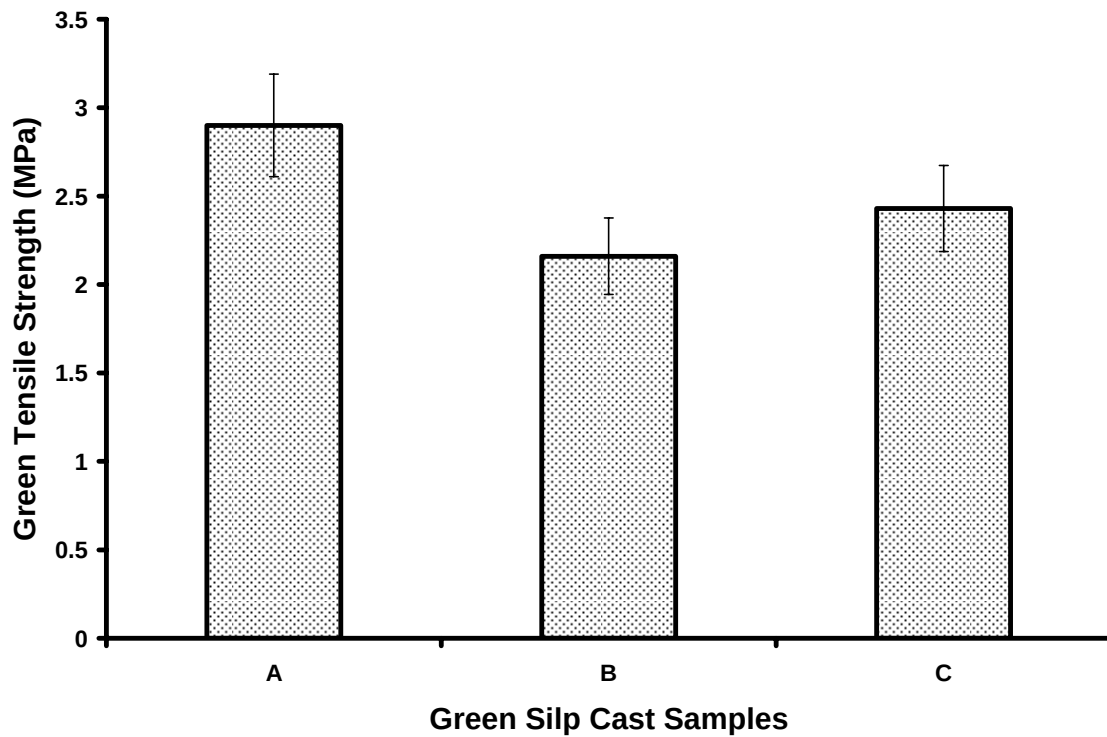


Figure 162: Variation of the green tensile strength values for the green (A) α -SiC/H₂O/ α -SiC samples (B) α -SiC/H₂O/LGG samples and (C) α -SiC/H₂O/ α -SiC (control) samples based polar slip cast dispersions samples

In each of the sample failures, the failure occurred along the vertical diametric axis as expected for the true tensile sample failures. The fracture surface further confirms that this splitting tensile test is a valid technique for determining the tensile strength of the α -SiC/H₂O/ α -SiC samples compared to the α -SiC/H₂O/LGG based polar slip cast dispersions samples.



Figure 163: Digital picture showing the sample failure along the diameter during the diametric compression test

For the sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar slip cast dispersions the results of the diametric compression testing measurements are presented in figure (164). There is a variation in the splitting tensile strength values for α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG samples seen. It is also observed that the sintered α -SiC/H₂O/ α -SiC based polar slip cast dispersions have a higher diametric compression strength values than the α -SiC/H₂O/LGG based polar slip cast dispersions. The better packing of the

particles for the α -SiC/H₂O/ α -SiC samples compared to the α -SiC/H₂O/LGG based polar slip cast dispersions samples as well as their higher density values could be a potential reason for this. Also the effect could be due to the greater amount of porosity in the α -SiC/H₂O/LGG based polar slip cast dispersions samples. It is also seen that compared to the green samples the tensile strength values for the sintered samples are higher.

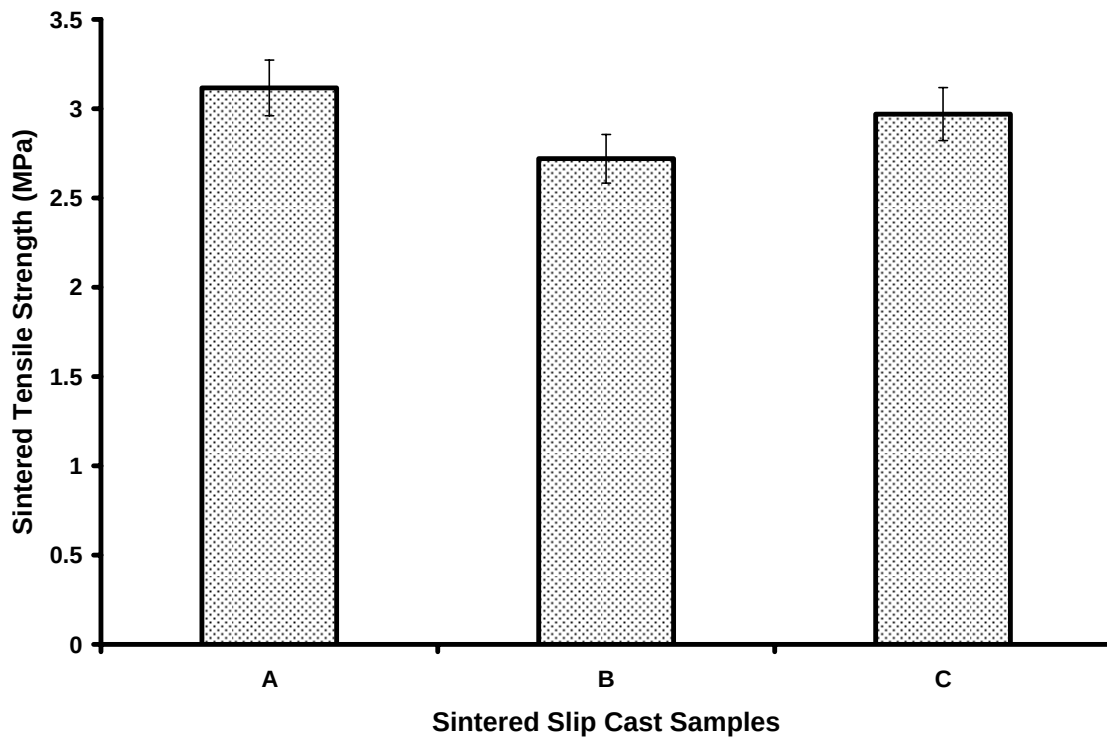


Figure 164: Variation of the sintered tensile strength values for the sintered (A) α -SiC/H₂O/ α -SiC samples (B) α -SiC/H₂O/LGG samples and (C) α -SiC/H₂O/ α -SiC (control) samples based polar slip cast dispersions samples

The amounts of binder added to the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar slip cast dispersions can also have an effect on the tensile strength values. Several scientists have been attempting to model the strength of ceramics and Onoda's model

which related the tensile force needed to break the inter-particle force depended on the amount of the binder and the packing fraction of the ceramic particles is given by the equation (90), which is the most commonly used (the equation is good only for green samples). [139]

$$\sigma = \frac{9\varphi}{8(1-\sigma)^{1/2}} (V_B)^{1/2} \sigma_B \quad (90)$$

where, ' σ ' is the tensile strength of the sample, ' V_B ' is the amount of binder in the sample relative to the ceramic material, ' φ ' is the solids loading of the sample and ' σ_B ' is the strength of the binder that is used.

From equation (90), it is seen that both the sample solids loading and the binder concentrations alter the sample tensile strength values as well.

From the statistical analysis of the samples using one-way ANOVA, it is calculated that the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar slip cast dispersions are not significant at the 99% confidence level but are significant at the 95% confidence intervals. The strength of the samples are lower compared to dense silicon carbide which has a tensile strength of 600 MPa. Compared to SiC filters for molten steel that have strengths of about 40 MPa, these were at lower strengths as well.

CHAPTER 5

SUMMARY

1. The electrostatic, van der Waals and the total interaction potential energies for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions were calculated and plotted. It was seen that there was a difference for the α -SiC/H₂O/LGG based polar dispersions from the α -SiC/H₂O/ α -SiC based polar dispersions in that the Hamakar constant values for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions were different by three orders of magnitude. It was also seen that the α -SiC/H₂O/LGG based polar dispersions were more repulsive than the α -SiC/H₂O/ α -SiC based polar dispersions.
2. Based on the Hamakar constant, a technique to determine the molecular weight of the dispersant to be used for the nano α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions was discussed and verified using experimental analysis. The novel technique was extended to non polar systems for the α -SiC/C₁₂H₁₄/ α -SiC and α -SiC/C₁₂H₁₄/LGG based non polar dispersions as well.
3. The approximate molecular weights for the poly acrylic acid to disperse the α -SiC nanoparticles in the α -SiC/H₂O/LGG based polar dispersions and the α -SiC and LGG particles in the α -SiC/H₂O/ α -SiC based polar dispersions were calculated to be 10^5 and 10^3 respectively.

4. The optimum amount of PAA-A and PAA-B required to cover the α -SiC nanoparticles in the α -SiC/H₂O/LGG based polar dispersions and the α -SiC and LGG particles in the α -SiC/H₂O/ α -SiC based polar dispersions were found to be 0.1 weight percent of PAA-A and 0.1 weight percent of PAA-B respectively. The zeta potential values also confirmed this result. The α -SiC/H₂O/LGG and the α -SiC/H₂O/ α -SiC based polar dispersions showed a shear thinning behavior with the addition of different weight percents of the dispersant. It was also seen that slurries with α -SiC/H₂O/ α -SiC based polar dispersions had a higher viscosity than the α -SiC/H₂O/LGG based polar dispersions with different weight percents of PAA.
5. The pH at the IEP for the various systems namely, α -SiC/H₂O/ α -SiC, α -SiC/H₂O/ α -SiC with PAA-A, LGG/H₂O/LGG, α -SiC/H₂O/LGG and α -SiC/H₂O/LGG with PAA-B were found to be 3.6, 1.5, 2.7, 1.4 and 1.9 respectively. Moreover, it was seen that for the case of the α -SiC/H₂O/ α -SiC polar based dispersion system with the addition of the dispersant PAA-A, at the pH value at the IEP for the case with α -SiC/H₂O/ α -SiC without the addition of PAA-A, the zeta potential value is – 22 mV. This value is in good agreement with the calculated mathematical analysis for the system. This result signifies that at the pH of 3.6 for the α -SiC/H₂O/ α -SiC polar based dispersion system, the PAA-A steric hindrance is significant enough to create the necessary repulsion in order to have a well dispersed suspension. A similar result is obtained for the case of the α -SiC/H₂O/LGG polar based dispersion system with the addition of the

dispersant PAA-B, at the pH value at the IEP for the case with α -SiC/H₂O/LGG without the addition of PAA-B, the zeta potential value is +10 mV. This value is in also in good agreement with the calculated mathematical analysis discussed in the previous sections. The result signifies that at the pH of 1.4 for the α -SiC/H₂O/LGG polar based dispersion system, the PAA-B steric hindrance is significant enough to create the necessary repulsion in order to have a well dispersed suspension. From the results obtained it is also seen that there is a sign difference for the cases with α -SiC/H₂O/ α -SiC and without α -SiC/H₂O/LGG in order to prepare stable suspensions. It is also seen that in the case of the α -SiC/H₂O/LGG systems since the system is more repulsive than the α -SiC/H₂O/ α -SiC polar based system, a lower zeta potential value is sufficient to create the required stable suspension.

6. The optimum range for Duramax B-1020 selected for the experimentation is found to be at around a binder weight percent of 0.25 for the α -SiC/H₂O/ α -SiC based polar dispersions. The addition of the Duramax B-1020 is seen to first increase the suspension viscosity for these samples and then with further additions of the binder the α -SiC/H₂O/ α -SiC based polar dispersions viscosity is reduced. It is also seen that the α -SiC/H₂O/ α -SiC based polar dispersions have a shear thinning behavior. The optimum range for Duramax B-1020 is found to be at around a binder weight percent of 0.25 for the α -SiC/H₂O/LGG based polar dispersions. These samples showed a shear thinning behavior as well. The viscosity variation for the α -SiC/H₂O/ α -SiC based polar dispersions is very large

compared to the α -SiC/H₂O/LGG based polar dispersions. It is also seen that there is not too much variation in the viscosity value for the α -SiC/H₂O/LGG based polar dispersions

7. The optimum range for PEG selected for the experimentation is found to be around a plasticizer weight percent of 0.25 for the α -SiC/H₂O/ α -SiC based polar dispersions. It can be seen that the α -SiC/H₂O/ α -SiC based polar dispersions have a shear thinning behavior. The optimum range for PEG is found to be around a plasticizer weight percent of 0.25 for the α -SiC/H₂O/LGG based polar dispersions. It is also seen that the α -SiC/H₂O/LGG based polar dispersions have a shear thinning behavior. The viscosity variation for the α -SiC/H₂O/ α -SiC based polar dispersions have higher viscosity values as compared to the α -SiC/H₂O/LGG based polar dispersions at the same weight percent of PEG.
8. It is also seen that the viscosity variation for the α -SiC/H₂O/ α -SiC based polar dispersions have higher viscosity values as compared to the α -SiC/H₂O/LGG based polar dispersions at the same solids loading value. The maximum solids loading for the α -SiC/H₂O/ α -SiC based polar dispersions at the various shear rates were obtained to be 16.7 vol% solids loading using the best fitting curve model. The maximum solids loading for the α -SiC/H₂O/ α -SiC based polar dispersions using the Liu model is at 17 vol% solids loading. The maximum solids loading for the α -SiC/H₂O/LGG based polar dispersions at the various shear rates were obtained to be 22.1 vol% solids loading using the best fitting model. From the

data it is seen that the maximum solids loading for the α -SiC/H₂O/LGG based polar dispersions is at 20 vol% solids loading using the Liu model. From the fitting curves the maximum solids loading for the α -SiC/H₂O/ α -SiC (control) based polar dispersions at the various shear rates were obtained to be 11.3 vol% solids loading and from the maximum solids loading model by Liu the α -SiC/H₂O/ α -SiC (control) based polar dispersions optimum solids loading was found to be at 11 vol%.

9. Based on the model similar to the 'Ball in Hand' ASTM standard the optimum solids loading for the slip and freeze casting the α -SiC/H₂O/ α -SiC and the α -SiC/H₂O/LGG based polar dispersions was found to be 12 vol% solids loading.
10. A novel technique to fabricate porous materials using biological agents as the pore forming agents is discussed. Preliminary experiments and characterization of the samples prepared with porcine circo virus 2, pseudomonas aeruginosa and single celled fungi with ceramic nanoparticles including Si₃N₄, SiO₂ and SiC (Appendix B) have been demonstrated. Also, SiC/H₂O/LGG based polar dispersions samples have been used for this novel technique to fabricate porous materials.
11. The α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions have been successfully slip and freeze cast. It is seen that near net shape features can be prepared using this technique. The digital and SEM images of the green and

sintered slip cast samples for the α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions are also presented.

12. The density characterization for the green and sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions is also presented and discussed. From the data obtained it is seen that for the case with the α -SiC/H₂O/ α -SiC samples the bulk density values are higher than that for the α -SiC/H₂O/LGG samples and so is the case with the relative bulk density values. It is also seen that for the α -SiC/H₂O/ α -SiC samples in general with an increase in temperature there is an increase in the density values.
13. The porosity characterization for the green and sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar dispersions is also presented and discussed. From the data obtained it is seen that for the case with the α -SiC/H₂O/ α -SiC samples the total porosity values are lower than that for the α -SiC/H₂O/LGG samples and so is the case with the apparent porosity values. It is also seen that for the α -SiC/H₂O/ α -SiC samples in general with a decrease in temperature there is an increase in the porosity values.
14. The electron microscopy images for the green and sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based slip cast dispersion samples are also presented. It is seen from the SEM micrographs that there is a significant increase in the amount of porosity in the α -SiC/H₂O/LGG based slip cast dispersion samples and that there

are numerous regions in the sample with porosity size in the size range of LGG.

It is seen that the freeze cast samples have a higher porosity and lower strength than the slip cast samples.

15. The diametric compression testing for the green and sintered α -SiC/H₂O/ α -SiC and α -SiC/H₂O/LGG based polar slip cast dispersions were also performed. It is seen that the green α -SiC/H₂O/ α -SiC based polar slip cast dispersions have a higher splitting tensile strength values than the α -SiC/H₂O/LGG based polar slip cast dispersions. This could be due to the higher density and better packing of the particles for the α -SiC/H₂O/ α -SiC samples compared to the α -SiC/H₂O/LGG based polar slip cast dispersions samples. It is also seen that the sintered α -SiC/H₂O/ α -SiC based polar slip cast dispersions have a higher splitting tensile strength values than the α -SiC/H₂O/LGG based polar slip cast dispersions. This could be due to the higher density and better packing of the particles for the α -SiC/H₂O/ α -SiC samples compared to the α -SiC/H₂O/LGG based polar slip cast dispersions samples. Also the effect could be due to the greater amount of porosity in the α -SiC/H₂O/LGG based polar slip cast dispersions samples. It is also seen that compared to the green samples the tensile strength values for the sintered samples are higher.

CHAPTER 6

CONCLUSIONS

The following are the major accomplishments from this work:

- A method has been developed to calculate the surface forces acting in a dispersion of α -SiC nanoparticles in an α -SiC/H₂O/ α -SiC based polar system and for α -SiC and LGG particles in an α -SiC/H₂O/LGG based polar system considering primarily the van der Waals forces.
- Developed a fundamental systematic analysis of the van der Waals force calculations for determining the molecular weight of the dispersant needed to prepare well dispersed polar and non polar nano-sized α -SiC/ α -SiC and α -SiC/LGG suspensions.
- Determined the optimum ranges for the zeta potential, pH, viscosity and for the amounts of dispersant, plasticizer, binder and solids loading to prepare dispersed systems containing nano-particles and biological agents.

CHAPTER 7

FUTURE WORK

Suggestions for the future work in this area include applying the mathematical analysis to different ceramic systems and testing for its validity. Different dispersants, plasticizers and binder combinations can also be experimented with for this technique. The dispersions prepared using this technique can be tested for various applications including targeted drug delivery and bio sensors and devices. Another area to work will be to develop a mathematical model for calculating the maximum solids loading for nano particulate systems. The optimization of the various experimental parameters can be studied.

APPENDIX A: VAN DER WAALS FORCES BASED NANO-SIZED ALPHA
SILICON CARBIDE-LACTOBACILLUS GG DISPERSIONS
IN A NON POLAR SOLVENT (DECAHYDRONAPHTHALENE)

In order to disperse the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems, we need to understand the forces that are acting on them in the system, and balance the forces, so that the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems do not aggregate. For simplifying the mathematical and theoretical understanding of dispersing α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems, let us make the following assumptions: [a] the forces acting between the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems (van der Waals) are attractive in nature, [b] the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems are perfectly spherical in shape [c] the LGG particles structure does not change with applied shear.

The van der Waals forces are the main forces for coagulation of nanoparticles in a non polar solvent, where only steric repulsion is present. [116] Hence in the system, an appropriate balance [V_T] between the van der Waals attractive force [V_A] and steric repulsive forces [V_R] are needed to disperse the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems as seen in equation (90).

$$V_T = V_A + V_R \quad (91)$$

This means that when the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems come close together, the attractive van der Waals forces becomes significant and these are the major component for causing agglomeration in the system. However, if we balance this attractive force [V_A] with a steric barrier [V_R], as shown in equation (90) [44, 117], a stable suspension will result. A schematic of the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems being separated by a steric barrier potential is shown in figure (165) and figure (166).

When the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems covered with the adsorbed polymer layer approach each other due to the inter-penetration of their polymer layers, a repulsive force is produced (steric stabilization). [116] When $V_A=V_R$, a balance between the repulsive and attractive forces will result and some optimum separation distance of ‘M’ and ‘N’ for the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems respectively. As shown in the figure (165) and figure (166), if we keep the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems are kept at a distance of ‘M’ and ‘N’ respectively from each other then the system is balanced with respect to the criteria mentioned above.

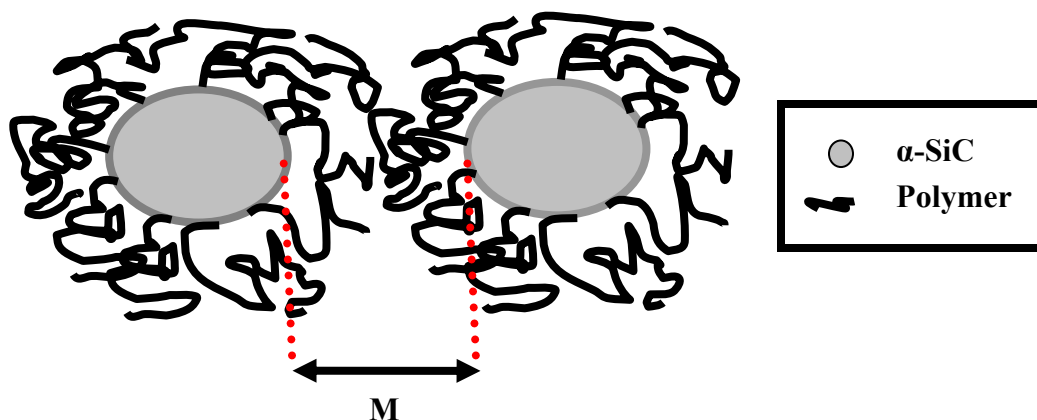


Figure 165: Sketch showing the α -SiC nanoparticles in α -SiC/ $C_{10}H_{14}$ / α -SiC non polar solvent based systems being separated by a steric barrier potential

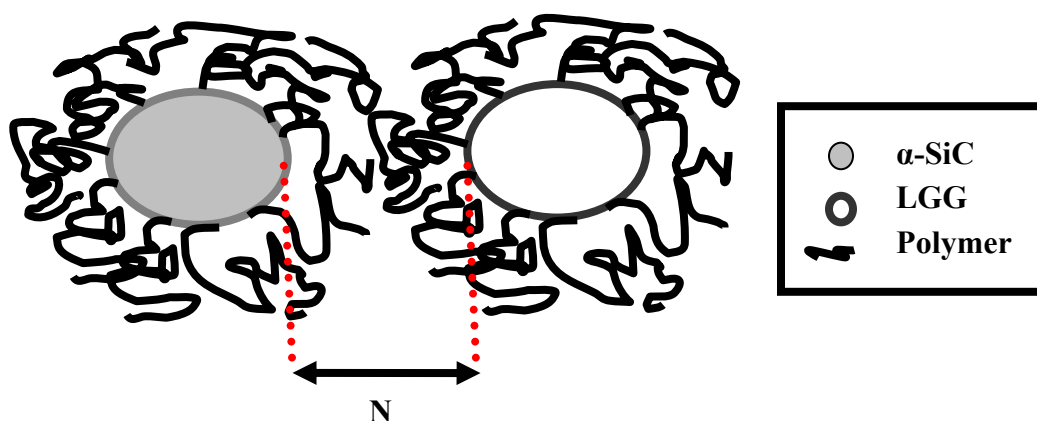


Figure 166: Sketch showing the α -SiC and LGG particles in α -SiC/ $C_{10}H_{14}$ /LGG non polar solvent based systems being separated by a steric barrier potential

For steric stabilization of a colloidal suspension the following criteria need to be met (as has been discussed earlier): (a) the polymer should firmly adhere to the surface of the particle; (b) the stabilization moieties should have a good solvent condition, (c) the adsorbed dispersant should be thick enough to overcome the attractive van der Waals forces; and (d) the polymer must cover the particle completely. [116] However, the

attractive van der Waals forces are difficult to quantitatively measure with any surface force technique [116], since the forces increase by orders of magnitude close to the surface. This causes a jump in the measuring probe and no data can be collected. Hence, it is important to determine theoretically the force balance discussed earlier.

Since we know the radius dimension for the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems equation (40) can be used to calculate the van der Waals interaction energy between the α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems. The Hamaker constants for a the α -SiC(1)/C₁₀H₁₄(3)/ α -SiC(1), and α -SiC(1)/C₁₀H₁₄(3)/LGG(2) non polar solvent based systems can be represented as (A_{131}) and (A_{132}) and can be obtained from the Tabor-Winterton approximation [118, 119] as shown in equation (53) and (55). This we believe is the first time biological material is used in such a system to develop the Hamaker constants.

However, when the radius of the particles is greater than the separation distance between the particle surfaces, the expression in equation (42) can be reduced to the commonly used form represented as seen in equation (42). [120]

Using equation (42), we can predict the variation of van der Waals separation distance between the spherical α -SiC nanoparticles in α -SiC/C₁₀H₁₄/ α -SiC, and α -SiC and LGG particles in α -SiC/C₁₀H₁₄/LGG non polar solvent based systems. An exponential curve

will result when plotting equation (42), since the van der Waals interaction varies inversely with separation distance. From this curve, we can approximately determine the minimum distance ($2r$) to keep the particles separated which will be the point on the curve the attraction becomes significant. Expanding this knowledge we can determine the molecular weight of the dispersant selected for experimentation based on similarities in solubility parameters of the solvent and the dispersant as discussed in the chapter 4. [119] Since the dispersant consists of repeated monomer units, calculating segment lengths between atoms by incorporating the radius of gyration equation as seen in equation (68), with ' r ' being half the minimum van der Waals distance calculated earlier, we can determine the appropriate order of magnitude for the molecular weight of the dispersant that can be used for experimentation. [38, 119, 121]

APPENDIX B: PRELIMINARY RESULTS FOR MICRO AND NANO POROUS MATERIALS FABRICATION USING NANO-BIO TECHNOLOGY

With the novel porous material fabrication process discussed in chapter 4, the preliminary experiments were conducted with various materials and biological agents to test the novel concept. The results from the experimentation are discussed in this section.

B1. Single Celled Fungi as the Biological Agent

B1.1 Clays

Two types of clay were used as the model ceramic systems, a high fire clay and a low fire clay. The single celled fungus, water, glucose, sodium chloride and clay were mixed in a beaker for small batches and in a Hobart mixer for larger batches. Many variations of the order of addition of the constituents to the mixture were investigated. In some cases, the single celled fungus, sugar, water, and sodium chloride were mixed in a beaker first and the single celled fungus mixture was allowed to stand for a few minutes. This mixture was then added to the clay mixture. In other cases, the single celled fungus, sugar, sodium chloride and water were added sequentially to the clay mixture. After mixing for a short period of time, the clay was formed into the desired shape. In general, the formed article was placed into a container with a small amount of water at the bottom to prevent drying of the surface of the clay during ‘rising’ of the single celled fungus. In other samples, the articles were covered with plastic wrap. The articles were placed into a drying oven at low temperature and allowed to rise for various times up to several hours.

The articles were then dried and in some case, fired and the resulting structures observed by a scanning electron microscope.

After firing the clay mixture, an article resulted which contained porosity in amounts up to approximately 70% volume porosity. An example of one of the articles processed in this manner is shown in figure (167). The large volume fraction of porosity can clearly be seen in this cut section of the sample. The porosity ranged in size from approximately several millimeters to below 100 microns.

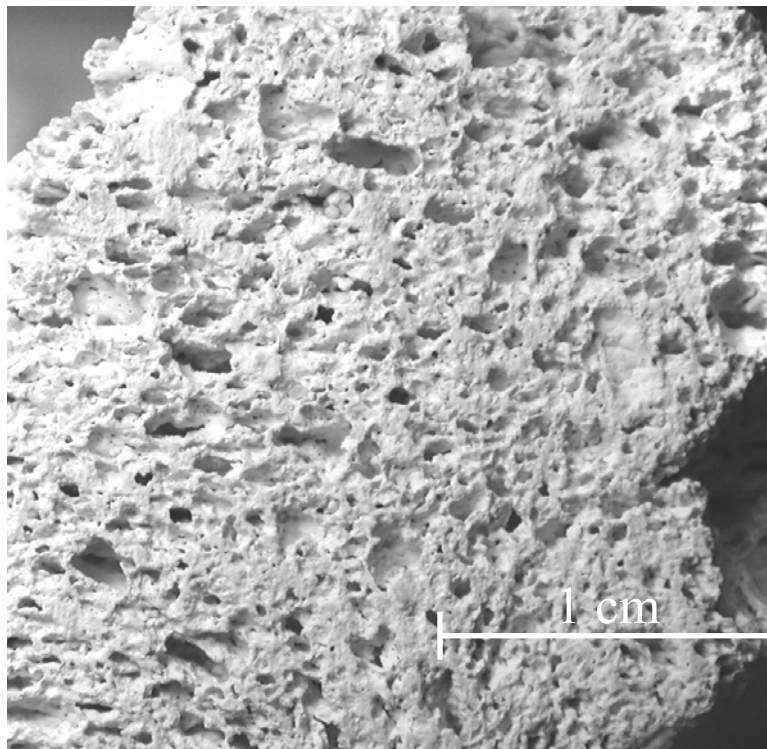


Figure 167: Porous ceramic article produced by biological agent incorporation

Figure (168.a), is an SEM image of the ceramic sample. The pore size ranges from a few hundred micrometers to a few nanometers.

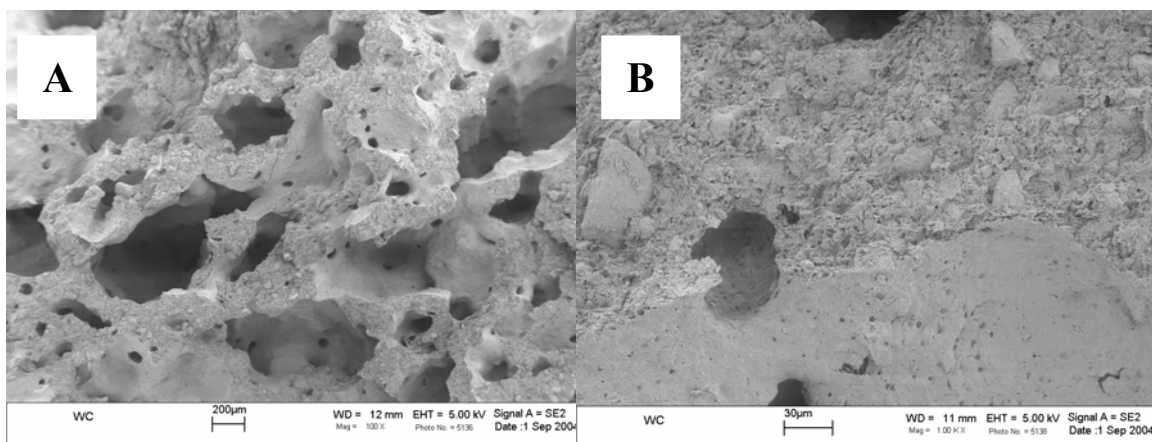


Figure 168: SEM image of the porous ceramic at (a) 1000X and (b) 100X magnification

Figure (168.b), is an SEM image of the ceramic sample at a higher magnification. The pores seem to vary in size from 50 micro meters to a few nanometers. The more interesting aspect is that we can see pores inside pores which indicate that the pores are interconnected.

B1.2 Ceramic Nanoparticles

The starting materials were nano sized silicon carbide, nano sized silicon nitride, nano sized silicon dioxide, glucose, sodium chloride, single celled fungus and de-ionized water. For this system, measured amounts of de-ionized water and the single celled fungus are taken in a beaker and hand mixed initially and then placed on a stirrer till the fungi gets dispersed in the carrier. This is followed by the addition of measured amounts of the nanoparticles (silicon carbide or silicon di oxide or silicon nitride), measured amounts of glucose and sodium chloride. The product is stirred well and left to air dry. To fasten the process of drying the samples could be placed in a furnace at elevated temperatures. Once the samples are dried the porous structures are characterized.

B1.2.1 Porosity Analysis Using Statistical Arrays

In this section we use statistical analysis to understand the effect of the contents of the nutrient media on the percent total porosity formed in the material. The amount and composition of the nutrient media play an important role in the pores produced in the material as this controls the reproduction and growth of the biological agent. The goal of this experimentation was to find out if the porosity in the material varies with the variations in amounts of the various additives added and if so what is the combination that can give us the maximum percent total porosity.

Table (21), shows the L4 statistical array that was used to study the effect of the different components of the nutrient medium on the percent total porosity for the nano sized silicon dioxide and silicon carbide material systems. The amount of sodium chloride was kept constant. The operating temperature was 30 °C and the calculated amounts of de-ionized water were added.

Table 21: An L4 array showing the levels and the factors

Factors	Level 1	Level 2
Nanoparticle [SiO ₂ or SiC]	1 g	2 g
Glucose	2 g	4 g
Single celled fungi	2 g	4 g

Accurate porosity measurements are an important part of characterizing the physical properties of porous materials. In this experiment, a liquid displacement method,

Archimedes' technique, was used to determine the percent closed porosity and the percent total porosity as seen in equation (80) through (88). These were calculated from precise measurements of the dry, saturated, and suspended weight of the porous material. The data obtained from these experimental analyses are in the tables (22) and (23).

Tables (22) correspond to structures fabricated using silicon di oxide as the nanoceramic material.

Table 22: L4 array of silicon dioxide based porous structures with data on the percent total porosity. The specifics of each level are seen in table (21)

	SiO ₂	Glucose	Single Celled Fungi	Percent Closed Porosity [%]	Percent Total Porosity [%]
A	1	1	1	9	39
B	1	2	2	33	72
C	2	1	2	16	86
D	2	2	1	16	87

From table (22), there is a huge difference in the percent total porosity values between the samples. For materials that need high porosity we can use a combination similar to sample D in table (21) and for materials that need low porosity, we can use a material combination similar to sample A in table (21), during preparation.

Tables (23) correspond to structures fabricated using silicon carbide as the nanoceramic material.

Table 23: L4 array of silicon carbide with data on the on the percent total porosity. The specifics of each level are seen in table (21)

	SiC	Glucose	Single Celled Fungi	Percent Closed Porosity [%]	Percent Total Porosity [%]
E	1	1	1	41	58
F	1	2	2	49	55
G	2	1	2	30	74
H	2	2	1	21	81

As with the case of silicon dioxide for silicon carbide samples too there is a huge difference in the percent total porosity values between the samples as seen in table (23). For materials that need high porosity we can use a combination similar to sample H in table (21) and for materials that need low porosity, we can use a material combination similar to sample E in table (21), during the sample preparation.

B1.2.2 Scanning Electron Micrographs

B1.2.2.1 Nano SiO₂ Based Structures

The SEM and EDX images of silicon dioxide based porous materials as fabricated in tables (21) and (22) are seen in figures (169), (170) and (171).

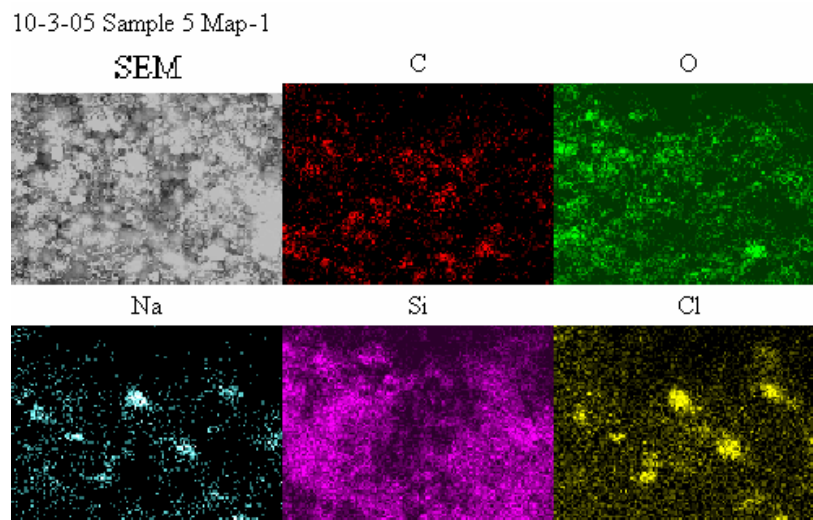


Figure 169: EDX image of the sample showing the pore formation due to the presence of the biological agent. (The regions where sodium and chlorine are present are the regions of the biological agent.)

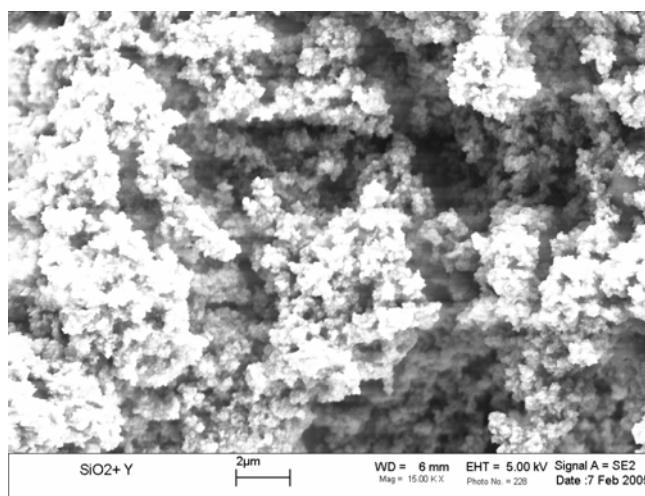


Figure 170: SEM image of sample D [see table (21) and (23) for sample contents]. The enormous amount of porosity in the material can be seen

Pores are formed in the material as the biological agent (in this case the single celled fungi) die or collapse as seen in figure (170). In some cases the biological agent is in the process of collapsing or shrinking to form the pore as seen in figure (171). The size of the pore formed is approximately the size of the biological agent—in this case around 1 micron, the size of a single celled fungus. The cracks on the surface of the fungus as seen

in figure (171) indicate that the biological agent structure is breaking. With time or on treating to elevated temperatures the formation of a pore is seen in the region where the fungus was once situated.

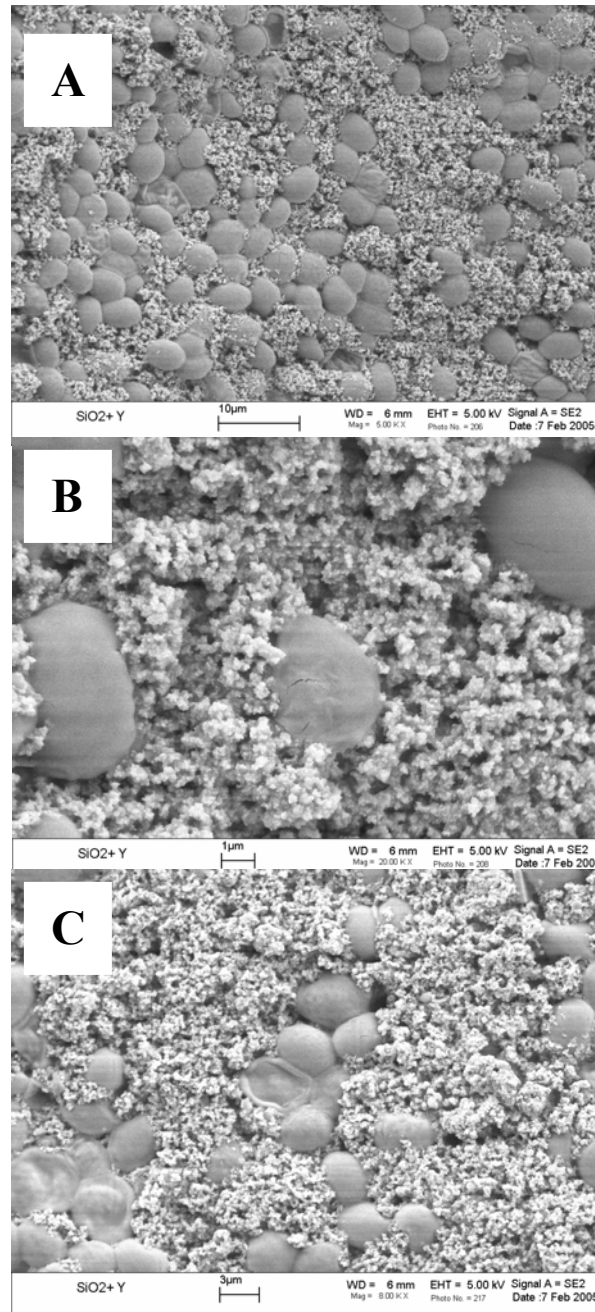


Figure 171: SEM images of sample A and B [see table (21) and (23) for sample contents]. (A) Sample A: dispersed single celled fungi and nanoparticles (B) Sample A: single celled fungi is breaking to generate the pore. (C) Sample B: pore formation by shrinking of the single celled fungi

B1.2.2.2 Nano α -SiC Based Structures

The SEM images of the silicon carbide based porous structures prepared in table (23) are seen in figure (172).

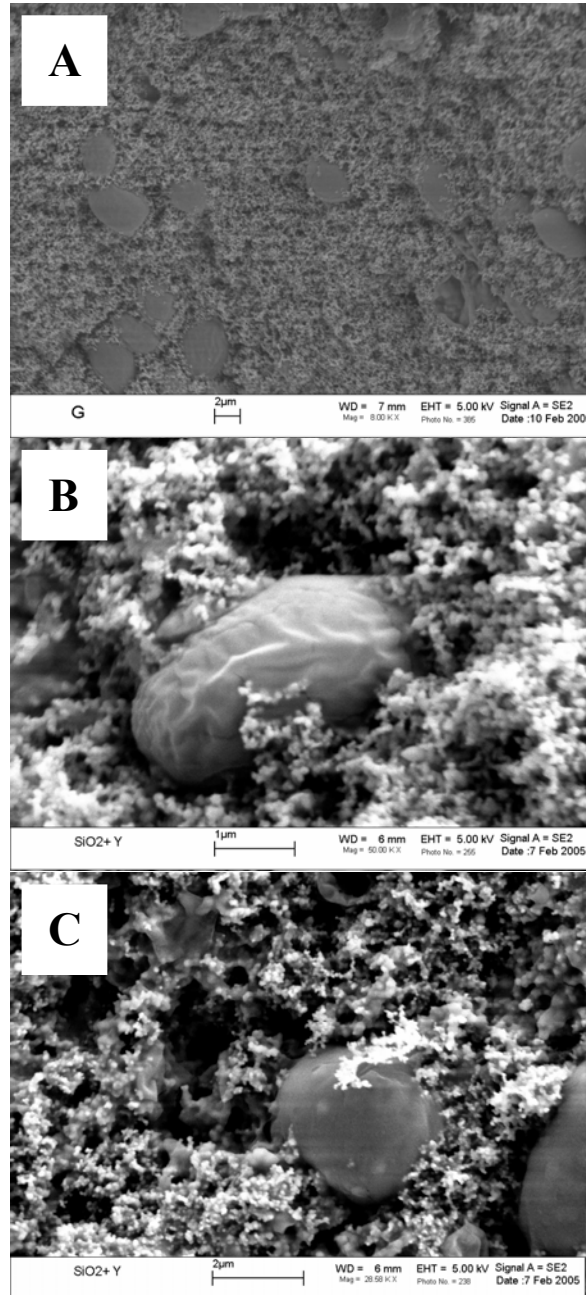


Figure 172: SEM image of sample H, G and E [see table (21) and table (23) for sample contents]. (A) Sample H: The biological agent and the nanoparticles. (B) Sample G: Biological agent is surrounded by the nanoparticles. The biological agent is shrinking to form the pore. (C) Sample E: Porosity in the material of the size of the biological agent

B1.2.2.3 Nano Si₃N₄ Based Porous Structures

The SEM images of porous structural material prepared using nano sized silicon nitride and single celled fungi are seen in figure (173). For the sample, the compositions of the starting materials included Si₃N₄, glucose, single celled fungi and sodium chloride. The silicon nitride nanoparticles surround the biological agent and with time the fungi die and the porosity that is left behind can be seen in figure (173).

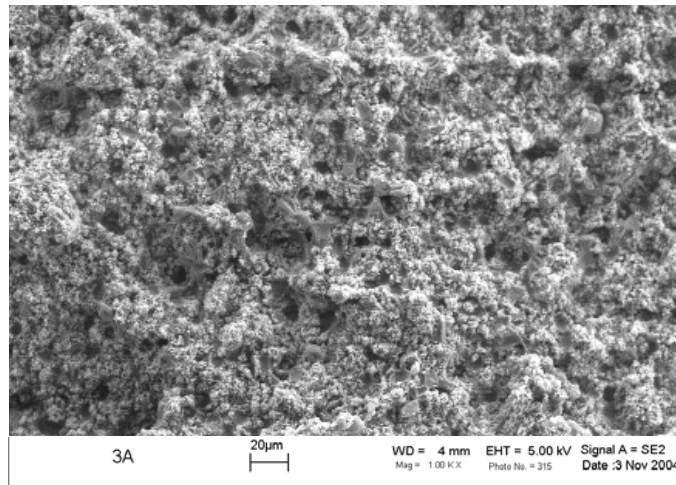


Figure 173: SEM images of the silicon nitride based porous material. (The large amount of porosity in the material is visible)

B2. Bacteria as the Biological Agent

The starting materials were silicon carbide, silicon nitride, silicon dioxide, glucose, sodium chloride, pseudomonas aeruginosa, cocci, nutrient media PAM9; which consists of sodium phosphate, sodium hydrogen phosphate, sodium chloride, ammonium chloride, magnesium sulphate, calcium chloride, iron sulphate, acetic acid and trace metals like zinc and molybdenum, and de-ionized water.

Silicon carbide was chosen for the experiments as of late there has been a lot of importance given to porous silicon carbide due to their unique combination of great oxidation resistance and thermal- shock resistance, as well as superior mechanical and chemical stability. Silicon nitride was chosen for the experimentation as the porous ceramic structural material made from this is reported to possess superior mechanical performance. Thus, offering an interesting combination of strength and stiffness. Being lighter they can be machined more easily than dense silicon nitride and hence can be used for different applications of assembled components, to reduce the thermal mismatch between the ceramic and the metal being used. Silicon dioxide was chosen as it was a widely used ceramic material.

Measured amounts of de-ionized water and the bacteria [*pseudomonas aeruginosa*] are taken in a beaker and manually stirred initially and then placed on a stirrer till the bacteria are dispersed in the carrier solution. This is followed by the addition of measured amounts of the nanoparticles (silicon carbide or silicon dioxide or silicon nitride). For making porous material based on the bacteria [*pseudomonas aeruginosa*] as the biological agent the nutrient medium was added to the suspension prepared earlier. The slurry hence prepared, is stirred well and left to air dry. For samples containing the bacteria cocci, the same procedure is followed without the addition of the nutrient media (PAM 9). To fasten the process of drying, some of the samples prepared were placed in a furnace and treated to elevated temperatures (200°C). Once the samples were dried the porous material was characterized using the scanning electron microscope.

The size ranges for fungi are between 1 and 6 microns. Protozoa's range from 1 to 300 microns in size. Bacteria range in sizes from 200 nanometers to 5 microns. Viruses have a size range of 5 to 100 nanometers.

The SEM images of samples fabricated with SiO₂ and bacteria are shown in figures (174.a) and (174.b).

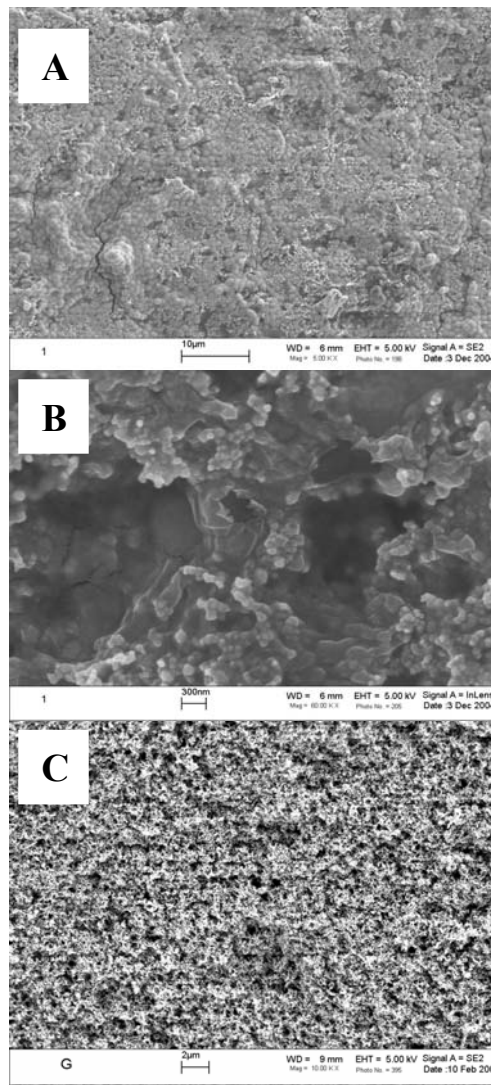


Figure 174: SEM images of SiO₂ and SiC based porous structures fabricated using cocci bacteria (A) SiO₂: The nanoparticles and the bacteria are seen. (B) SiO₂: The breaking of the bacteria is seen. (C) SiC: Showing the enormous amount of porosity in the silicon carbide based structures made using the bacteria *pseudomonas aeruginosa*

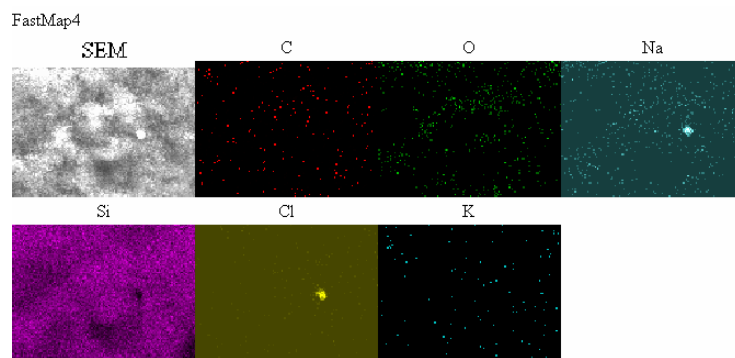


Figure 175: EDS showing the presence of the biological agent in the high amounts of sodium and chlorine in the silicon carbide based structures made using *pseudomonas aeruginosa*

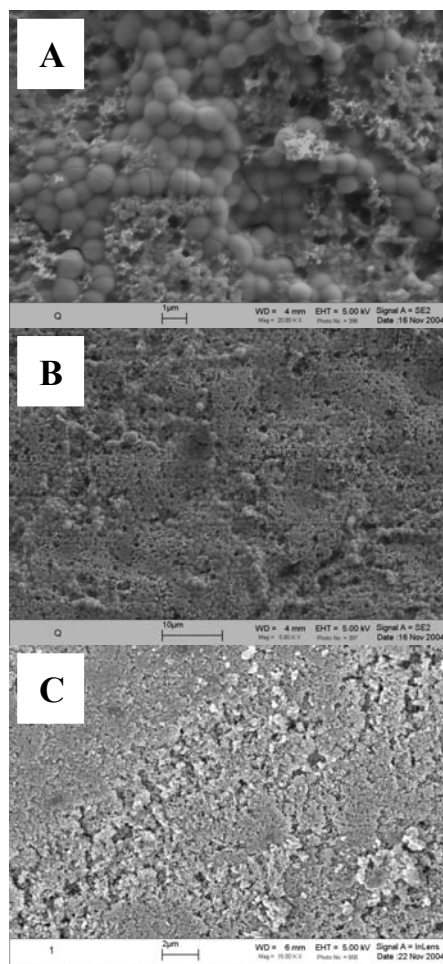


Figure 176: SEM image of porosity in silicon carbide using cocci bacteria. (A) Multiplication of the bacteria. (B) Long chains of bacteria formed in the material (C) After drying the long chain of bacteria disappears, leaving a material with porosity in long chains

The EDX and SEM images of samples fabricated with SiC and bacteria are seen in figures (175) and (176), respectively. Figures (177) through (181) are SEM and EDX images of porous samples prepared using silicon nitride and bacteria.

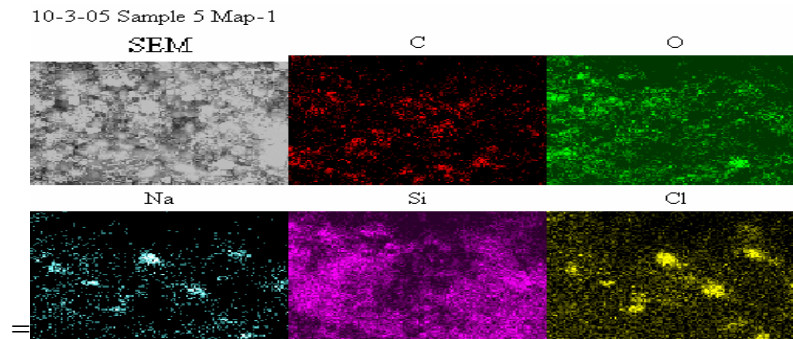


Figure 177: EDS image of silicon nitride samples using bacteria *pseudomonas aeruginosa*. Bacteria is present in the regions showing sodium and chlorine

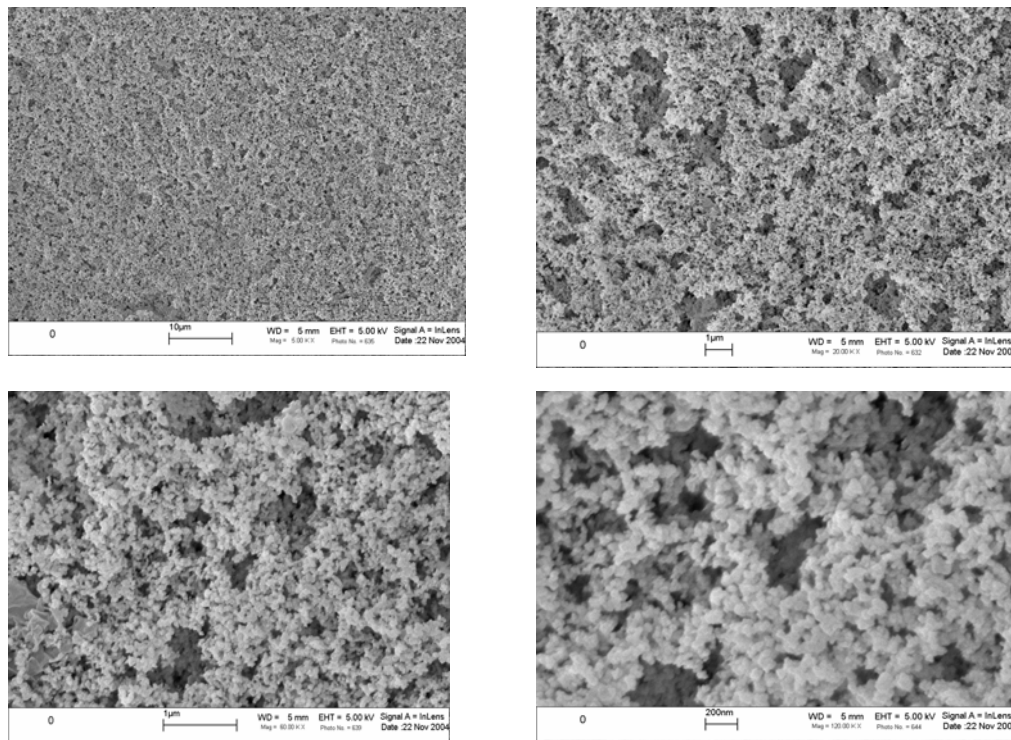


Figure 178: SEM image showing porosity in the silicon nitride samples using bacteria *pseudomonas aeruginosa* with increasing magnification

[140]. The virion is icosahedral, nonenveloped, has a diameter of 17-22 nm, and a molecular weight of 0.58×10^6 g/mol [140]. The genome has three main protein encoding open reading frames (ORF); ORF 1 which encodes Rep proteins that are responsible for viral replication, ORF 2 which encodes the virus capsid protein, and ORF 3 which has recently been described to induce apoptosis [141-143]. PCV2 is the causative agent of Postweaning Multisystemic Wasting Syndrome (PMWS) in pigs [144-146]. Some characteristics of PMWS include progressive weight loss, labored breathing, enlarged lymph nodes, lymph node lymphoid depletion, diarrhea, and jaundice in swine [147].

The complete genomic DNA of PCV2 isolate number 40895 [148] was excised from an infectious DNA clone of PCV2 cloned in the pBluescript II SK+ vector using the enzyme *SacII*, and the restriction enzyme digestion product was run on a 1% agarose gel. The 1.7 kilo base (kb) virus genomic DNA band was excised, purified using the GeneClean Spin Kit (Q-biogene Inc., Morgan Irvine, CA), and subsequently analyzed on a 1% agarose gel using molecular weight ladder, Hyperladder I (Biolone USA Inc., Randolph, MA). T4 DNA ligase (Stratagene Coop.) was then used to concatomerize the purified virus genomic DNA in an overnight ligation at 4°C. Approximately 12 µg of concatomerized PCV2 genomic DNA were transfected into three T-25 flasks of 70% confluent PK-15 cells using Lipofectamine and Plus Reagent (Invitrogen Inc., Carlsbad, CA) as previously described [149]. PCV2 virus was harvested by freezing and thawing each flask three times, and PCV2 infectivity titration was performed to determine the infectious titer of the virus stock by indirect immunofluorescence assay as previously described [149]. The

final infectious titer for the PCV2 virus stock was determined to be $0.5 \times 10^{5.0}$ ₅₀/ml tissue culture infectious dose.

The starting materials were nano sized silicon carbide, nano sized silicon dioxide, PCV2 (as prepared) and de-ionized water. To prepare the samples, the frozen PCV2 virus stock test tube was placed in a beaker with cold water for few minutes. The tube was then rubbed between the hands so as to thaw the frozen virus stock. A change in color confirmed the presence of the completion of thawing. This was followed by the addition of measured amounts of the nanoparticles (silicon carbide or silicon dioxide) to the solution containing the PCV2 virus. The product was stirred well and left to air dry for 48 hours. To fasten the process of drying the samples could be treated to elevated temperatures. Once the samples were dried, the structural porous ceramic was characterized using the scanning electron microscope.

Shown in figure (182) are samples in which SiC nanoparticles were used for the porous ceramic fabrication. Two images at different magnifications (low and high) show the porosity produced in the material. Pores in the same size of the size range of a few nanometers are seen, which are of the size of the porcine circovirus 2 that were used for the experimentation. It is envisioned that the pore formation is due to the removal of the PCV2 at elevated temperatures (200 °C).

In figure (183), silicon dioxide nanoparticles were used to prepare the samples. The large amount of porosity in the material can be seen in the micrographs.

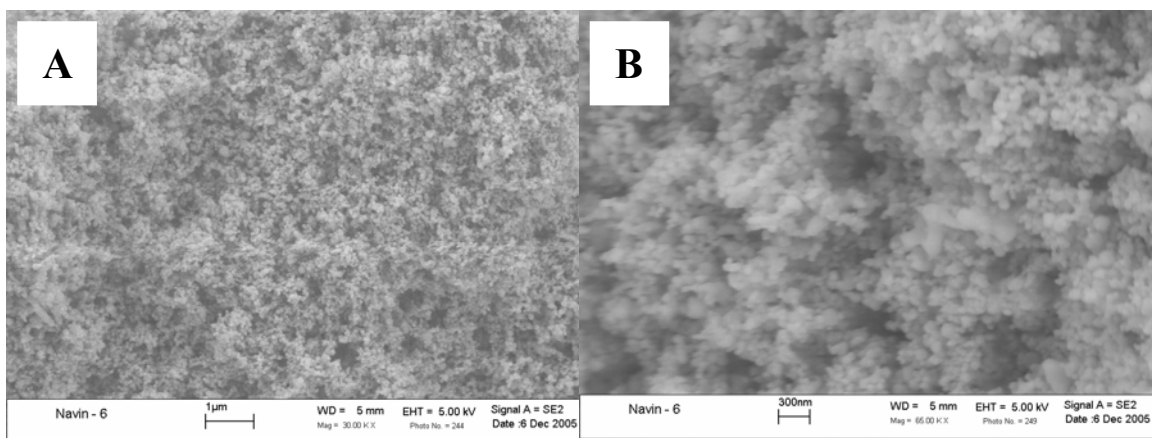


Figure 182: SEM images of the porous silicon carbide structure made using PCV 2

However, due to agglomeration of the nanoparticles and the virus because of insufficient mixing the porosity in the material is not uniform. We believe this can however be rectified by careful control of the rheology of the system.

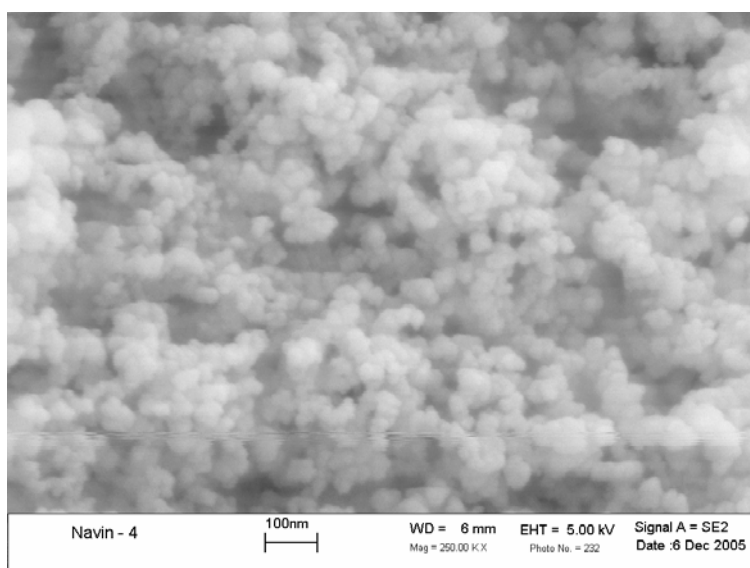


Figure 183: SEM image of the porous silicon dioxide structure made using PCV 2

APPENDIX C: APPLICATIONS OF NANO-BIO TECHNOLOGY II: TARGETED DELIVERY OF CARBON NANOTUBES AS TOOLS FOR INTRACELLULAR ANTIBIOTIC DELIVERY

The majority of the current commercial nanoparticle based applications in medicine deal with drug delivery. [150] There is a keen interest in pursuing different types of intracellular molecular transporters for drug, gene or protein therapeutics due to the high impermeability of the cell membranes to foreign substances. [3, 151] Due to their low toxicity, non-viral nanoparticles systems have gained interest within therapeutics for macrophage targeting. [152] The advantages of these systems are that they can be designed by conjugating them with specific ligands to meet specific physiochemical requirements and be targeted to a desired cell type or tissue or organ. Recent research [3, 153, 154] has shown that carbon nanotubes can penetrate mammalian cells and deliver or act as transporters of nucleic acids, proteins or small peptides to the cell.

However, the exact mechanism of the nanotube entering a cell is of considerable debate. Some researchers [153-155] believe that the nanotube pierces the cell membrane and hence by a process of insertion enters into the cell. Some others [153, 156] believe that the nanotubes enter the cell by an endocytosis process. The exact mechanism is not yet understood. The colloidal processing and the dispersion of the nanotubes are also essential to prevent any cytotoxic effect to the cell when used for the drug delivery process.

For this application too it is essential to have a well dispersed suspensions of carbon nanotubes which can be prepared as discussed in chapter 4.

C1. Research Motivation

Brucella species, *Salmonella species*, and *Mycobacterium species*, (which are intracellular bacteria pathogens) evade the killing by host phagocytic cells thereby leading to chronic infections. These infections require long term anti-microbial therapy in order to effect treatment. The reason for this being that the drugs delivered outside the cells are not effective in killing all the bacteria as the drugs do not penetrate the cells and target the bacteria effectively. This is because the cell recognizes the drug as a foreign body. The targeted delivery of antimicrobials to the infected cells using nanoparticles may effectively address the abovementioned issues and also help in the reduction of antimicrobial dose and duration required to control such intracellular pathogens. [157]

C2. Introduction and Novel Concept

In this research carbon nanotubes (CNTs) are used as a tool to deliver drugs to salmonella infected macrophages.

Carbon nanotubes (CNTs) are allotropes of carbon and have well-ordered fullerene structures [C_{60}] with high aspect ratios. These nanotubes can be single walled (one central nanometric diameter tube only) [SWNT] or multi-walled (a central nanometric diameter tube surrounded by graphitic layers separated by 3.4 Å) [MWNT]. [158, 159] Both these variants are ultra-light weight, have high tensile strength and excellent chemical and mechanical stability. [160]

The chemical modification of the CNT if done efficiently has stimulated the preparation of soluble CNT's that can be used for several biological applications and particularly drug delivery. [161] The CNT acts as a carrier for the drug to the bacteria inside the cell. The attachment of the ligands to the CNT surface guides the CNT to the infected cell and kills the bacteria.

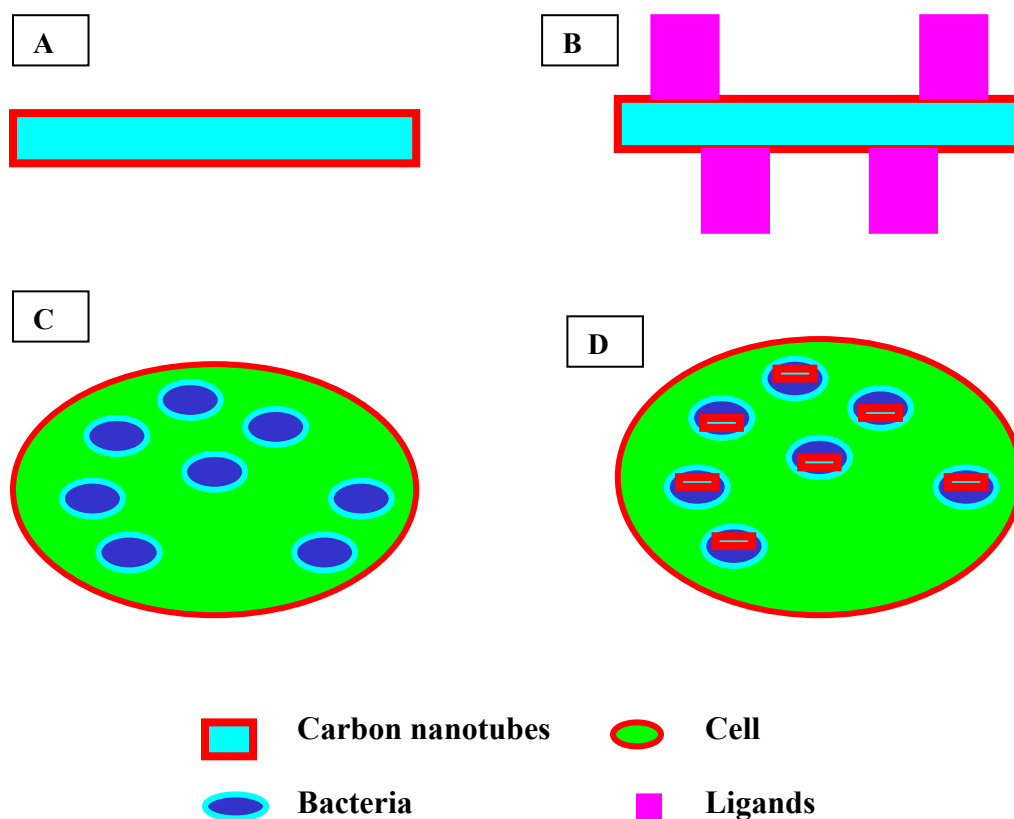


Figure 184: Schematic of the drug delivery concept. Ignore the scale in this schematic

However, the dispersion of CNT's has not been clearly understood and especially as it relates to its use in biological systems. The strong inter-tubular forces (both van der Waals and electrostatic) promote aggregation of the nanotubes. Hence, it is important to

understand the forces acting on these tubes to have better dispersion. There have been many investigations on dispersing nanotubes both in a polar solvent [for polymeric interactions] and in aqueous solvents [for drug delivery]. Some of the successful techniques include sonication, using a surfactant or dispersant for stabilization and covalent functionalization. [160] Sonication can be done using an ultrasonic horn or probe or an ultrasonic bath. In this case there is no need for any chemical modification as the CNT's disperse and stable suspensions have been reported. [160, 162] However, other researchers have found aggregated nanotubes even after sonication. [151, 160, 163, 164] Sodium dodecyl sulphate (SDS) and TritonTM X-100 are the most commonly used surfactants to disperse the nanotubes. Biomolecules have also been used as dispersing agents. Functionalizing the CNT surface is another method to disperse nanotubes. This can be done by covalently attaching the requisite group such as peptides, genes, polymers, etc. to the carbon nanotube surface. The attachment is carried out through –COOH bonds that are generated on the CNT structures by amidation or esterification. [160]

Figure (184), is a schematic showing the concept of the research. The CNT's are dispersed initially by sonication as seen in figure (184.a). The dispersed nanotubes are treated with specific chemicals so as to form sites on the CNT surface for the antibody and the antibiotic to bind to as seen in figure (184.b). Figure (184.c) is a cell containing bacteria. As the bacteria multiply the cell will die. Hence, the goal is to target the functionalized nanotubes (f-CNT's) to the bacteria inside the cell so that the bacteria die and the cell lives as seen in figure (184.d). The antibody targets the f-CNT's to the cell.

The antibiotics need to be delivered to the bacteria that are inside the cell for it to kill the bacteria and keep the cell alive.

Reference [165] shows how a CNT is oxidized using a strong acid (H_2SO_4) resulting in a reduction in their overall length and producing carboxylic groups which enhance their dispersability in aqueous solutions. [161] Reference [166], shows the structure of EDC and reference [167], shows the amide formation mechanism with the CNT. The formation of an amide using carbodimide is straightforward but with several side reactions that complicate the process. Certain additives like N-hydroxybenzotriazole can be added to increase yields and decrease the side reactions taking place. The antibody attached to the EDC is responsible for transporting the nanotube to the infected macrophage. The reason for this is that the antibody is basically a negative of the site that needs to be targeted (in this case the infected macrophage).

The structure of antibiotics Gentamicin and Centiofur Sodium (NAXCEL) are seen in reference [166]. The antibiotic attaches to the nanotubes also at the carboxylated end and are responsible for killing the intracellular bacteria.

Other carriers for delivering the drug are also being pursued which are biodegradable and hence can be effectively used in the body as they can be made to dissolve in a controlled fashion over time. [157]

C3. Potential Advantages

This technique of targeted delivery of antimicrobials to the infected cells using nanoparticles should effectively address treatment for intracellular bacteria pathogen (*Brucella sp.*, *Salmonella sp.*, and *Mycobacterium sp.*) based chronic infections. Also, targeting intracellular pathogens using this technique may have an enormous potential especially in dealing with drug resistant pathogens requiring long term therapy.

C4. Preliminary Results and Discussion

C4.1 Mathematical and Theoretical Basis

For the dispersion of the carbon nanotubes for drug delivery the same concepts as discussed in chapter 4, based on the van der Waals forces that correspond to the shape of the nanotubes can be used. If we consider the nanotubes to be parallel cylinders we can use the equations (50) and calculate the van der Waals forces that are necessary to overcome to keep the particles separated by a distance (M), as schematically shown in figure (185).

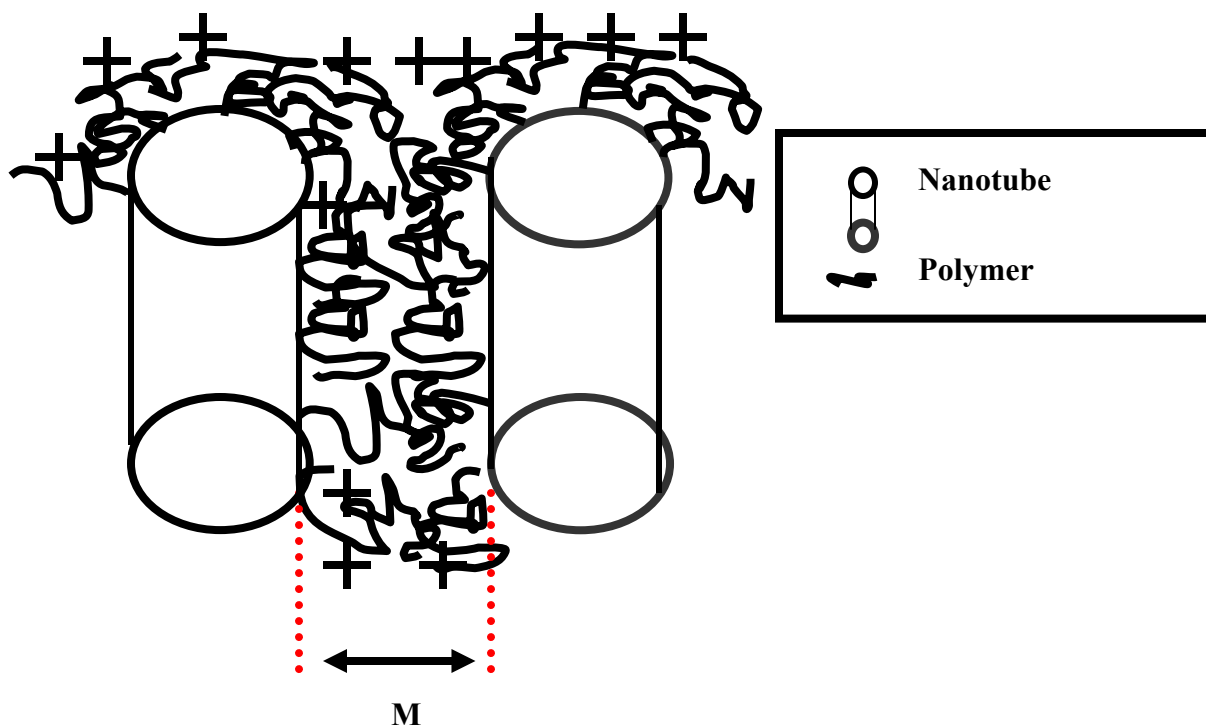


Figure 185: Schematic for dispersing nanotubes in a liquid medium using electro-steric repulsion

From these figures and the equations described in chapter 4, we can determine the appropriate amounts of dispersants needed to obtain a well dispersed slurry. The balance of the van der Waals forces with a combination of the steric barrier and the electrostatic forces is the governing condition to keep the particles dispersed in the polar medium.

C4. 2 Transmission Electron Microscope Images

Transmission electron microscope images for the preliminary results obtained using this technique are presented and compared to similar data obtained from the literature in this section. Figure (186), shows the TEM images of carbon nanotubes that we characterized and can be compared with that seen in the literature. [168]



Figure 186: TEM image of carbon nanotubes

Figure (187) is the TEM images of CNT-antibody/antibiotic complex that we prepared and it can be compared with the CNT-DNA complex seen in literature. [169]

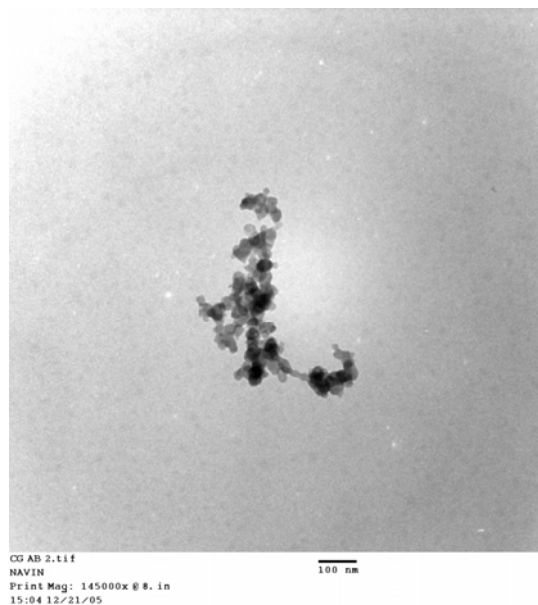


Figure 187: TEM image of carbon nanotubes-antibody/antibiotic complexes

Figure (188), is the TEM images of salmonella infected macrophage that we prepared and we can compare this with that of the Guinea Pig alveolar macrophage infected with *Legionella pneumophila* as seen in the literature. [170]

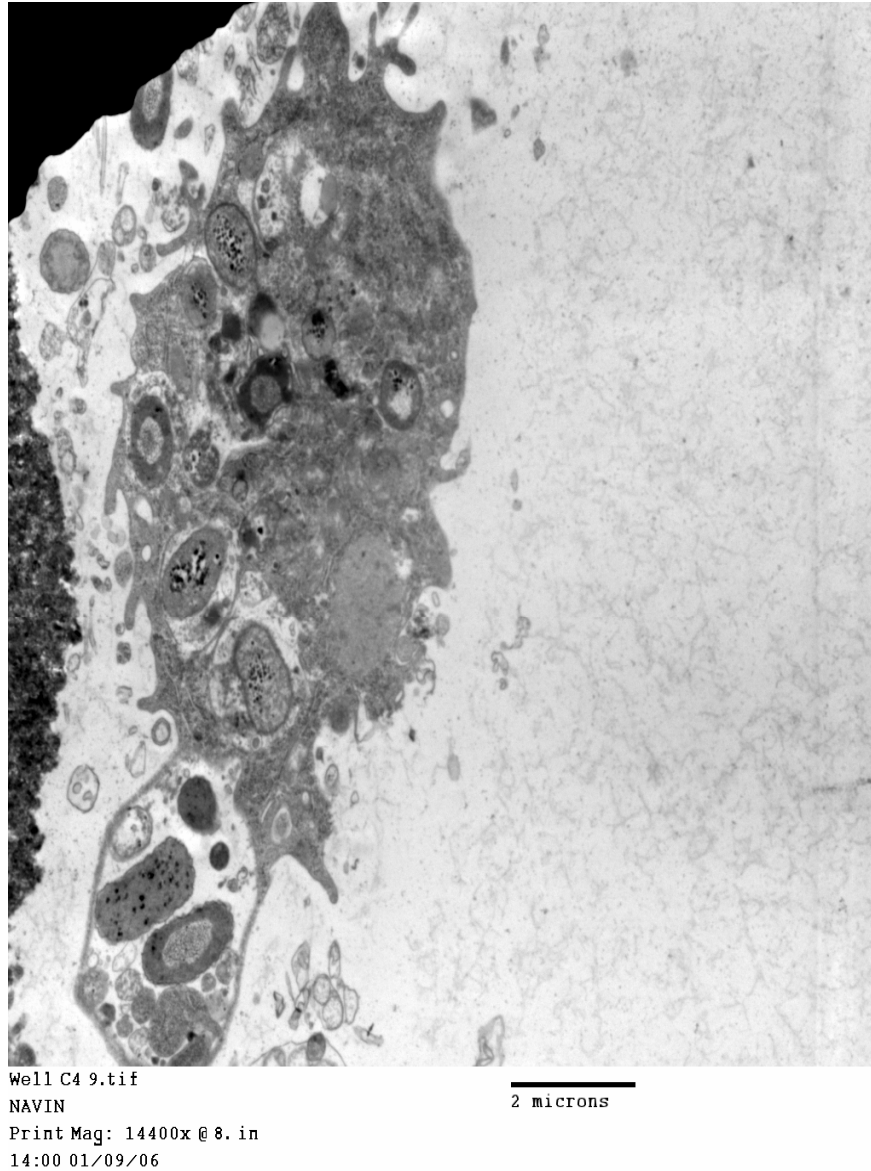
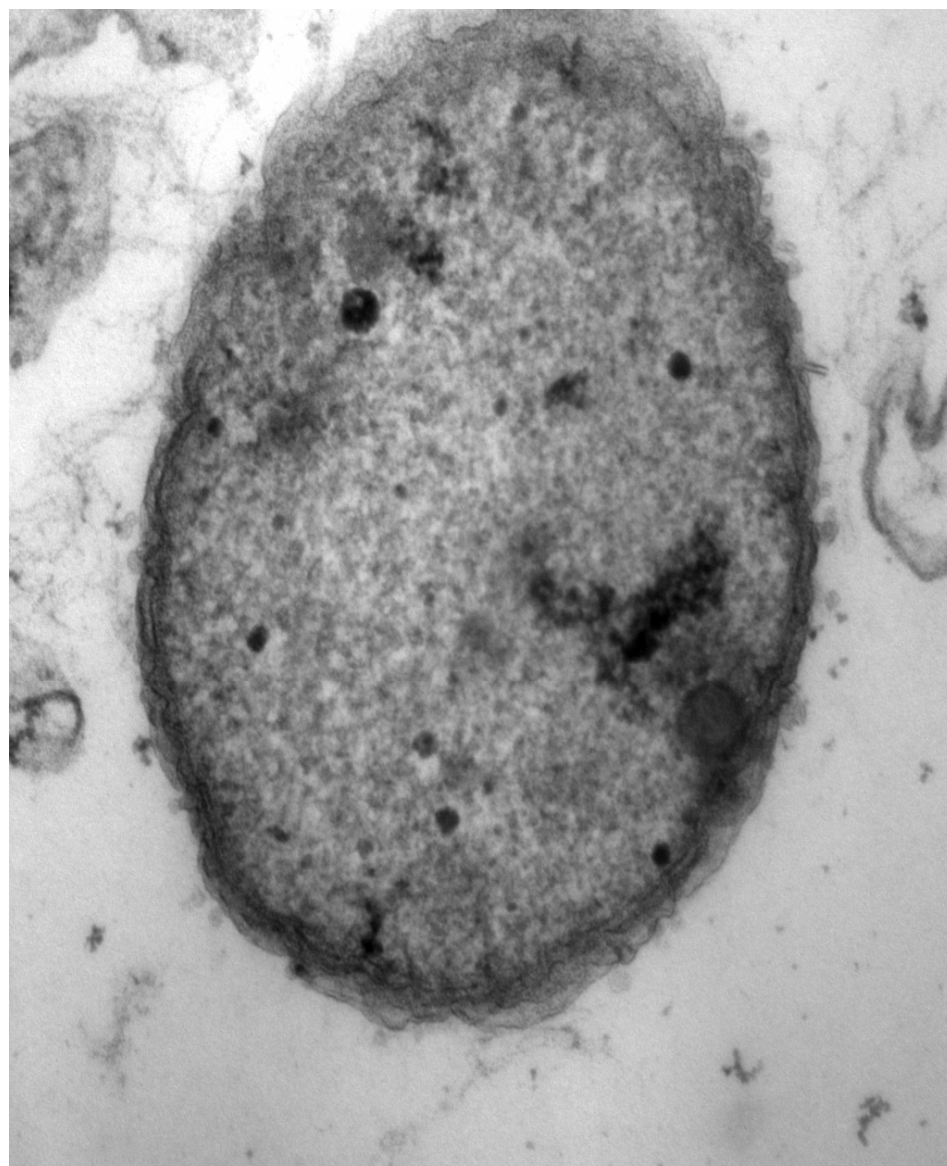


Figure 188: TEM picture of bacteria infected macrophage

Figure (189), is the TEM images of CNT as seen by us inside the bacteria and it can be compared to the magnesium oxide nanoparticles seen inside *E. coli* bacteria in literature.

[171]



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100 nm

Figure 189: TEM picture of salmonella bacteria containing carbon nanotubes

It is important to mention here that the elemental data characterization on these TEM images has not been found in the literature. The reason is because it is difficult to analyze biological samples under a TEM. However, TEM confirmed the phagocytosis of CNT by the macrophages as seen in figure (193).

In conclusion, the preliminary results suggest that we can deliver antibiotics using CNTs to control intracellular pathogens. Targeting intracellular pathogens using this technique may have an enormous potential especially in dealing with drug resistant pathogens requiring long term therapy.

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VITA

Navin was born on the fourth of July in Ankamaly, a small village in the outskirts of Cochin, Kerala, India. Being brought up in a middle-class family his opportunities to learn was scarce. However, right from his childhood he was fascinated by the wonderful world of mathematics and physical sciences. Constant presentations at science exhibitions and interactions with scientists and faculty enhanced his interest which led to him receiving scholarships for his entire schooling. Besides academics, he was also ranked in the top hundred in singles and doubles in men's tennis in India and also participated at the Indian nationals in enterprise class sailing and water-skiing. His first steps towards an engineering career came in May 1997 with his admission into the prestigious National Institute of Technology (NIT), Warangal, Andhra Pradesh, India (the oldest of the NITs). A consistently high academic record helped him secure the 'Naval Foundation' scholarship for his entire undergraduate program in Metallurgical Engineering. He graduated from NIT, Warangal with the 'Alumni Association Gold Medal', for being the best outgoing student and all-rounder (valedictorian) and also the 'Sri Kabadi Subalu Silver Medal', for being the best outgoing sportsperson among the students graduating in the year 2001. He was the first student in NIT Warangal history (since it was founded in 1959) to win both these prestigious medals. After graduation, a decision had to be made between joining Mahindra British Telecomm (MBT) or to go in for higher studies. A graduate research assistantship with Dr. Wolfgang Sigmund in Materials Science and Engineering at the University of Florida (UF), Gainesville, starting in Aug 2001, made the decision easier. After securing his masters degree from UF in

May 2003, Navin worked at the materials research labs at CAU and AMPAC before coming to Virginia Tech (in Aug 2004) to pursue his Ph.D. in Materials Science and Engineering with Dr. Gary Pickrell. At Blacksburg too, Navin has continued to involve himself with the student government and the international community. He has held several leadership positions on campus including being the graduate student representative to the Virginia Tech Board of Visitors (the governing authority of Virginia Tech) and the President of the Council of International Student Organizations (representing more than 110 countries and 50 student organizations). Based on his academic, leadership and service to the university community; he has been presented several awards including the '2006 Outstanding Student Award', '2006 Paul E. Torgerson Ph.D. Research Excellence Award' and the '2006 Graduate Student Service Commendation Award'. Navin has also filed for three patent disclosures, published more than fifteen peer reviewed publications and has presented at more than thirty international, national and local conferences and meetings. He has also been inducted into several honorary, academic and leadership societies including the 'Alpha Epsilon Lambda', 'Omicron Delta Kappa', 'Who's Who', 'Order of the Gavel' and 'William Preston Honor Society'. He is also a Virginia Tech Citizen Scholar. He has also been a founding member of the Journal of Undergraduate Materials Research (JUMR), Graduate Speaker Series at the Graduate Life Center, Graduate Scholars Society and the International Education Week at Virginia Tech. Navin has accepted an offer to work for Siemens Corporation after graduation.