# Influence of Interface on the Properties of Silicone Nanocomposites

by

Faisal Aldawsari

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Electrical and Computer Engineering

Waterloo, Ontario, Canada, 2018

# AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

# Abstract

The increase in voltage levels and electrical stresses of the electrical equipment have resulted in demands for electrical insulations that have high breakdown strength, low losses, high thermal conductivity, and high mechanical performance. Use of dielectric polymer nanocomposites is a promising approach as nanocomposites have superior properties over traditional materials. The improvements of electrical, mechanical and thermal properties are related to the plurality of interfaces introduced with nanoparticles as fillers. Addition of fillers to the polymer materials not only enhance their performance but also reduce the cost. In this thesis, influence of interface on the electrical properties of silicone nanocomposites has been investigated.

Poor interaction between nanoparticles and base polymer, and particle agglomerations limit the performances and applications of nanocomposite materials unless the fillers are dispersed and distributed uniformly. Base polymers, nanofillers, surface treatment of the fillers, filler concentrations, and dispersion techniques are the main factors that determine dispersion status and overall properties of the composites.

In this study, filler loading levels, surface treatment of nanofillers and different processing techniques are investigated. Incorporation of treated and untreated nano-alumina into RTV 615 silicone rubber with different weight percentages of nanofillers 5wt %, 7.5wt% 10wt%, and 20wt% has been investigated. Surface treatment are used to change the hydrophilic surface of nano-alumina to hydrophobic and to enhance the dispersion. Electrostatic disperser (ES) and high shear (HS) methods have been used to obtain further improvements in the properties of the composites.

Dielectric spectroscopy, thermographic analysis (TGA), laser erosion tests, and mechanical performance evaluations are used to study the effect of the interface on the electrical, mechanical and thermal properties of nanocomposites.

Results obtained with the above techniques, and scanning electron microscopy (SEM) images have demonstrated that treated nano-alumina prepared by high shear (HS) and electrostatic disperser (ES) have a better filler dispersion and distribution than untreated nano-alumina. Also treated nano-alumina composites showed less dielectric loss and high erosion resistance than those composites with untreated nano-alumina. Results further confirm that particle dispersion using ES mixing is better than that using HS mixing.

Filler polymer interactions and dispersion can be analyzed by using dielectric spectroscopy, in specific using the frequency responses below 0.01 Hz. The low frequency spectra can reveal the interfacial polarization, hence the reflected permittivity. The present result indicate that treated nano-alumina filled silicon rubber has lower permittivity than untreated nano-alumina at very low frequency because of the restriction of polymer chain mobility. In addition, untreated fillers being hydrophilic can absorb moisture and have resulted in composites that show high permittivity values particularly at frequencies below 0.001Hz.

# Acknowledgements

I would like to express my thanks to Allah for blessing me and my family. All praises are due to Allah for giving me the ability and knowledge to complete this thesis.

I would like to express my sincere gratitude and appreciation to my supervisor, Professor Shesha Jayaram, for her continuous support, encouragement, and precious guidance throughout my master study.

I also like to thank Dr. Chitral Angammana for his great support in the beginning of this work. I also extend my thanks to Prof. Ayman El-Hag and Prof. Siva Sivoththaman to be a part of my master committees. I would like to express my appreciation to Mohana Krishnan for his great help.

I give my appreciation to my friends in the High voltage groupmates for their support and for the moments we spent together. I would like to express my thanks to Arathi Sharma and Dr. Khadija Khanum for their great cooperation and useful discussion during this work. I would to express my gratitude to all my friends in Waterloo and in Saudi Arabia especially Abdullah Alshehri, Ahmed Alqurashi, Mohammed Aldosary, Nizar Alshrief, Mohammed Fekri, Ahmed Marof, Hassn Alrajhi, Majed Alotaibi and Abdulrahman Aloraynan for their help and care.

I would like to express my deepest thanks to my parents, my brothers, my sisters for their prayers, patient and supports during my master journey. A special and an exclusive thanks to my mother for her love and motivation.

# Dedication

**To my dear parents**

**To my beloved wife and adorable daughter**

**To my brothers and sisters**

# Table of Contents

# List of Figures

x

# List of Tables

# Chapter 1
# Introduction

## 1.1 Emergence of Nanocomposite Materials

The demand for new approaches to improve and optimize electrical insulation materials has gained attention in the last two decades. It is expected that the improvements of electrical insulation allow them to operate at higher temperature and electrical stresses. Recent advancement in polymer nanocomposites shows interesting results and new developments applied to electrical insulation. The terms nanodielectrics was introduced for the first time by Lewis in 1994 which is now the most cited paper in this field [3]. However, it was not clear how it could improve electrical insulation until Nelson and his team did series of experimental works in 2002 to understand the different properties of nanocomposites [1]. Subsequently, many studies have been conducted to investigate electrical, thermal, mechanical and optical properties of these nanometric materials and also on their different fabrication techniques. The number of publications has increased gradually since 2002 as shown in Figure 1.1. For the field of electrical insulation, nanocomposite materials are defined as structures that consist of nanofillers having at least one dimension less than 100 nm dispersed usually in some base polymer. Nanocomposite consists of three main phases: fillers, base polymers and the interface between fillers and matrix. The base materials can be classified into three main categories: thermoplastics (e.g. polyethylene, polyvinyl chloride (PVC) and polypropylene), thermosets (e.g. epoxy resin, polyester resin and polyimide) and elastomers (e.g. silicone rubber, polyacrylic rubber, and epichlorohydrin rubber). These base materials have also been used widely for nanocomposites because they are easy to fabricate, have light weight and are relatively low cost. Nanoparticles or nanofillers that are commonly used in electrical insulation can be classified into four main group: silicon oxides (silica), metallic oxides and hydroxides (alumina, hydrotalictes); nanoclays (montmorillonite, hectorite); and carbon nanotubes [1-6]. The interface that exist between the two phases, fillers and base polymers, play a significant role in defining the final product, the nanocomposite. Therefore, understanding the effect and mechanism of interface is very important to modify the composite performance.

Despite the advantages of polymeric materials, they deteriorate faster than ceramic and glass insulators, and could lose their hydrophobicity under certain condition [7,8]. Therefore, in order to improve the performance of polymeric materials, inorganic nanofillers are introduced to polymer

1

matrix. Incorporation of nanofillers into base polymers overcome the limitations of neat polymer materials in electrical insulation [2].
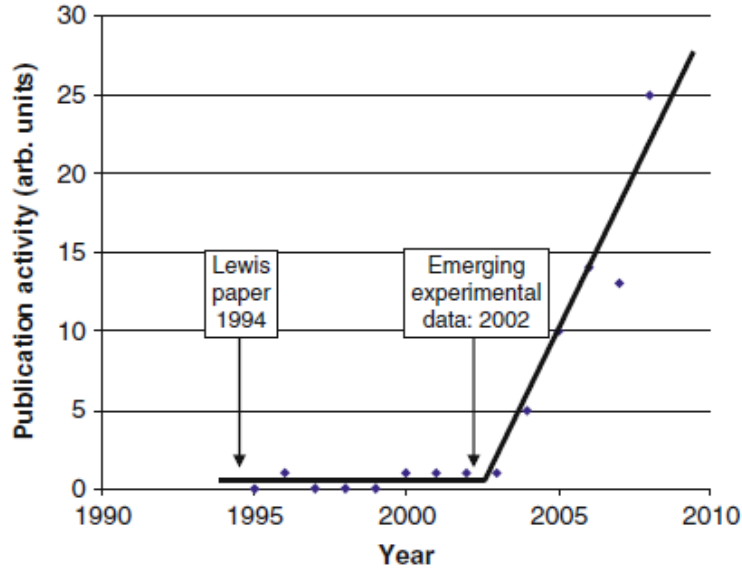


**Figure 1.1** Publication Activity in the field of Nanocomposites [1].© Springer, 2010.

## 1.2 Nanofillers

Inorganic nanofillers such as alumina ($Al_2O_3$), silica ($SiO_2$), titanium dioxide ($TiO_2$), boron nitride (BN), zinc oxide (ZO) are incorporated into different polymer matrix such as epoxy resin (ER), polypropylene (PP), silicone rubber (SiR), polyamide (PA) to gain specific electrical, mechanical and thermal properties such as improved relative permittivity, breakdown strength, thermal stability, tensile strength, etc. Nanofiller can be classified into three categories according to their dimensions [2,9]:

- One dimension such as plates and shells.

- Two dimensions such as nanotubes and nanofibers.

- Three dimensions such as spherical nanoparticles.

These nanofillers are homogeneously dispersed in polymers with a quantity in the range of 1-20 wt%. Nanocomposite fillers are distinguished from micro-composite fillers in their low loading level (up to 20 wt% for nanofiller, and exceeding 50 wt% for micro-fillers) and their large specific surface area to volume ratio [2]. The properties of nanocomposites are determined by shape, size, chemical nature, loading level, and dispersion of nanofillers, nature of polymer matrix and the interphase between base

2

polymer and fillers. The choice of nanofillers depends on their electrical, mechanical, optical and thermal properties. In electrical insulations, past experimental works have shown promising results in terms of electrical breakdown strength, relative permittivity, dielectric losses, space charge behavior, erosion resistance, tracking and electrical tree resistance, thermal conductivity and tensile strength respectively [1,2,7,10,11,12,13, 14].

## 1.3 Surface Treatment

Nanoparticles agglomerate due to their high surface energy and this agglomeration or cluster formation limits the properties and applications of nanocomposite materials. As such homogeneous dispersion of nanoparticles into polymer matrix that brings favorable properties to polymers is essential. However, homogenous dispersion cannot be achieved unless inorganic nanoparticles have proper surface treatment because of poor chemical bonding between inorganic nanoparticles and base polymers as inorganic nanoparticles are hydrophilic and base polymer are hydrophobic in most cases.

Surface modification of nanofillers not only improve the dispersion of nanofillers, but also improve the interface between nanofillers and host polymers. Therefore, it is important to modify the surface of nanoparticles to obtain excellent properties and better bonding between nanofillers and base polymers. Surface treatment of nanofillers opens new ways of enhancement and improvement of nanocomposite materials' properties. There are many methods that have been used to modify the surface of nanofillers which improve the adhesion between nanofillers and polymer matrix such as chemical method, grafting method and plasma treatment method.

Chemical treatment method of nanoparticles surface is a very important method to reduce aggregation and allows better dispersion of nanofillers. In this method, different coupling agents like silanes, titanates, zircoaluminates and zirconates are used to change the surface polarities of the fillers. Grafting of functional polymeric molecules to the hydroxyl groups of the surface of fillers is another important method used to overcome the incompatibility between organic and inorganic nanocomposites. In addition, Plasma method is used to make the fillers' surface more or less wettable, harder, and more conducive to adhesion [2,15,16,17, 18].

3

## 1.4 Filler Dispersion

Homogeneous dispersion of nanofillers in the base polymers lead to a large volume fraction between atoms which cause strong interfacial interaction between nanofillers and polymer matrices. As a result, the nanocomposite with a large number of interfaces provide enhanced performance to the polymers. However, nanoparticles tend to agglomerate due to incompatibility of hydrophobic polymer matrices and hydrophilic nanoparticles and due to high surface energy of nanofillers which will result in poor interfacial interactions [19]. Geometry of the fillers is a significant factor that influences the state of dispersion of nanofillers [20]. Good dispersion of nanoparticles into base polymers is not enough to gain excellent properties because the nanoparticles may disperse very well, but the distribution of the particles in the base polymer is bad. Dispersion of nanofillers determines whether the particles are agglomerated; whereas, distribution of nanofillers determine whether the nanoparticles are distributed uniformly inside the base polymer. Figure 1.2 illustrates the distribution and dispersion state of nanoparticles [21].
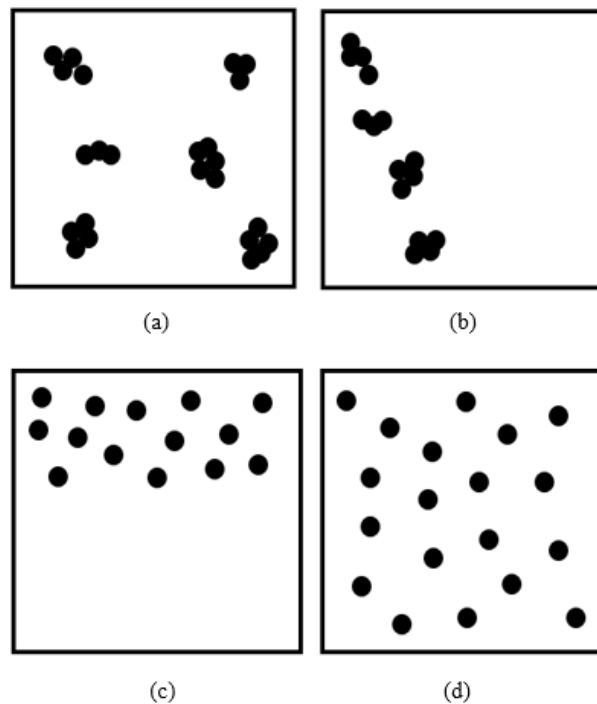


Figure 1.2 illustration of the distribution and dispersion state of nanoparticles:
(a) Poor dispersion but good distribution (b) Poor dispersion and poor distribution.
(c) Good dispersion but poor distribution (d) Good dispersion and good distribution [33].

4

There are several techniques that have been used to obtain a good dispersion and distribution of inorganic nanofillers into base polymers [1,2, 7,45]:

- Sol-gel method

- Melt blending

- Solvent Method

- In situ polymerization

- High-shear method

- Electrospinning method

Reference [1,2] describes in details the first four techniques used in preparing nanocomposites, and reference [7,45] has described the general principle of high-shear and electrospinning mixing techniques.

## 1.5 The Role of the Interface

An important aspect of changes in properties is related to the plurality of interfaces introduced through the use of nanoparticles as fillers. As the particle size reduces, the specific surface area becomes very large; hence the interfacial area forms a significant volume fraction of the polymer in nanocomposites. The interfacial area surrounding the filler has properties different from both the bulk polymer and the filler. Therefore, materials can be engineered for improved specific functionality by effectively dispersing nanoparticles into polymer matrix [22].

The large surface area surrounding the fillers is very important because the bonding between nanofillers and polymer matrix will be stronger and the number of interfaces between them will be larger [23]. Therefore, as the particle size is reduced the materials are dominated by the properties corresponding to the interaction zone [24].

Several publications aim to explain the role and structure of interface between nanoparticles and polymer matrix. In the model proposed by Lewis [25], the interface ab between two uniform material phases A and B, is described as shown in Figure 1.3. An increasingly dominating interface in nanocomposite materials as filler size reduces is illustrated in Figure 1.4. Thus, as the filler size reduces, the property typical for bulk material can be gradually diminished.

5

In such a scenario, more of the particles reside in interface states under the influence of interfacial forces, which differ from the bulk forces [25]. Therefore, in the vicinity of each particle, or clusters of particles, the interfacial region modifies the properties of the material. The thickness of this interaction zone is between 5 to 20 nm and it shows dependence on concentration, shape, and size of the nanoparticles [24]. More importantly, the dispersion of particles in polymer matrix as defined by mixing methods ultimately defines the properties of composites [23, 26].
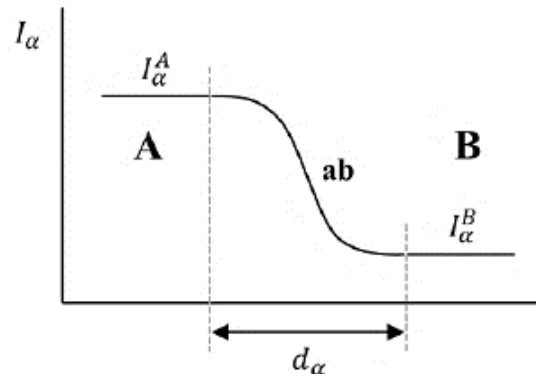


Figure 1.3 Representation of an interface ab between two phases A and B with intensities $I_\alpha^A$ and $I_\alpha^B$. The parameter α is a chosen property changing over the interface with thickness, dα [25]© IEEE 2004.
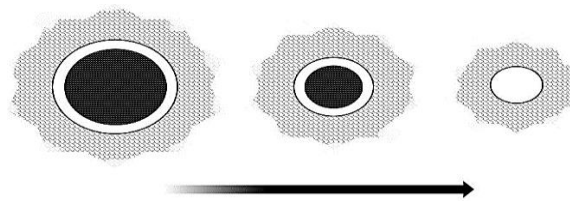


Figure 1.4 Illustration of an increasingly dominating interface as the particle or filler size reduces in nanocomposite materials [25] © IEEE 2004.

## 1.6 Polarization

The dielectric materials are polarized when they are exposed to the external electrical field. Polarization is responsible for dipole formation and alignment of electric charge along the direction of the electric field. Under electric field, complex dielectric permittivity $\varepsilon^*$ is given by [8],

$$\varepsilon^* = \varepsilon' - j\,\varepsilon'' = \varepsilon_0\,\varepsilon_r - j\,\varepsilon'' \qquad\qquad \textbf{1. 1}$$

Where $\varepsilon'$ is the relative permittivity which is related to amount of polarization, and $\varepsilon''$ is the imaginary part of permittivity which is the dielectric loss during dipole formation. Measurement of real and imaginary permittivity over a wide range of frequency and temperature can identify moisture, aging process and other contaminants. Dissipation factor (tan δ) is given by equation 1.3 which is used to evaluate the quality of dielectric materials [8].

$$\textbf{tan δ} = \varepsilon'' / \varepsilon' \qquad\qquad \textbf{1. 2}$$

There are four modes of polarization mechanisms: Electronic polarization, ionic polarization, orientation or dipolar polarization and interfacial polarization. All four types of polarization are shown in Figure 1.5. Polarization (P) is the sum of all dipole moment per unit volume. As given by following equation [8].

$$\textbf{P} = (\,P_{electronic} + P_{ionic} + P_{dipolar} + P_{Interfacial})\,/\,\textbf{Volume} \qquad\qquad \textbf{1. 3}$$
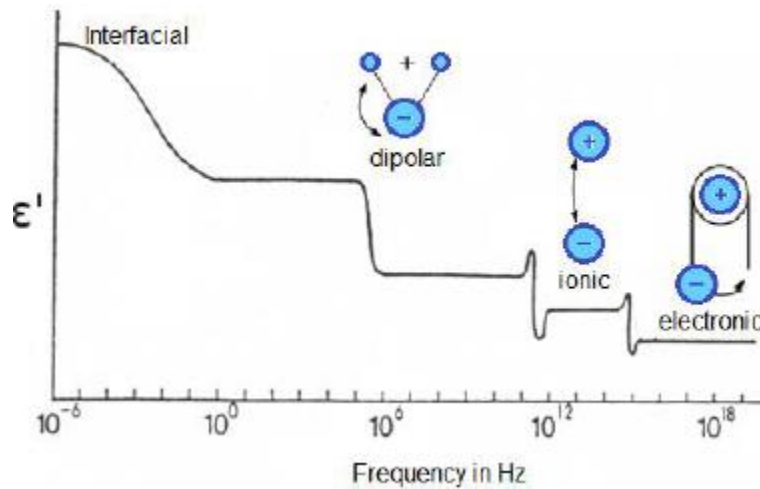


Figure 1.5 Variation of relative permittivity (or dielectric constant) of dielectric materials versus frequency [23].

7

Electronic polarization occurs in all atoms and molecules. When an electrical field is applied, there is a shift of electrons that occur within molecules. Thus, the center of positive and negative charge is separated by distance d, as shown in Figure 1.6 [8] . Comparing with other polarization mechanisms, magnitude of electronic polarization mechanism is relatively small and it occurs at UV frequencies.



Electron Cloud                    Electron Cloud

(a)                                    (b)
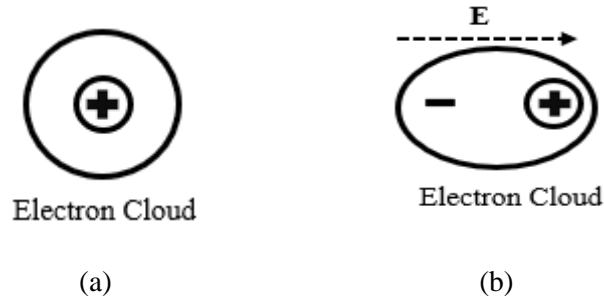
**Figure 1.6** Electronic polarization: (a) without electric field (b) with electric field.

Ionic polarization occurs in ionic materials such as NaCl and $BaTiO_3$. Without an electric field, there is no net dipole moment of these materials. Displacement of cations and anion in opposite direction occur when an electric field is applied which leads to unequal charge separation as shown in Figure 1.7 [8]. Ionic polarization response is slower than electronic polarization. Ionic polarization can lead to noticeable change in dielectric constant.



(a)

E

(b)
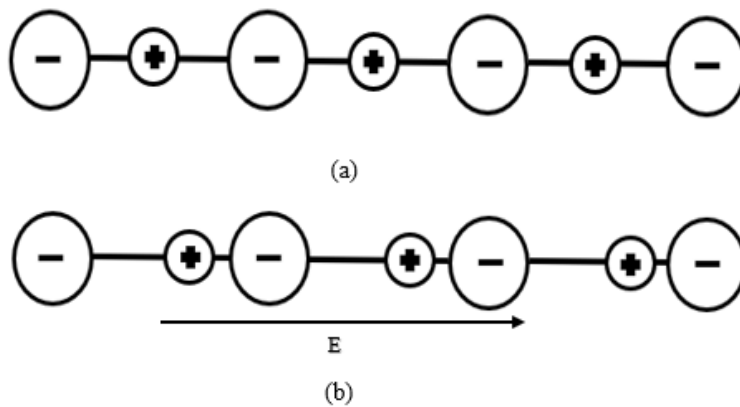
Figure 1.7 Ionic polarization: (a) without electric field (b) with electric field [8].

Orientational or dipolar polarization occurs in dielectric materials that have polar molecules. Polar molecules have permanent dipole moment. Before the application of electric field, there is no net dipole moment because dipoles are randomly oriented. Under the application of electric field, randomly oriented dipoles align with the direction of electric field as shown in Figure 1.8 [8].



(a)                                      (b)
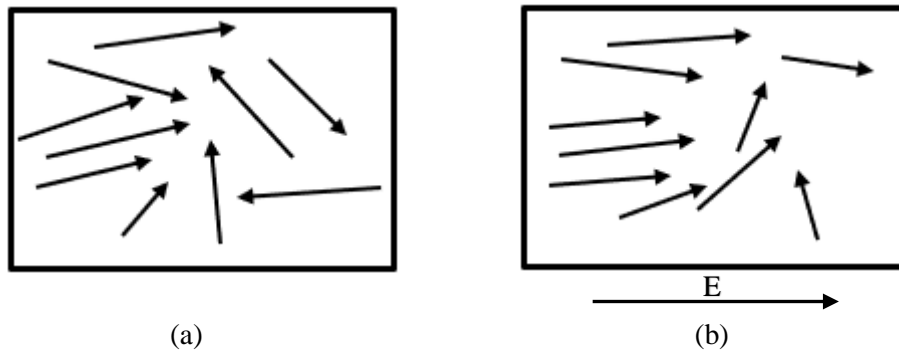
Figure 1.8 Orientational polarization: (a) without electric field (b) with electric field [8].

Interfacial or space charge polarization occurs in heterogeneous materials where there are multiple phases or regions. For example, in polymer nanocomposites, electrical charges accumulate between polymers matrix and fillers which has a huge effect on their properties. Interfacial polarization effect is also seen at the dielectric and electrodes. In the absence of electric field, there is no net separation between positive and negative charges. with the application of an electric field, charge carriers will migrate over a distance through the material. The charges are trapped at the interface of a material as shown in figure 1.9 [8]. The accumulation of these charges increases the relative permittivity. Interfacial polarization occurs at very low frequency below 1Hz.
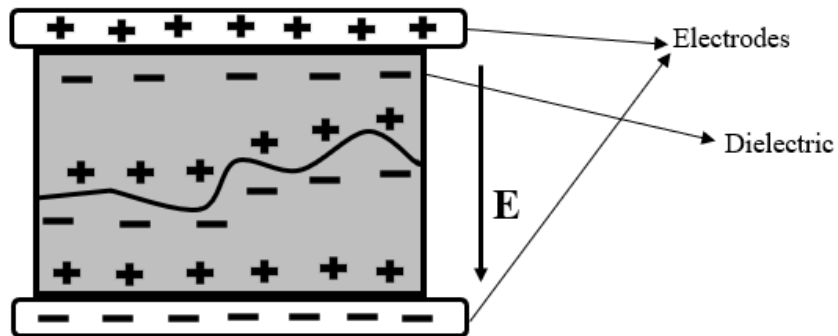


Figure 1.9 Interfacial polarization at the presence of electric filed [8].

### 1.6.1 Dielectric spectroscopy

Dielectric spectroscopy measures the complex permittivity and dissipation factor or dielectric loss (tan δ) as a function of frequency and temperature which can provide information about polarization process of the composite and any manufacturing contaminates. Therefore, dielectric spectroscopy is a powerful tool to improve the quality of the nanocomposite materials. Dielectric spectroscopy is very important for studying nanocomposite materials, especially at a very low frequency where the Maxwell-Wanger effect starts to appear [1].

## 1.7 Base Polymer

Due to unique properties of polymer materials such as high electrical resistance and breakdown strength, light weight, less dielectric loss and tunable flexibility compared to glass and ceramic materials, polymers have been used widely in electrical insulation applications. In the dielectric nanocomposite field, the polymer matrix can be classified into three major categories: thermosets, thermoplastic and elastomers. Thermosets are 3D cross-linking structure which brings favorable mechanical performance and thermal stability. The 3D structure can be cured by heat (above 200 ℃) or by high energy irradiation. Thermosetting materials such as epoxy resin, polyester resin, and urea formaldehyde cannot be melted and reused. However, Thermoplastic materials can be melted by increasing the temperature and solidify upon cooling. The typical examples of thermoplastic are poly (methyl methacrylate) (PMMA), polypropylene (PP), and polyvinyl chloride (PVC). These kinds of materials can be reprocessed multiple times. Compared to thermosetting materials, thermoplastics materials have lower thermal resistance. Elastomers are flexible polymers that have soft structure and low glass transition temperature (Tg). Comparing with thermoplastics and thermosetting polymers, elastomers have better damping and sealing performance. Many researches have conducted to study elastomers as base polymers in nanocomposite due to their outstanding recoverable deformation [1,2,7,8]

An example of elastomers is silicone rubber (SiR) which has very high thermal and chemical stability. Silicone rubber has been used widely in distribution lines, transmission lines, electronic devices, cable accessories, and gate dielectrics. Silicone rubber exhibit stable resistance to UV radiation, ozone, corona and heat because it has stronger bonding between polymer chain compared to other polymers. However, due to dust, wetting, and arcing, silicone rubber may temporarily lose their hydrophobicity. In addition, silicone rubber has very thermal conductivity and poor erosion resistance.

There are three kinds of SiR: RTV (room temperature vulcanizing), LSR (liquid silicone rubber), and HTV (room temperature vulcanizing) silicone rubber [7,8,27].

## 1.8 Literature Review

Different kinds of fillers have been added to base polymers to overcome the limitations of polymers and to improve their electrical, mechanical and thermal performance. This literature focuses on the applications of nanocomposites in electrical insulations.

### 1.8.1 Electrical, Thermal and Mechanical properties of Nanocomposites

Roy et al. [28] demonstrated that incorporation of 5% nanosilica into cross-linked polyethylene (XLPE) have a higher breakdown strength and voltage endurance compared to 5% microsilica. The authors found that nanosilica treated with vinylsilane is more effective at higher stress levels comparing with untreated nanosilica where there exists a weak bonding between fillers and polymer matrix. For similar loading level (5%), microsilica fillers showed a significant increase in relative permittivity, while there is a reduction in permittivity for the nanosilica comparing with microsilica and base resin. The loss tangent (tan $\delta$) found to be lower with nanosilica when compared to microsilica because nanofillers reduce the chain movement of the polymers through physical bonding. Roy et al. [12] also studied the behavior of 5 wt % $SiO_2$ filled XLPE with different surface treatment to see the influence of the interface between matrix and nanofillers. Nanofillers were functionalized with hexamethylisilazane (HMDS), aminosilane, and triethoxyvinylsilane agents. Treated and untreated nanocomposites showed better breakdown strength and endurance than base resin. At room temperature, all treated nanocomposites had higher breakdown strength than untreated nanocomposite. Nanofillers treated with triethoxyvinylsilane agents showed the largest increase in breakdown strength.

Another study has been conducted by Sun et al. [10] on epoxy/silica nanocomposite and microcomposite with higher loading level of 20%. Relative permittivity and loss tangent (tan $\delta$) were found to be higher for nanocomposite than epoxy resin and microcomposite. The authors indicated that the higher dielectric loss is due to the increased ionic conductivity caused by contaminants from the sol-gel synthesized nanofillers.

Nelson et al. [29] reported a reduction in space charge and an increase in dielectric strength for 10% titanium dioxide nanofillers filled epoxy resin over a 10% titanium dioxide microfillers filled epoxy. This study showed that titanium dioxide nanofillers filled epoxy resin has higher voltage

endurance than micron size titanium dioxide filled epoxy resin. Microcomposites showed higher relative permittivity than both nanocomposite and epoxy resin. Nanocomposites have a lower relative permittivity than epoxy resin because nanofillers may restrict the movement of the side-chain or end-chain of the epoxy molecules.

Calebrese et al. [30] investigated the effect of incorporation of nano-alumina with different concentration level 2.5 wt%, 5 wt%, 7.5 wt% and 10 wt% into polyamideimide. Alumina/Polyamideimide nanocomposites showed increase in breakdown strength and real permittivity. However, a reduction in breakdown strength and permittivity was obtained at higher loading 10 wt%, which could be due to filler agglomeration. Increase in dielectric constant for nanocomposites also reported in many other research studies [31,32,33].

Kochetov et. al [34,35] incorporated different type of particles such as alumina, aluminum nitride, magnesium oxide, boron nitride, and silica into epoxy resin. The surface of the particles was treated to obtain a good adhesion between organic polymers and inorganic nanoparticles. The dissipation factors of the composite did not change significantly with increasing nanoparticles up to 5wt%. The relative permittivity of epoxy filled with 0.5wt%, 2wt%, 5wt%, 10wt% MgO, 0.5wt%,2wt%, 5wt% $Al_2O_3$ and 0.5wt%, 2wt% AIN found to be lower than neat epoxy. Whereas, relative permittivity of epoxy filled with 0.5wt%, 2wt%, 5wt%, 10wt% $SiO_2$ , 10wt% $Al_2O_3$, and 5wt%, 10wt% AIN is higher than unfilled epoxy. The authors assumed that higher relative permittivity can be due to presence of byproduct inside epoxy resin after preparing the composite by in-situ or it can be due to different preparation process of the samples, while the reduction in relative permittivity is caused by restriction of the chain mobility of epoxy resin. Thermogravimetric (TGA) results showed that treated $Al_2O_3$ and MgO have higher weight loss than untreated particles because particles treated with silane coupling agent have an organic chain that degrades at high temperature, thus higher weight loss was observed for treated fillers. Surface treatments of particles react with OH group and this reaction makes boding between particles and base polymers stronger. Therefore, the chain mobility will be restricted in the vicinity of nanoparticles.

El-Hag et al. [36] evaluated the erosion resistance of SiR with nano and micro silica. The addition of nanosilsica to SiR increase the erosion resistance. Erosion resistance increases proportionally with the increase of filler concentrations. Nanosilica filled SiR has higher erosion resistance comparing to microsilica filled SiR.

Ramirez et al. [11] analyzed erosion resistance of RTV 615 SiR with nano fumed silica, nano natural silica, and nano alumina. Triton$^{TM}$ X-100 surfactant has been used to achieve good dispersion of the filler into SiR matrix. At same amount of surfactant and concentration, fumed silica showed higher eroded resistance than natural silica and alumina nano fillers. There is no significant difference observed in erosion resistance between nano natural silica filled SiR and nano alumina filled SiR.

Han et. al. [13] studied the thermal conductivity of epoxy resin nanocomposite with different type of particles such as alumina, boron nitride, silicon carbide, diamond and silicon nitride with different sizes from micro to nano. The thermal conductivity of epoxy resin filled with boron nitride increases exponentially with filler concentrations. Filler sizes of boron nitride did not show a big difference in thermal conductivity. All other fillers showed a little enhancement in thermal conductivity, but it was not comparable to boron nitride.

Yasmin et. al. [37] analyzed the mechanical and thermal properties of 2.5wt% and 5wt% graphite platelet dispersed in epoxy resin. Tensile strength of the composite with 2.5wt% graphite showed about by 21% enhancement over the pure epoxy. However, tensile strength of the composite with 5wt% graphite is increased by only 9% compared to neat epoxy. The elastic modulus of the composite increased by increasing the addition of the fillers. Moreover, both 2.5wt% and 5%wt graphite composites showed higher thermal stability than epoxy.

With above literatures, it was shown that dielectric constant and dissipation factor can increase or decrease with the introduction of nanofillers. The result of real permittivity and loss factor depend on many factors such as the base polymer, nanofillers, surface treatment of the fillers, filler concentrations, filler agglomerations and dispersion techniques. Nanoparticle added to the base polymer to improve specific properties. Strong interactions between base polymer and nanofillers are attributed to improve thermal stability of the composite. It has been reported that incorporation of nanofillers into base polymer improve tensile strength and elongation at break of composite. However, nanofillers tend to agglomerate easily due to electrostatic force during mixing in base polymer and incompatibility between hydrophilic nanoparticles and hydrophobic base polymer resulting in weak interaction between them. In addition, scanning electron microscopy (SEM) can provide a good insight into

particles agglomeration, but it is not able to give enough information about the interaction between base polymers and nanoparticles [47]. Therefore, it is difficult to achieve desirable improvements without a proper fillers dispersion and distribution in base polymer.

## 1.9 Objective and Organization of the Thesis

Polymer nanocomposites have received a great attention in the last few years due to their significant improvements in electrical, thermal and mechanical properties over traditional polymer materials. These improvements are attributed to an interfacial region between nanofillers and base polymers. However, depending on the strength of interface between nanofillers and base polymers, the improvements of the composites can be very high or very low. Therefore, there is a great need to investigate the effect of interface on the properties of nanocomposites.

The interfacial interactions determine the status of the dispersion and the amount of the interfacial area [38]. Fillers agglomerations limit the interactions between base polymers and nanofillers. Therefore, in order to obtain strong interfacial interactions between polymer matrices and nanofillers, good dispersion and uniform distribution are required which can be achieved by either using surface treatments of nanofillers or by using effective mixing method.

This study is focused on the influence of interface between nanofillers and base polymers and their effect on electrical and thermal properties. Treated and untreated nano alumina were selected to investigate the effect of interface on the properties of the silicone rubber nanocomposite. Both conventional mixing, and electrostatic disperser methods have been used to analyzed the effect of mixing. Nanocomposites were prepared with different filler concentrations to study the impact of inorganic fillers on the properties. Furthermore, dielectric spectroscopy was used to measure the relative permittivity and dissipation factor of the composite on a large range of frequency. It has been demonstrated that the trends observed using dielectric spectroscopy are informative for composite materials especially at very low frequency where particle agglomeration and the Maxwell-Wanger effect start to influence the polarization [1].

The main objectives of this thesis are as follows:

- To study the influence of interaction zone between nanoparticles and base polymers.

- To investigate the effects of surface modifications in the properties of the nanocomposites.

- To understand the impact of different processing on the properties of the composite.

- To analyze and evaluate the role of filler concentrations in the composites.

In view of above objectives, the remaining sections of the thesis is organized into the following chapters:

- ❖ Chapter 2 presents the specification of the materials and preparation methods used in this work. Thermal gravimetric analysis (TGA), laser ablation test, scanning electron microscopy (SEM), tensile strength and dielectric spectroscopy have been used to evaluate the properties of the nanocomposites.

- ❖ Chapter 3 shows the electrical, mechanical and thermal results of the nanocomposite that have been gained from different experiments.

- ❖ Chapter 4 discusses the electrical, mechanical and thermal results of the nanocomposites. In addition, the effect of interface on relative permittivity and loss factor have been described in this chapter.

- ❖ Chapter 5 provides the conclusion of this thesis and suggestion for the future works.

# Chapter 2
# Materials and Experimental Setup

As shown in literature, the improvements in the properties of polymer materials can be achieved by introducing nanofillers to base polymers. However, nanofillers agglomeration and weak interaction between nanofillers and base polymers have negative impact on in the composites properties. Therefore, to enhance the properties of the composites and to overcome these limitations, various mixing techniques have been used in order to obtain homogenous dispersion and uniform distribution of the nanofillers. Moreover, surface treatments of nanofillers have been applied to attain strong interaction between nanofillers and base polymers.

This chapter describes material specifications, and composite preparations and the performance assessments of the composites. The assessments include dielectric spectroscopy, thermographic analysis (TGA), infrared laser test, tensile strength and scanning electron microscopy (SEM) analyses.

## 2.1 Materials specifications

The host polymer material used in this work is a two-parts silicone rubber (SiR) RTV 615 manufactured by General Electric. It consists of a clear liquid silicone rubber (part A) and curing agent (part B) (see Table 2.1). These two parts are clear and colorless liquid which can cure at room temperature. This kind of SiR was chosen because of its low viscosity, low cost, low weight, containing no fillers or solvents in their chemical composition. In addition, curing rate of RTV 615 can be accelerated by heat for fast productions.

Alumina ($Al_2O_3$) is used widely in dielectric polymer nanocomposites as filler to improve both electrical and thermal properties. It has high thermal conductivity (18-35 W/m.K), low thermal expansion and relatively high dielectric constant. In this work, two different types of alumina particles manufacture by Evonik; AluC 805 treated with organosilane and untreated AluC shown in Table 2.2 were used with different weight percentages; 5wt%, 7.5wt%, 10wt%, and 20wt% respectively for investigations.

**Table 2.1 Characteristics of the base polymer**

| Polymer matrix | Viscosity (cps) | Mixing Ratio by weight | Curing Temperature ($^o$C) used. |
|---|---|---|---|
| Silicon Rubber RTV 615 | 4000 | 1 :10 | 150 $^o$C |

**Table 2.2 Properties of alumina particles**

| Filler | Material loss on drying (%) | Specific surface area (m$^2$/g, BET) | Density (g/cm$^3$) @ 20 $^o$C |
|---|---|---|---|
| Aeroxide® Alu C | 5 | $100 \pm 15$ | 3.27 |
| Aeroxide® Alu C 805 | $\leq 2$ | $90 \pm 15$ | 2.6 |

## 2.2 Composite Preparations

Silicone composites were prepared by dispersing nano particles using two different methods of dispersion. The first method dispersed the particles by using a high shear (HS) mixer (RossTM model HSM-100LSK), Figure 5. The speed of the mixing blade is calculated as:

$$\text{rpm} = \frac{\text{Peripheral velocity} \left(\frac{\text{m}}{\text{sec}}\right) \times 60 \times 1000}{\text{d(mm)} \times \pi} \qquad \text{2. 1}$$

The mixing ratio is 10:1 by weight and that is 10 parts RTV615 (part A) to one-part RTV 615 (part B). First, the nanofillers were added gradually to part A silicon rubber and mixed it at a speed of 12,000 rpm for approximately 20 minutes. During this process, high speed of mixer and friction of materials cause the composite to heat, hence the composite was kept in a cooling bath for five minutes. Subsequently, part B was added to the composite and mixed for 5 minutes. In the second method, an electrostatic disperser (ES) (Figure 2.1 (b)) was used [45]. First, nanoparticles were added gradually to RTV615 part A and stirred until the particles becoming wet. Then, the compound was

17

mixed with electrostatic disperser until there is no visible of lumps. After dispersing nano alumina particles in RTV615 part A, RTV615 part B was added to the mixture and stirred for 5 minutes. Both compounds from different mixtures were degassed in a vacuum oven at 28 inHg to remove bubbles form the compound. The resulting blends from both high shear (HS) and electrostatic disperser (ES) were poured separately into different aluminum moulds and hot pressed at 1200 psi and 150 ºC for 15 minutes to obtain cured slabs.



(a)                                                              (b)
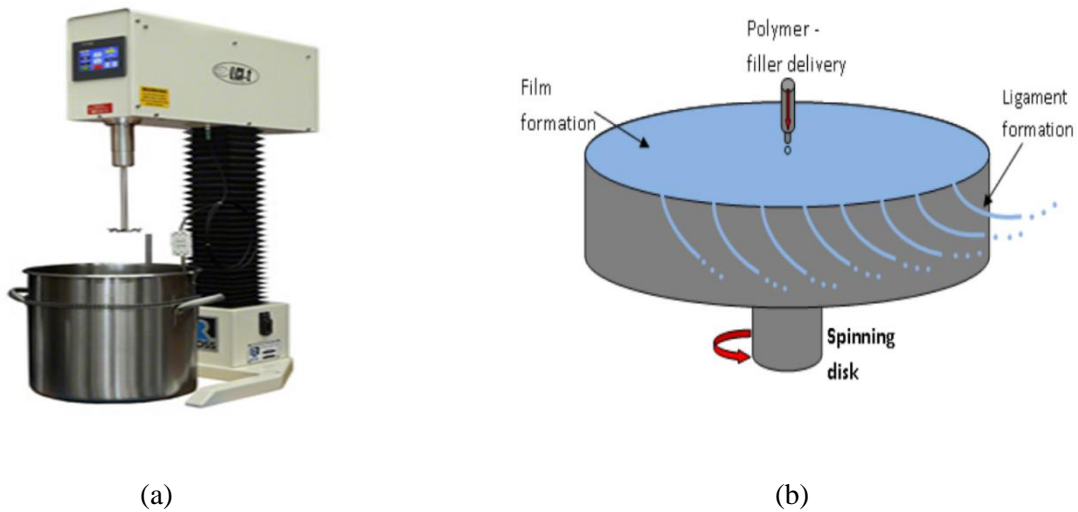
Figure 2.1 (a) High shear mixer (HS) (b) Electrostatic disperser (ES).

## 2.3 Dielectric Spectroscopy Analysis

Dielectric spectroscopy is used to monitor the behavior of relative permittivity, imaginary permittivity and dissipation factor as a function of frequency. Dielectric spectroscopy provides an informative information about presence of moisture, air bubble and aging process in composite materials. In this work, it is shown the dielectric spectroscopy can be used as an effective method to get an insight into the filler polymer interaction and strength; hence to study the dispersion and the interface effects. An insulation diagnostic analyzer, Megger™ IDAX 300 which works based on dielectric spectroscopy, was used to investigate the dielectric properties of the prepared composite slabs, through which the effects of dispersion of nano particles in silicone rubber matrix has been analyzed. A custom-made guarded electrode system (Figure 2.2) was used to measure the dielectric properties of composite slabs to minimize the fringe effects and other disturbances during

measurements. The capacitance and dissipation factor of prepared composites were measured over a frequency range from 0.1 mHz to 1 kHz at 200 V to study the effects of interfacial polarization on dielectric properties such as the permittivity. The relative permittivity of composite samples was calculated based on the value of measured capacitance.
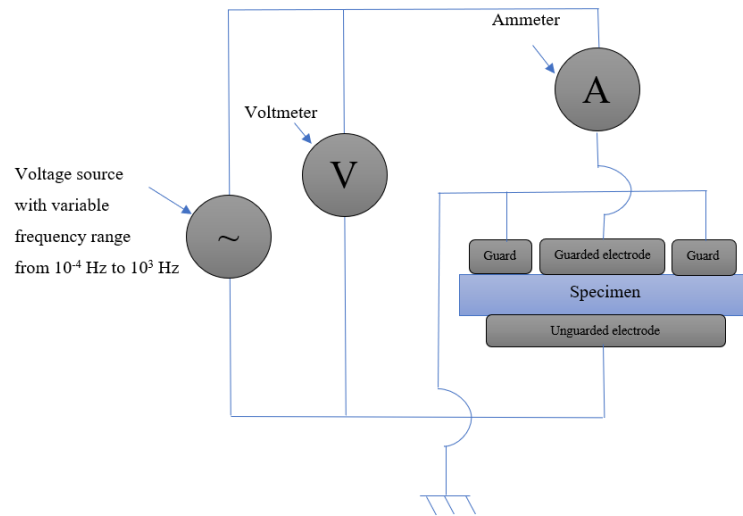


**Figure 2.2** Schematic diagram of IDAX® 300 connections.

## 2.4 Thermal Characterization

### 2.4.1 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) is used for recording the weight loss of the martials as a function of temperature or time in a controlled atmosphere. TGA can provide useful information about thermal stability, composition and decomposition of materials, oxidation of materials, volatiles and moisture content of materials, filler content of materials and life time estimations of materials [42]. In this work, approximately 9 mg of samples were treated to temperature from 200 to 800 $^{\circ}$C at a heat rate of 20 $^{\circ}$C/min in an air atmosphere using thermogravimetric analyzer (TGA-Q500) from TA instruments (see Figure 2.3) to analyze thermal stability and to confirm existence of surface treatments on the fillers. The onset of thermal degradations represents temperature point that the materials starts to degrade and it is used to evaluate the thermal stability of the materials as shown in Figure 2.4. Final decomposition temperature gives information about the amount of materials residues left and filler content of materials.



Figure 2.3 TGA-Q500 instrument
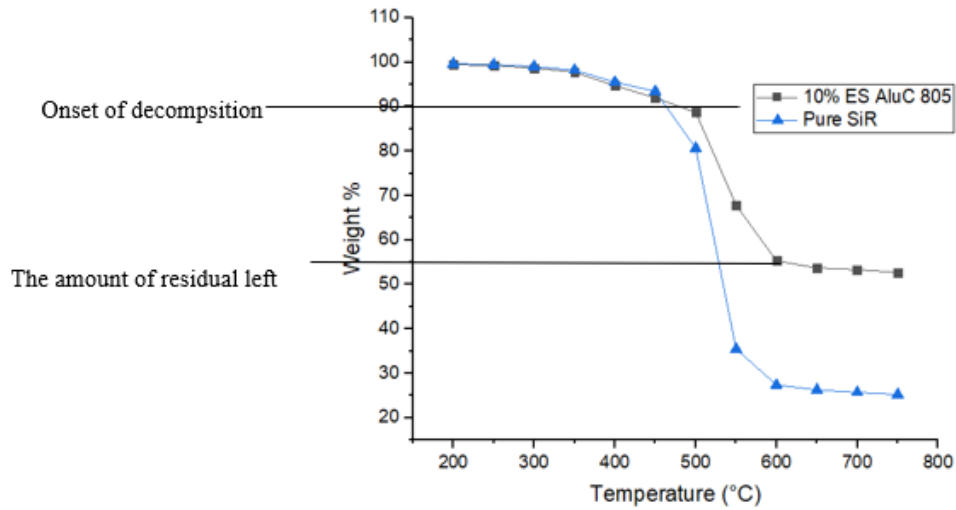
**Figure 2.4** An example of the thermal degradation of pure silicone rubber and 10wt% treated nano-alumina filled silicone rubber by using electrostatic disperser methods (ES).

## 2.4.2 Infrared Laser Test

Laser erosion test is conducted to measure the erosion resistance of composite materials [46]. To measure the eroded mass of the samples, infrared laser from Coherent was operated in a continuous wave mode at wavelength of 802 nm with a current of 17.5A. The infrared laser was applied for 7 minutes and the samples were located 5 cm from the laser source as shown in Figure 2.4. As these nanocomposite samples do not absorb the laser radiation because they are white in color, the samples were mixed with 5% red iron oxide ($Fe_2O_3$) of nanofillers percentage. Red ion oxide was used because decomposition temperature of red ion oxide ($Fe_2O_3$) is higher than SiR. Also, adding 5% $Fe_2O_3$ did not show any noticeable adverse effect on the properties of the composites. The samples weight was measured before and after applying the laser by using AC 211S-00MS balance from Sartorius with an accuracy of 1 mg. Each sample was tested three times to get the average of eroded mass.

Figure 2.5 The experimental setup of laser erosion resistance measurement.

## 2.5 Scanning Electron Microscopy (SEM)

LEO 1530 FE-SEM system was used to investigate nano particles dispersion inside polymer matrix. SEM uses high energy electron beam to produce variety of signals at the surface of nanocomposites samples that contain information about composition and morphology of the composite. Before the test, the samples were cut into small pieces and then coated with thin layer of gold to provide earth path for electrons. Considering the cost and complexity of using SEM analysis, only selected samples were analyzed. The composite with 7.5wt% treated and untreated nano-alumina prepared by ES and HS and 10wt% treated and untreated nano-alumina prepared HS were chosen for investigations.

## 2.6 Mechanical properties

Improvements in the mechanical properties of SiR composites were also analyzed. The tensile strength and elongation at break were measured based on ASTM D1708 standard using a Q series Mechanical Test machine. For each formulation, five specimens (thickness <3.2 mm) were tested at room temperature. The test speed used was 100 mm/min (speed D). The tensile strength was calculated as:

$$\sigma = \frac{f}{A_0} \qquad\qquad 2.2$$

where $f$ is the applied force, and $A_0$ is the initial cross-sectional area of the sample.

# Chapter 3

Silicone composite were studied to investigate the effect of interface on various properties of the composites, prepared by both high shear and electrostatic disperser described in section 2.2, and different evaluation methods mentioned in sections 2.3 to 2.7. This study focused on the influence of interface between nano-alumina and SiR and their effect on electrical, mechanical and thermal properties. Treated and untreated nano alumina were selected to investigate the effect of interface on the properties of the silicone rubber nanocomposite. Nanocomposites were prepared with different filler concentrations, in order to study the impact of inorganic fillers on the properties. Dielectric spectroscopy was used to measure the relative permittivity and dissipation factor of the composite. Dielectric spectroscopy is very significant for nanocomposite materials specially at very low frequency where particle agglomeration and the Maxwell-Wanger effect start to appear. Therefore, treated and untreated nano-alumina were investigated using dielectric spectroscopy over wide range of frequency. In addition, thermogravimetric analysis (TGA) and heat erosion resistance were used to analyze thermal properties of the composites. Moreover, the dispersion morphology, tensile strength and elongation at break are presented in this chapter.

## 3.1 Dielectric Spectroscopy

Frequency domain spectroscopy was used to measure dielectric loss (tanδ), and relative permittivity in the frequency range of $10^{-4}$ to $10^3$ Hz. Different weight percentage of treated and untreated nano-alumina 5wt%,7.5wt%,10wt%, and 20wt% were investigated using high shear method.

### 3.1.1 The effect of nano-alumina on Relative Permittivity

The behavior of relative permittivity as a function of frequency for treated nano-alumina filled SiR with different concentration and pure SiR at 25 °C using high shear (HS) is shown in Figure 3.1. The relative permittivity of pure SiR remains constant with the increase in frequency as expected because the interfacial polarization occurs in the heterogenous materials.

As reported in the literature, the effects of interface properties on relative permittivity become increasingly prominent, below 0.1Hz. Therefore, there is no major difference observed with increasing filler concentrations at higher frequencies; however, relative permittivity increases proportionally with increasing filler concentrations at lower frequencies. As the loading level of nanofillers increases, the number of interfaces between nanofillers and base polymer increases which results in more charge

accumulation at the interfaces. In addition. agglomeration effects is also noticed with increasing higher concentrations. Nanofiller agglomerations showed slower response to align with electric filed.



Figure 3.1 relative permittivity for treated nano-alumina (AluC 805) filled SiR at different weight percentages and pure SiR as a function of frequency using high shear method (HS).

Untreated nano-alumina composite results obtained under similar test conditions are presented in Figure 3.2. For untreated nano-alumina prepared by HS, relative permittivity is higher than pure SiR at low frequency due to the presence of interfacial polarization effect. As the addition of untreated nano-alumina increase, the effect of interfacial polarization increases resulting in high relative permittivity. However, at high frequency, the permittivity is showing similar behavior to pure SiR.

Comparing the dielectric response of treated and untreated nano-alumina composites shows that the relative permittivity of treated nano-alumina composite is almost one order of magnitude lower than untreated nano-alumina composite. These differences are believed to be related to the interaction between nano-alumina and base SiR; and hydrophilic versus hydrophobic nature of fillers [35,37].

24

Furthermore, the higher value of relative permittivity of untreated nano-alumina composites compared to treated nano-alumina composite are related to particle agglomerations and presence of water within the particles clusters.



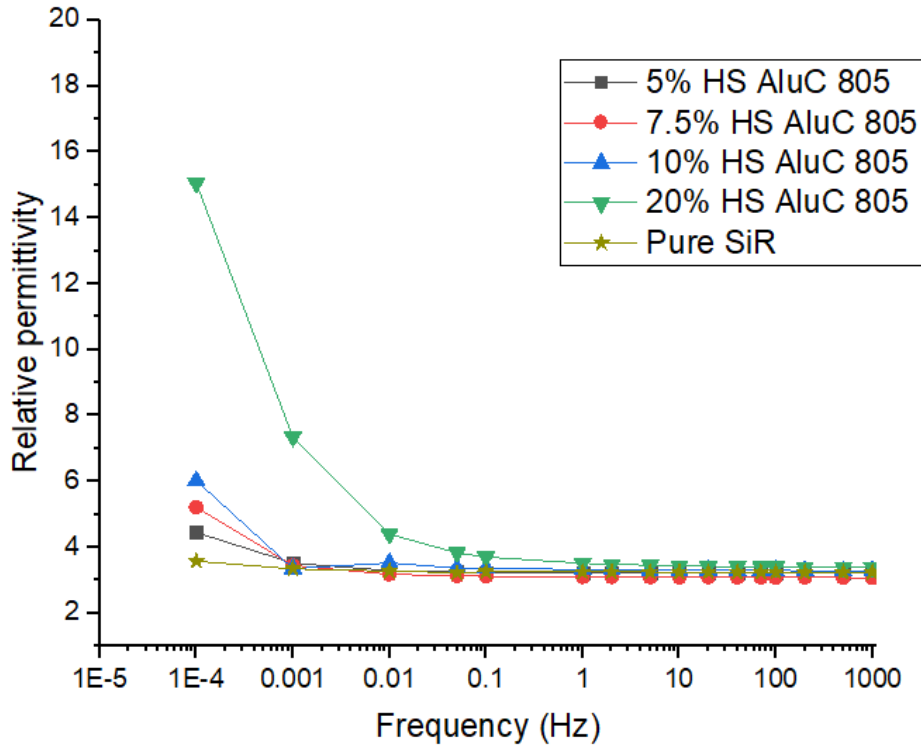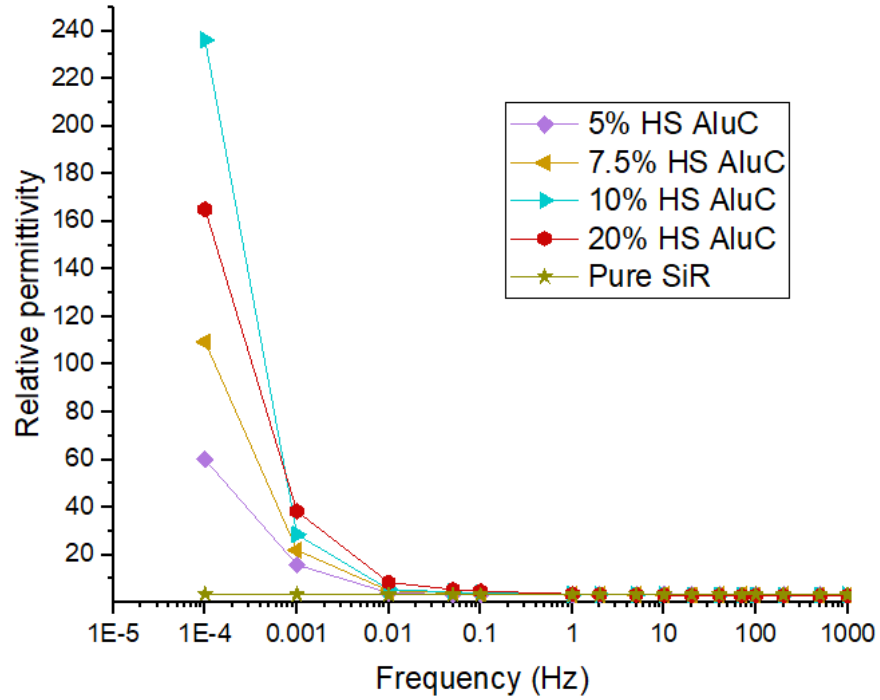Figure 3.2 relative permittivity for untreated nano-alumina (Alu C) filled SiR at different weight percentages and pure SiR as a function of frequency using high shear method (HS).

### 3.1.2 The effect of nano-alumina on Dielectric Loss (tanδ)

Dielectric loss for treated and untreated nano-alumina filled SiR at different weight percentages and pure SiR as a function of frequency using high shear method (HS) are shown in Figures 3.3 and 3.4 respectively. The higher loss tangent of nano-alumina composite was observed because of charge carriers. Since the addition of nanofillers increase the role played by the interface, the loss tangent of 20 wt% composite is the highest compared to pure SiR and other compositions. The behavior of loss tangent of 5 wt% and 7.5 wt% treated nano-alumina composites is similar to that of pure SiR. Treated nano-alumina has lower tan δ than untreated nano-alumina shown in Figure 3.4 because the surface treatment of nanoparticles makes the bonding between treated filler and base polymer stronger. Good physical bonding between nanofillers and base polymer restrict the chain movements of the polymer. Higher dielectric loss of pure SiR at $10^{-4}$ Hz is due to the interfacial polarization between the electrodes and the dielectric materials.
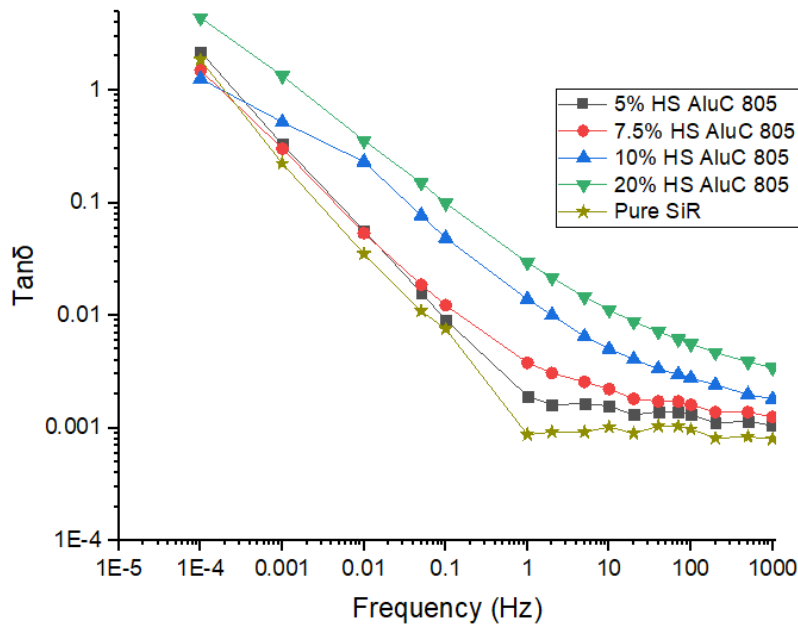
Figure 3.3 Dielectric loss for treated nano-alumina (AluC 805) filled SiR at different weight percentages and pure SiR as a function of frequency using high shear method (HS).

26
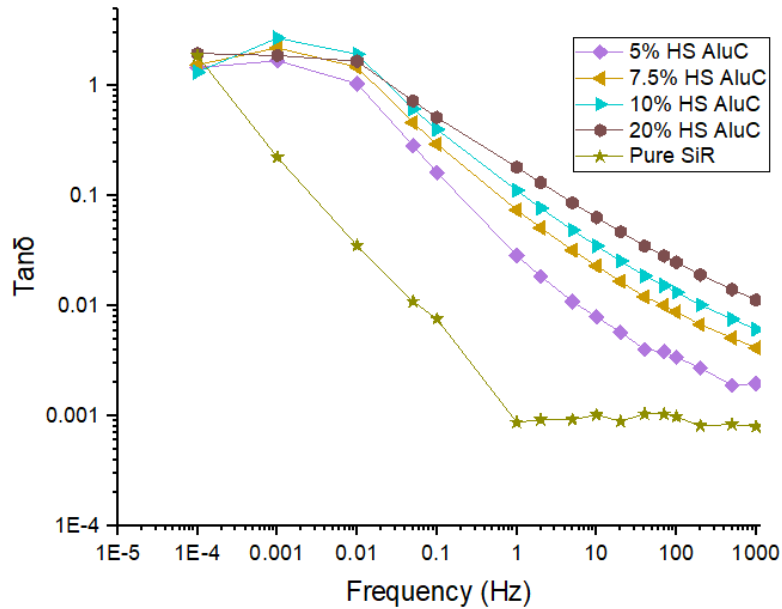
Figure 3.4 Dielectric loss for untreated nano-alumina (AluC) filled SiR at different weight percentages and pure SiR as a function of frequency using high shear method (HS)

## 3.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is conducted to monitor the weight loss of the composites and pure SiR with respect to increase in temperature which gives the information about the thermal stability of the composites and pure SiR. As shown from TGA plots in Figure. 3.5 and Figure 3.6, that treated nano-alumina nanocomposites have higher residual weight than pure SiR with both HS and ES methods. The residual weight observed for pure SiR is about 27%. There is a significant increase in the residual weights with the increase in percentage loading of fillers from 5wt% to 20wt%. All the composite samples showed higher thermal stability over pure SiR.

Figure 3.5 Thermal degradation of pure silicone rubber and treated nano-alumina filled silicone rubber with different weight percentage by using high shear methods (HS).



Figure 3.6 Thermal degradation of pure silicone rubber and treated nano-alumina filled silicone rubber with different weight percentage by using electrostatic disperser methods (ES).

Furthermore, comparing high shear (HS) and electrostatic disperser (ES) methods, the 20wt% treated nano-alumina filled SiR has 10% less weight loss for composites prepared using electrostatic disperser. This is due to the better dispersion and bonding of the filler with SiR [26].

The results of untreated nano-alumina prepared with both HS and ES are also tested for comparison as shown in Figure 3.7 and Figure 3.8. Pure SiR has less residual weight than untreated nano-alumina with both methods.

The result shows that treated and untreated nano-alumina composites have higher thermal stability than the pure polymer. The residual weight of untreated nano-alumina filled SiR prepared by HS is slightly higher than treated nano-alumina composites. These differences can be due to degradation of the silane group coating of surface treated nano-alumina particles at elevated temperatures [34]. However, 10wt% and 20wt% treated nano-alumina composites showed higher residual weight than 10wt% and 20wt% untreated nano-alumina composites by using ES. The improvements of treated nano-alumina composites at high loading level by using ES method are assumed due to better fillers dispersion and distribution into the base polymer.
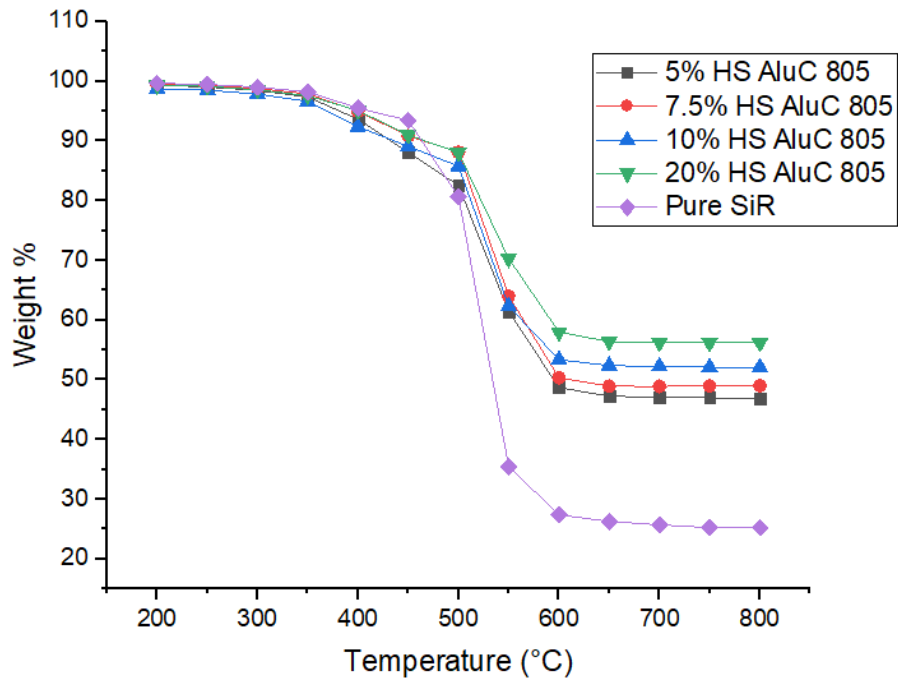


Figure 3.7 Thermal degradation of pure silicone rubber and untreated nano-alumina filled silicone rubber with different weight percentage by using high shear methods (HS).
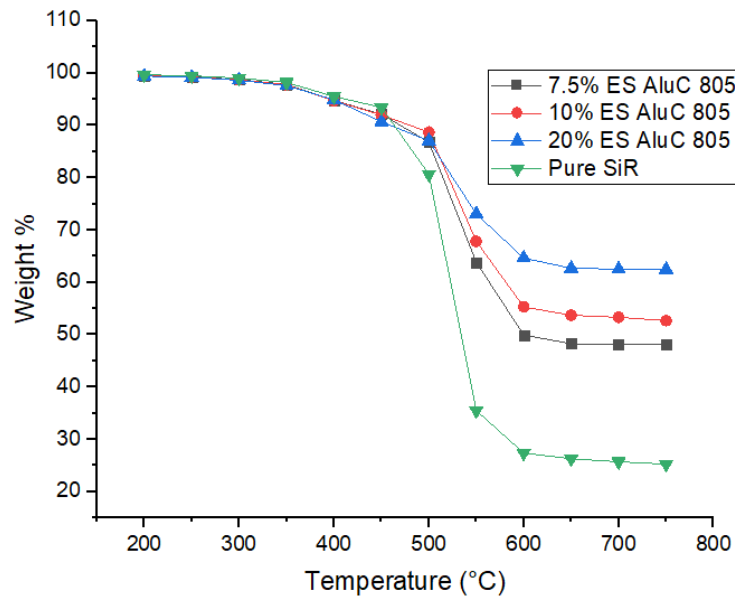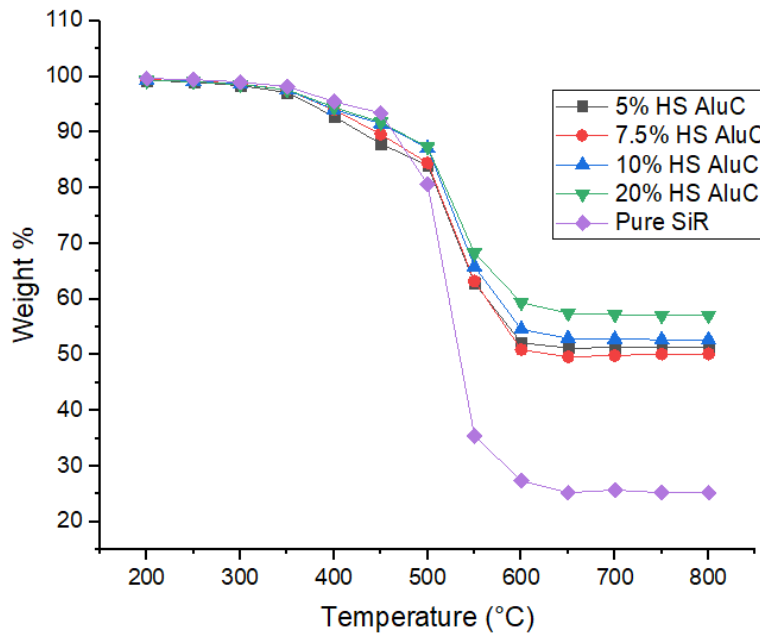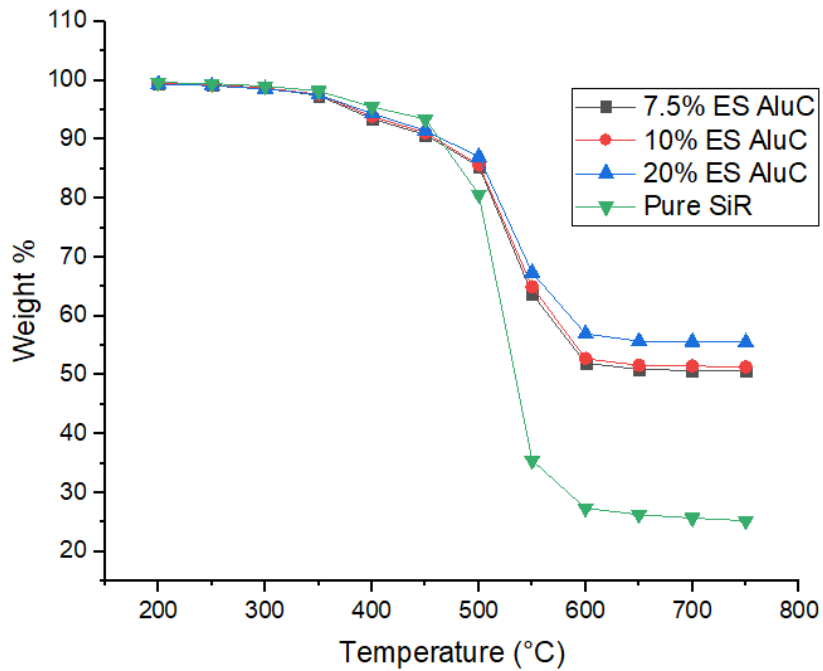
Figure 3.8 Thermal degradation of pure silicone rubber and untreated nano-alumina filled silicone rubber with different weight percentage by using electrostatic disperser methods (ES).

## 3.3 Laser Erosion Resistance Test

Figure 3.9, shows the eroded mass for treated nano-alumina (AluC 805) and untreated (AluC). The samples containing 10wt% treated nano-alumina (AluC 805) mixed using the electrostatic disperser (ES) technique had ~40% less eroded mass than its high shear counterpart (HS). This shows that the samples have better erosion resistance and can withstand the heat better than HS composite samples. The composite containing 10wt% untreated nano-alumina (AluC) mixed using high shear technique had ~24% higher eroded mass than electrostatic disperser technique. At higher loading of 20% treated nano-alumina (AluC 805), electrostatic disperser composites had ~46% less weight loss than the high shear composites. The result also shows that the 20% untreated nano-alumina had higher eroded mass than with these samples prepared using electrostatic disperser.

These observations indicate improved dispersion of the filler in the polymer matrix achieved by mixing using the electrostatic disperser technique. Additionally, the eroded mass of HS and ES alumina composites increased with increasing concentration of the fillers from 10 to 20%. At high loadings of alumina, viscosity is very high that high shear mixing becomes difficult leading to more

agglomerations and poor dispersion of filler in the rubber matrix. For all test composites, treated nano-alumina has lower eroded mass than untreated one because the surface treatments of nano-alumina help to improve the dispersion of nanoparticles.
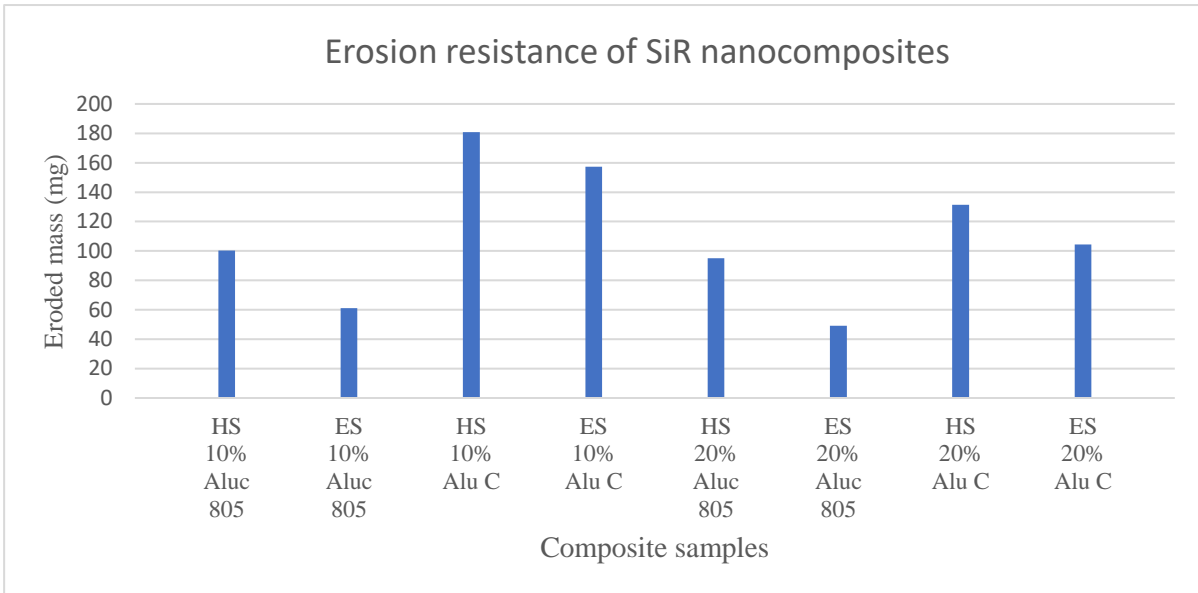


Figure 3.9 Eroded mass of silicone rubber composite exposed to infrared laser.

## 3.4 Mechanical Properties

The mechanical properties of the nanocomposites are depending on many factors such as the type of filler, filler concentration and the dispersion of fillers in silicone rubber matrix. The tensile strength of pure SiR is reinforced with the addition of 5wt%, 7.5wt, and 10wt% nano-alumina as shown in Table 3.1. It can be seen from Table 3.1 that the composite shows higher tensile strength and elongation at break than pure SiR obtained by high shear (HS) and electrostatic disperser (ES). The tensile strength of high shear samples increased with increasing loading of the filler at 7.5wt% and decreased with increasing loading of the filler at 10wt% for both treated (AluC 805) and untreated nano-alumina (AluC), which can be due to the nanofiller agglomerations present at such high loadings. The composite reinforced with 5wt% treated nano-alumina obtained by HS showed about 28% increase in elongation at break compared to pure SiR; whereas, the composite reinforced with 7.5wt% treated nano-alumina showed about 66% increase in elongation at break over pure SiR. There is no much difference observed between treated and untreated nano-alumina prepared by HS in terms of tensile strength. Tensile strength and elongation at break of treated nano-alumina filled SiR are slightly higher than untreated nano-alumina filled SiR prepared by ES. It can be assumed that the high loading level of treated nano-alumina prepared by HS made the composite more brittle.

**Table 3.1** The mechanical properties of the silicone rubber (SiR) nanocomposites.

| Composite Sample | Tensile Strength (MPa) | Elongation @ Break (%) |
|---|---|---|
| Pure SiR | 3.5 | 126.8 |
| HS 5% AluC 805 | 5.5 | 155.3 |
| HS 7.5% AluC 805 | 6.4 | 193.7 |
| HS 10% AluC 805 | 4.6 | 128.1 |
| ES 7.5% AluC 805 | 4.8 | 194.1 |
| ES 10% AluC 805 | 5.6 | 179.6 |
| HS 5% AluC | 5.8 | 174.9 |
| HS 7.5% AluC | 6.3 | 181.8 |
| HS 10% AluC | 5.2 | 168.0 |
| ES 7.5 AluC | 3.8 | 137.9 |
| ES 10% AluC | 4.8 | 171.4 |

## 3.5 Scanning Electron microscopy (SEM) Observation

Nano-alumina dispersion and distribution in the base SiR is analyzed by scanning electron microscopy (SEM). The cross-sections of treated and untreated nano-alumina prepared with high shear (HS) and electrostatic disperser (ES) is presented in Figure 3.9 and Figure 3.10 respectively. As shown in Figure 3.9 (a) and (b), treated nano-alumina composites showed good dispersion using both electrostatic disperser and high shear methods. However, treated nano-alumina composites prepared by ES method have better filler distributions inside base polymers comparing this with treated nano-alumina composites prepared by HS method. Comparing both ES and HS techniques shown in Figure 3.10 (a) and (b), the untreated nano-alumina composites obtained by HS forms lager particles agglomeration as shown in Figure 3.10 (b). It can be observed that electrostatic disperser (ES) method helps to obtain good dispersion and distribution of nanofillers compared to high shear (HS) method. In addition, it is clear that surface treatment of nano-alumina reduced particles agglomerations. Figure 3.11 (a) and (b) showed surface treatment effect on dispersion. Due to incompatibility between

hydrophilic nanofillers (untreated nano-alumina) and hydrophobic base polymer (SiR), nanofillers agglomerate and form cluster as shown in figure 3.11 (b).
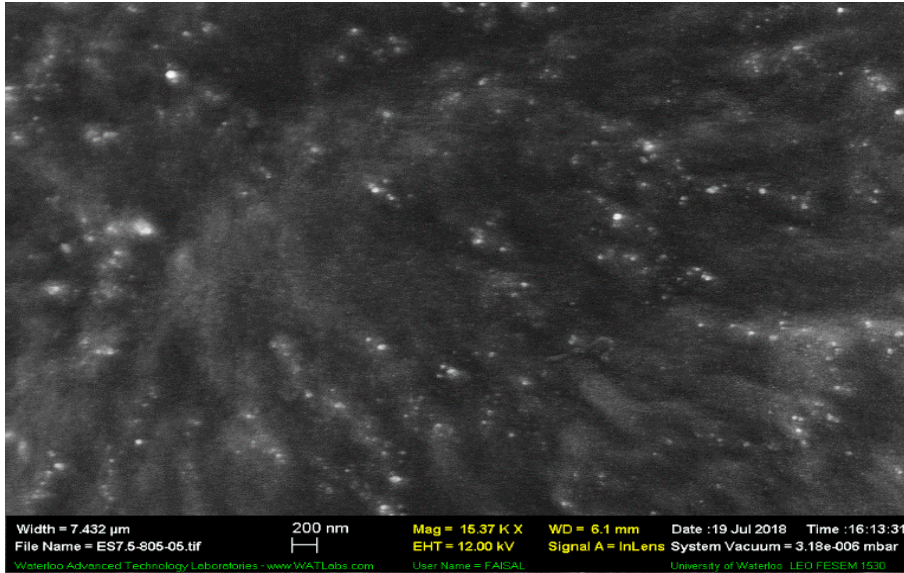


(a)
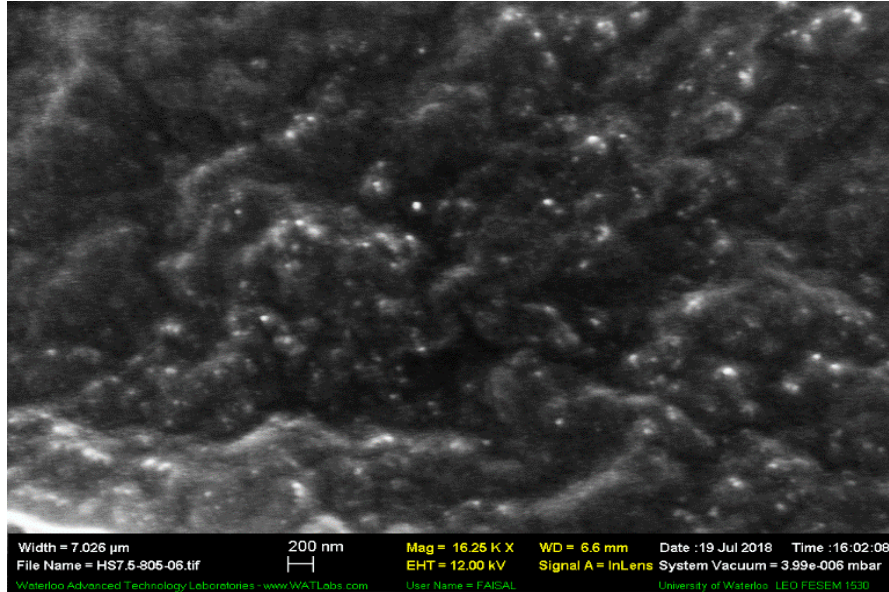


(b)

**Figure 3.10** Cross-sectional morphology of silicone rubber nanocomposite with treated nano-alumina by using two methods, (a) 7.5 wt% treated nano-alumina obtained by ES, (b) 7.5 wt% treated nano-alumina obtained by HS.

(a)



(b)

**Figure 3.11** Cross-sectional morphology of silicone rubber nanocomposite with untreated nano-alumina by using two methods, (a) 7.5 wt% untreated nano-alumina obtained by ES, (b) 7.5 wt% untreated nano-alumina obtained by HS.
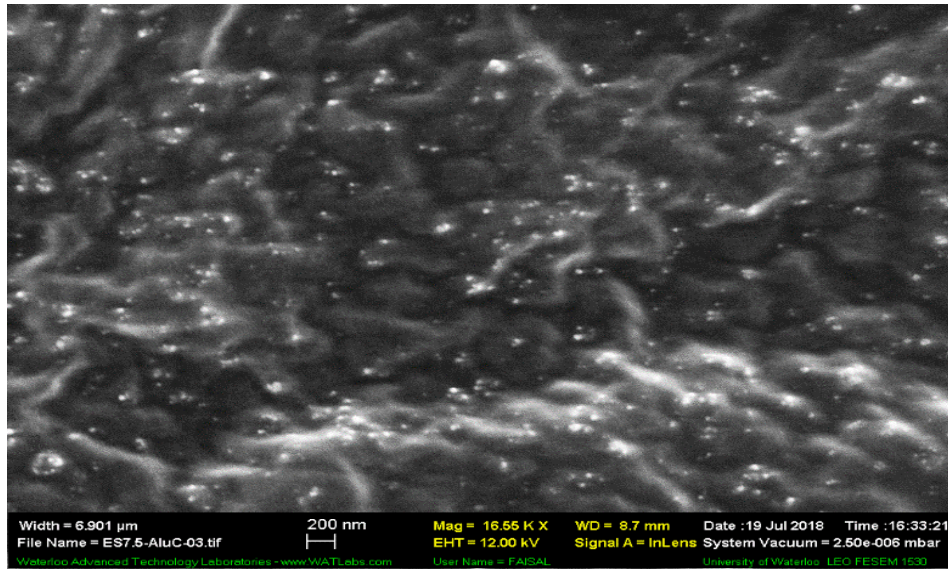
(a)



(b)

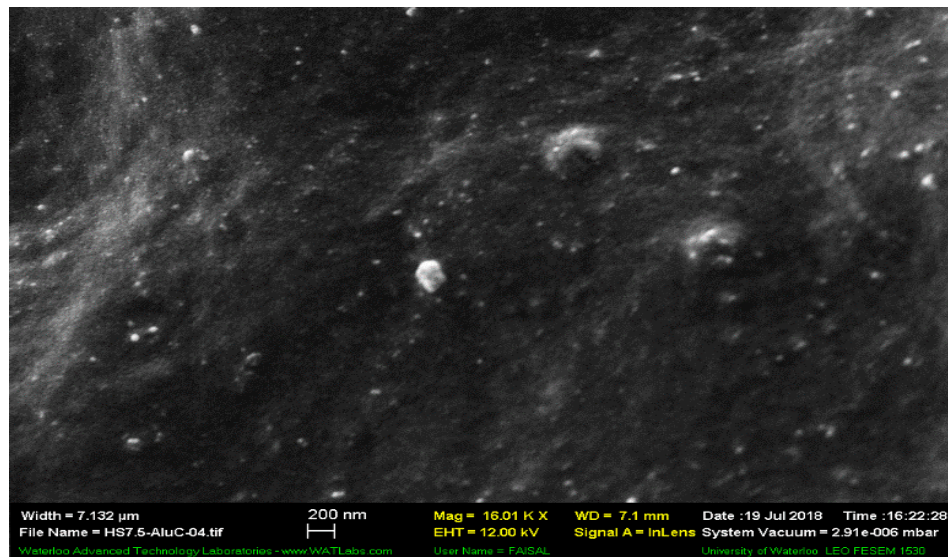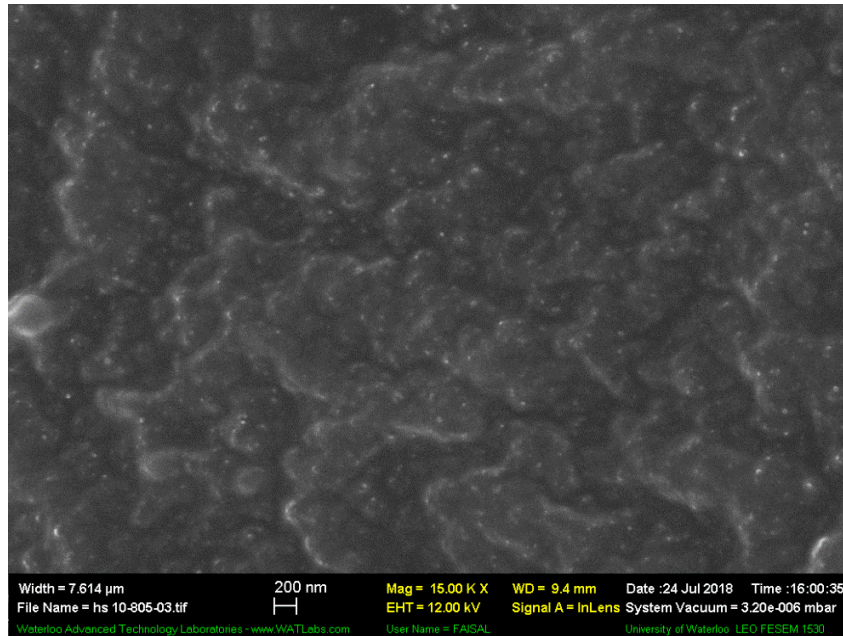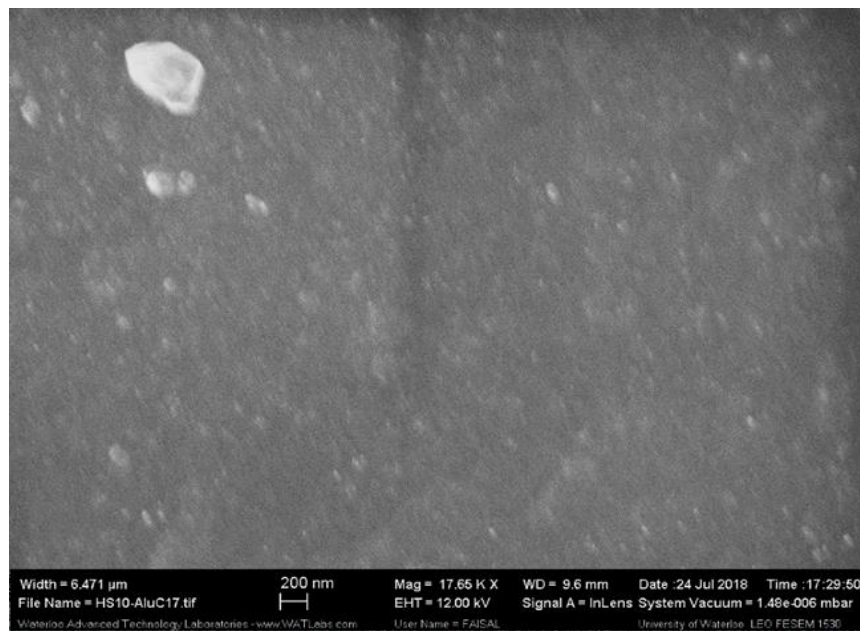**Figure 3.12** Cross-sectional morphology of silicone rubber nanocomposite with treated and untreated nano-alumina by using HS method, (a) 10 wt% treated nano-alumina, (b) 10 wt% untreated nano-alumina.

# Chapter 4

# Discussion

Uniform dispersion and good distribution of nano-alumina into SiR were successfully obtained by treating the surface of nano-alumina. In addition, strong interaction between nanofillers and base polymers are essential to attain better improvements in the properties of nanocomposites as shown in chapter 3. It is shown that electrostatic disperser (ES) technique can disperse nanoparticles into base polymer more uniformly than high shear (HS) technique. Dielectric spectroscopy is a powerful method to get an insight into the interface effects on the properties of nanocomposites materials. Both thermal and mechanical properties analyzed to understand the effect of fillers dispersion on composites properties.

## 4.1 The effect of interface on relative permittivity and loss factor (tanδ)

Surface treatment of nanofillers has a great influence on the interface between nanofillers and base polymer by changing the surface of fillers from polar to nonpolar and vice versa [1]. The results show that relative permittivity and loss factor depend on filler concentrations and frequency. The relative permittivity of pure SiR remains constant because the interfacial polarization occurs in heterogenous materials where there are multiple phases or regions as mentioned earlier [8]. The higher relative permittivity and loss factor at very low frequency are associated with the presence of interfacial effect (Maxwell-Wanger effect). When voltage is applied to the samples, the electric charge will accumulate at the interface between different materials resulting in interfacial polarization phenomena. Therefore, as the nanofillers concentration increases, the number of interfaces will be larger and the charge accumulation will be higher [41]. Treated nano-alumina restrict the chain movement of the polymer through physical bonding, so it has lower relative permittivity and loss factor in comparison with untreated nano-alumina [1]. The very high relative permittivity and loss factor of untreated nano-alumina can be related to the presence of moisture in the composite. Since the untreated nano-alumina is hydrophilic in nature, it could attract the moisture in the atmosphere. Surface treatment of nanoparticles reduce the amount of absorbed water in the composite [43].

Relative permittivity and loss factor are sensitive to any change in the composite interface. In order to demonstrate this, the effect of moisture and air bubble on permittivity were analyzed (see Figures 4.1 and 4.2). The treated nano-alumina composites were immersed in deionized water for three weeks to study the effect of water absorption in the interface of treated nano-alumina filled SiR. In

addition, to investigate the influence of air bubble samples of treated nano-alumina composite was cured without degassing. These experiments were conducted deliberately with introducing air pockets (bubbles) and moisture in the test samples, so as to demonstrate the use of dielectric spectroscopy in analyzing both interface and dispersion effects.



Figure 4.1 The effect of moisture and air bubbles on relative permittivity for 5wt% treated nano-alumina filled SiR as a function of frequency using high shear method (HS).
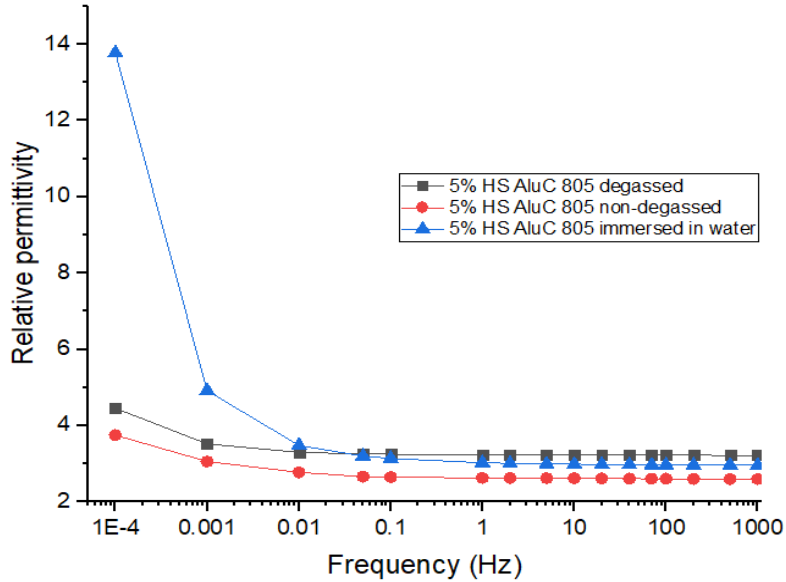


Figure 4.2 The effect of moisture and air bubble on relative permittivity for 10wt% treated nano-alumina filled SiR as a function of frequency using high shear method (HS).

All the samples immersed in water showed higher relative permittivity at low frequency than degassed samples and non-degassed samples without additional moisture. The samples that are not degassed with 5wt% and 10wt% treated nano-alumina have the lowest relative permittivity. The tanδ of degassed samples shown in Figures 4.3 and 4.4 have less dielectric loss compared to non-degassed sample and the samples immersed in water. The samples that immersed in water with 5wt% and 10wt% nano-alumina have higher loss than degassed and non-degassed samples.

The increase in loss factor and permittivity of the sample immersed in water are attributed to presence of hydroxyl groups on the surface of nanofillers. Even though, the surface of nanofiller is hydrophobic because it is treated with organosilane, there will be some water absorption due to incomplete surface treatment. Very small amount of water in the sample will have its effect on relative permittivity because the relative permittivity of water is ~80. The presence of water in dielectric material is undesirable as it has negative impact on the dielectric properties [40]. In addition, it is important to make sure to avoid any air bubble during processing because the air bubble cause partial discharge to incept and eventually a complete failure of the composite. Since air bubbles have very low relative permittivity equal to one, the non-degassed samples have the lowest relative permittivity.
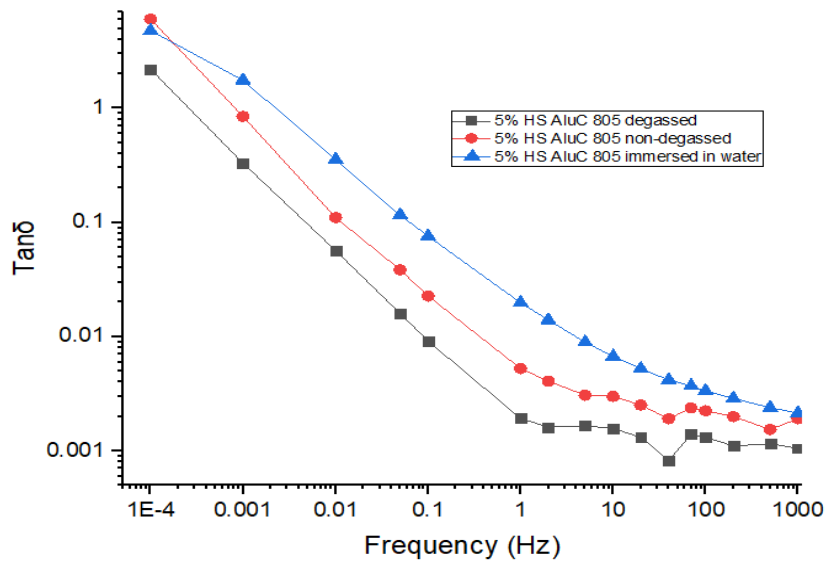


Figure 4.3 The effect of moisture and air bubble on Tanδ for 5wt% treated nano-alumina filled SiR as a function of frequency using high shear method (HS).

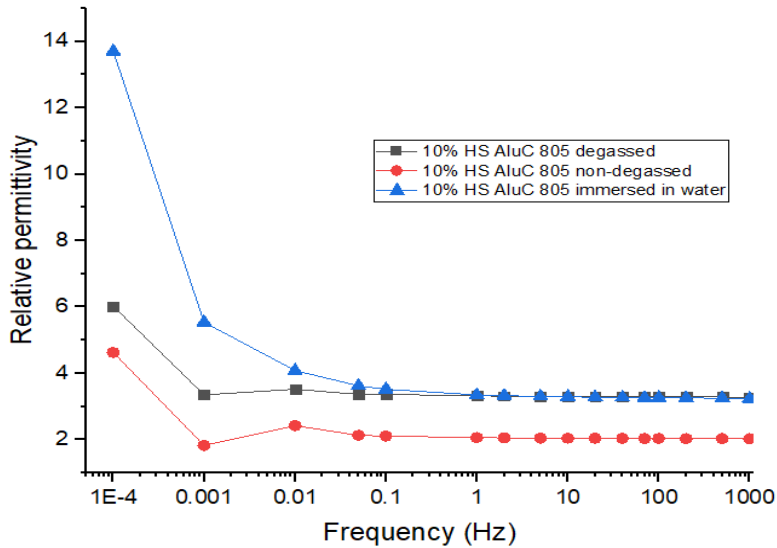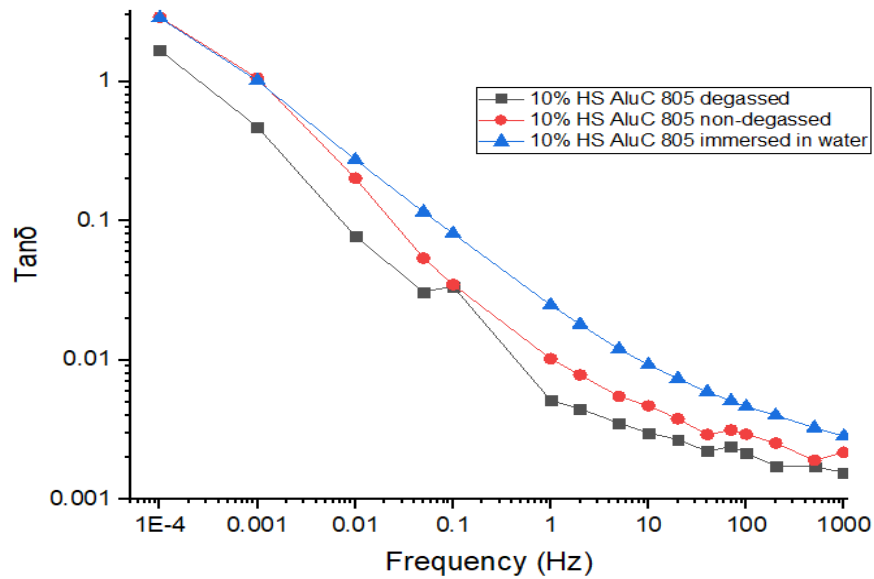Figure 4.4 The effect of moisture and air bubble on Tanδ for 10wt% treated nano-alumina filled SiR as a function of frequency using high shear method (HS).

## 4.2 Thermal Stability of the Composite

Treated and untreated nano-alumina with different weight percentage enhance the thermal stability of pure SiR as shown in chapter 3. Thermal stability increases with increasing the addition of nanoparticles because the nanoparticle forms an isolation layer over the base polymer and prevent any gas diffusion during decomposition process [1,7,42]. The residual weight of untreated nano-alumina composites is slightly better than the treated nano-alumina composites; but the difference is very small. This difference can be due to degradation of the silane group coating of surface treated (AluC 805) particles at elevated temperatures. The samples prepared by electrostatic disperser has higher thermal stability than the samples prepared by high shear. It is could be because the nanoparticles prepared by electrostatic disperser has better dispersion and uniform distribution as shown in Figures 3.9 (a) and 3.10 (a), compared to those samples prepared using high shear mixing.

## 4.3 Heat Erosion Resistance of the composite

The treated nano-alumina composites showed significant enhancements in erosion resistance compared to untreated nano-alumina composites. The composite prepared by high shear-filled with 10wt% treated nano-alumina had ~80% less eroded mass than 10wt% untreated nano-alumina composites. In addition, 10wt% treated nano-alumina filled SiR prepared by electrostatic disperser had ~96% less eroded mass than untreated nano-alumina at same filler concentrations. These improvements are attributed to surface treatment of nanoparticles. Higher filler concentrations increase the resistance of SiR. Electrostatic disperser technique showed around 20-40% improvements compared to high shear technique. The electrostatic disperser method has proven to be the most effective in improving the dispersion of nanofillers in polymer matrix compared to high shear method. It can be concluded that eroded mass of the composite is affected by processing, filler concentrations and surface treatment of fillers for a given polymers.

## 4.4 Dispersion improvement

Nanofillers agglomerate because of their high surface energy and incompatibility between hydrophilic fillers and hydrophobic base polymers [16]. Therefore, the purpose of treating the surface of nanoparticles to get better filler dispersion and better interaction between nanoparticles and base polymer is important to enhance the properties of the composite. Organosilanes provide better filler dispersion, and strong interaction between polymer and filler [44]. Treated nano-alumina filled SiR results confirm that surface treatment of nanofillers is beneficial and has positive impact on the properties. Particle agglomeration can be detected clearly in case of 10wt% untreated nano-alumina filled SiR by using SEM as shown in Figure 4.5. At same amount of filler loading, the composite with treated nano-alumina is showing better filler dispersion and distribution as shown in Figure 3.11 (a) and (b). Therefore, this demonstrates that surface treatment of nanofillers is an important part of the compound of dielectric nanocomposite materials [1]. In addition, dielectric spectroscopy is an effective method to get an insight into dispersion of nanofillers in base polymer.

# Chapter 5

# Conclusions and suggestions for Future Work

## 5.1 Conclusions

The recent developments of electrical equipment raise the demands for new dielectric materials with high breakdown voltage, high thermal conductivity, high tensile strength, high erosion resistance, and selective relative permittivity. Introducing inorganic nanofillers to base polymers has been identified as a promising technique to overcome the limitations of traditional materials. The interface between filler and matrix, affects the properties of nanocomposites because of the high ratio of surface area to volume of nanofillers, in comparison to micro-fillers as the interfacial area forms a significant volume fraction between particles and base polymer. The interfacial area has properties different from both the bulk polymer and the filler. As such, in this study, electrical, mechanical and thermal properties of silicone rubber nanocomposites were investigated to give a better understating of the interface between SiR and nanoparticles.

Nanoparticles agglomerate due to electrostatic force during mixing in base polymer and incompatibility between hydrophilic nanoparticles and hydrophobic base polymer resulting in weak interaction between them. The dispersion of nanoparticles depends on many factors such as the base polymer, nanofillers, and surface treatment of the fillers, filler concentrations, and dispersion techniques. To understand particle agglomeration and cluster formation in composites, surface treated fillers and untreated fillers have been used.

In this thesis, effects of filler concentration, filler surface treatment, and mixing method on the dielectric properties are investigated. Surface treatment of nanoparticles is used to change the filler dispersion and the interaction between nanoparticles and base polymer. In addition, electrostatic disperser method and high shear method have been used to investigate the effect of processing on the filler dispersion and distribution.

The SEM image confirms that surface treatment of nanoparticles can be used to eliminates the agglomeration of nanofillers. Dielectric spectroscopy results showed that relative permittivity and dielectric loss of treated nano-alumina composites are lower than untreated nano-alumina composites. In addition, treated nano-alumina filled silicon rubber had higher erosion resistance compared to untreated nano-alumina. Thermal stability and erosion resistance of pure SiR enhanced by the addition

of nano-alumina. The samples prepared by ES method can withstand the heat better than samples prepared by HS method.

In summary, the results showed that surface treatment of nanofillers can be used to improve the dispersion of the nanoparticles in silicone rubber. Dielectric spectroscopy is an effective method to get an insight into the filler polymer interaction; hence to study the dispersion and the interface effects. Erosion resistance, dispersion and thermal stability of treated nano-alumian filled SiR enhanced significantly. Electrostatic disperser technique effectively improved the nanofiller dispersion and distribution; thus, showed improved material characteristics in composite prepared using this technique.

## 5.2 Suggestions for Future Work

The interfacial area between nano-alumina and silicone is the key factor to improve the properties of composite. Even though, surface treatment enhances the dispersion of nanoparticles, it is difficult to avoid the agglomeration especially at high loading level. Trying another surface treatment may be helpful to avoid particles agglomeration. Scanning electron microscopy used to determine the state of dispersion, but it is not able to give enough information about the interfacial area. It is therefore necessary to study different polymer fillers compositions using dielectric spectroscopy to confirm its applicability in evaluating the interfacial bonding. Processing is important because homogeneous dispersion of nanoparticles in the base polymers lead to a large volume fraction between nanoparticles and base polymer. As a result, alternative dispersion methods should be investigated to have a comprehensive idea about processing techniques. The focus of this thesis was on evaluating the relative permittivity, loss factor and erosion resistance and thermal degradation. But other electrical, thermal and mechanical properties such as hardness, corona resistance and space charge accumulation needs to be investigated, in an effort to develop practical insulating materials. In addition, inclined plane test (IPT) and dielectric breakdown strength should be studied, if it is applied to electrical insulation industry. In industry, combination of both nano and micro fillers are used; hence such hybrid composites needs to be studied.

# References

1. J. K. Nelson, *Dielectric Polymer Nanocomposites,* Springer, Boston, 2010.

2. I. Pleşa, P. V. Noţingher, S. Schlögl, C. Sumereder, and M. Muhr. "Properties of polymer composites used in high-voltage applications," *Polymers,* vol. 8, *(5),* pp. 173, 2016.

3. T. Lewis, "Nanometric dielectrics," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 1, *(5),* pp. 812-825, 1994.

4. T. Tanaka, "Dielectric nanocomposites with insulating properties," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 12, *(5),* pp. 914-928, 2005.

5. P. H. C. Camargo, K. G. Satyanarayana and F. Wypych, "Nanocomposites: synthesis, structure, properties and new application opportunities," *Materials Research,* vol. 12, *(1),* pp. 1-39, 2009.

6. T. Tanaka, G. Montanari and R. Mulhaupt, "Polymer nanocomposites as dielectrics and electrical insulation-perspectives for processing technologies, material characterization and future applications," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 11, *(5),* pp. 763-784, 2004.

7. S. Bian, "A Study of the Material Properties of Silicone Nanocomposites Developed by Electrospinning," PhD thesis, University of Waterloo, 2013.

8. K. Zhong and B. Li, *Polymer Nanocomposites for Dielectrics.* CRC Press, 2017.

9. T. ISO, "27687 Nanotechnologies-Terminology and definitions for nano-objects," *Nanoparticle, Nanofibre and Nanoplate,* 2008.

10. Y. Sun, Z. Zhang and C. Wong, "Influence of interphase and moisture on the dielectric spectroscopy of epoxy/silica composites," *Polymer,* vol. 46, *(7),* pp. 2297-2305, 2005.

11. I. Ramirez, E. A. Cherney, S. Jayaram, and M. Gauthier."Nanofilled silicone dielectrics prepared with surfactant for outdoor insulation applications," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 15, *(1),* 2008.

12. M. Roy, J. Nelson, R. MacCrone, L. S. Schadler, C. Reed, and R. Keefe. "The influence of physical and chemical linkage on the properties of nanocomposites," in *Electrical Insulation and Dielectric Phenomena, CEIDP'05. 2005 Annual Report Conference on,*pp. 183-186, 2005.

13. Z. Han, J. Wood, H. Herman, C. Zhang, and G. Stevens. "Thermal properties of composites filled with different fillers," in *Electrical Insulation, 2008. ISEI 2008. Conference Record of the 2008 IEEE International Symposium on,*pp. 497-501, 2008.

14. M. G. Danikas and T. Tanaka, "Nanocomposites-a review of electrical treeing and breakdown," *IEEE Electr. Insul. Mag.,* vol. 25, *(4),* pp. 19-25, 2009.

15. R. Hong and Q. Chen, "Dispersion of inorganic nanoparticles in polymer matrices: Challenges and solutions," in *Organic-Inorganic Hybrid Nanomaterials* Anonymous Springer,pp. 1-38, 2014.

16. I. Ramirez Vazquez, "A study of nanofilled silicone dielectrics for outdoor insulation," PhD thesis, University of Waterloo, 2009.

17. S. Kango, S. Kalia, A. Celli, J. Njuguna, Y. Habibi, and R. Kumar. "Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites—a review," *Progress in Polymer Science,* vol. 38, *(8),* pp. 1232-1261, 2013.

18. M. Z. Rong, M. Q. Zhang, Y. X. Zheng, H. M. Zeng, R. Walter, and K. Friedrich. "Irradiation graft polymerization on nano-inorganic particles: An effective means to design polymer-based nanocomposites," *J. Mater. Sci. Lett.,* vol. 19, *(13),* pp. 1159-1161, 2000.

19. M. Rong, M. Zhang and W. Ruan, "Surface modification of nanoscale fillers for improving properties of polymer nanocomposites: a review," *Materials Science and Technology,* vol. 22, *(7),* pp. 787-796, 2006.

20. C. Sun, *Controlling the Rheology of polymer/silica Nanocomposites,* 2010.

21. J. Lu, *High Dielectric Constant Polymer Nanocomposites for Embedded Capacitor Applications,* 2008.

22. J. Seiler and J. Kindersberger, "Insight into the interphase in polymer nanocomposites," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 21, *(2),* pp. 537-547, 2014.

23. M. Paredes, C. J. Angammana and S. H. Jayaram, "Experimental study of dielectric properties of fumed silica/silicone composites," in *Electrical Insulation and Dielectric Phenomena (CEIDP), 2016 IEEE Conference on,* pp. 683-686, 2016.

24. M. Todd and F. Shi, "Dielectric characteristics of complex composite systems containing interphase regions," in *Advanced Packaging Materials: Processes, Properties and Interfaces, 2004. Proceedings. 9th International Symposium on,* pp. 112-117.

25. T. Lewis, "Interfaces are the dominant feature of dielectrics at the nanometric level," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 11, *(5),* pp. 739-753, 2004.

26. S. Bian, S. Jayaram and E. A. Cherney, "Electrospinning as a new method of preparing nanofilled silicone rubber composites," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 19, *(3),* 2012.

27. S. Kumagai and N. Yoshimura, "Hydrophobic transfer of RTV silicone rubber aged in single and multiple environmental stresses and the behavior of LMW silicone fluid," *IEEE Trans. Power Del.,* vol. 18, *(2),* pp. 506-516, 2003.

28. M. Roy, , J. Nelson, R. MacCrone, L. S. Schadler, C. Reed, and R. Keefe. "Polymer nanocomposite dielectrics-the role of the interface," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 12, *(4),* pp. 629-643, 2005.

29. J. K. Nelson and J. C. Fothergill, "Internal charge behaviour of nanocomposites," *Nanotechnology,* vol. 15, *(5),* pp. 586, 2004.

30. C. Calebrese, J. K. Nelson, L. S. Schadler, and D. Schweickart. "Polyamideimide-alumina nanocomposites for high-temperatures," in *10th IEEE International Conference on Solid Dielectrics (ICSD),* 2010.

31. S. Xie, B. Zhu, X. Wei, Z. Xu, and Y. Xu. "Polyimide/BaTiO3 composites with controllable dielectric properties," *Composites Part A: Applied Science and Manufacturing,* vol. 36, *(8),* pp. 1152-1157, 2005.

32. C. A. Grabowski *et al*, "Dielectric performance of high permitivity nanocomposites: impact of polystyrene grafting on BaTiO3 and TiO2," *Nanocomposites,* vol. 2, *(3),* pp. 117-124, 2016.

33. H. Li, G. Liu, B. Liu, W. Chen, and S. Chen. "Dielectric properties of polyimide/Al2O3 hybrids synthesized by in-situ polymerization," *Mater Lett,* vol. 61, *(7),* pp. 1507-1511, 2007.

34. R. Kochetov *et al*, "Anomalous behaviour of the dielectric spectroscopy response of nanocomposites," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 19, *(1),* 2012.

35. R. Kochetov, "Thermal and Electrical Properties of Nanocomposites, Including Material Properties," Master thesis, Lappeenranta University of Technology, 2012.

36. A. El-Hag, L. Simon, S. Jayaram, and E. Cherney."Erosion resistance of nano-filled silicone rubber," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 13, *(1),* pp. 122-128, 2006.

37. A. Yasmin and I. M. Daniel, "Mechanical and thermal properties of graphite platelet/epoxy composites," *Polymer,* vol. 45, *(24),* pp. 8211-8219, 2004.

38. A. N. Netravali and K. Mittal, *Interface/Interphase in Polymer Nanocomposites.* John Wiley & Sons, 2016.

39. M. G. Todd and F. G. Shi, "Characterizing the interphase dielectric constant of polymer composite materials: effect of chemical coupling agents," *J. Appl. Phys.,* vol. 94, *(7),* pp. 4551-4557, 2003.

40. K. Y. Lau, *Structure and Electrical Properties of Silica-Based Polyethylene Nanocomposites,*Phd thesis, University of  Southampton, 2013.

41. X. Huang, P. Jiang, C. Kim, Q. Ke, and G. Wang. "Preparation, microstructure and properties of polyethylene aluminum nanocomposite dielectrics," *Composites Sci. Technol.,* vol. 68, *(9),* pp. 2134-2140, 2008.

42. A. Choudhury, A. K. Bhowmick, C. Ong, and M. Soddemann."Effect of various nanofillers on thermal stability and degradation kinetics of polymer nanocomposites," *Journal of Nanoscience and Nanotechnology,* vol. 10, *(8),* pp. 5056-5071, 2010.

43. C. Zou, J. C. Fothergill and S. W. Rowe, "The effect of water absorption on the dielectric properties of epoxy nanocomposites," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 15, *(1),* 2008.

44. S. K. Mealey, B. Thomas and D. Corning, "Past, present and future of organosilane treatments for fillers," *Rubber World,* vol. 12, pp. 32-34, 2005.

45. C. Angammana and S. Jayaram, "A study of free surface electrospinning process to enhance and optimize the nanofibre production," in *Proc. 2012 Electrostatics Joint Conference,* 2012.

46. L. H. Meyer, S. H. Jayaram and E. A. Cherney, "A novel technique to evaluate the erosion resistance of silicone rubber composites for high voltage outdoor insulation using infrared laser erosion," *IEEE Trans. Dielectr. Electr. Insul.,* vol. 12, *(6),* pp. 1201-1208, 2005.

47. Wang, Qi. The effect of nano size fillers on electrical performance of epoxy resin,Phd thesis, University of Southampton, 2012.