CHAPTER 1

INTRODUCTION

1.1. RECENT TRENDS IN INSULATION TECHNOLOGY

Numerous researches have been carried out on composite dielectric materials using conventional micron sized fillers for the use of electrical insulation in high voltage applications. These fillers help to overcome the defect of the conventional insulation material by improving its physical, mechanical, thermal and electrical properties. Further improvements of materials using micron-sized fillers are not possible nowadays because, mixing of the viscous compositions has reached the limitations of current processing technology.

In the recent years, the interest in the addition of nanofillers has grown and many research papers have been published in the area of electrical properties of nanocomposites. Polyamide 6/clay nanocomposite (Fukushima & Inagaki1987) was the first engineering plastic manufactured on a commercial basis by Toyota in 1990. Compared to micronized fillers, nanometric fillers, have large specific surface area and multi fold number of nanoparticles within the same volume fraction (Lewis, 1994). Hence, the interfacial effects dominate over the volume and depending on the polymer filler interaction, the presence of such interfaces governs the macroscopic behaviour of the composite and hence the dielectric properties (Lewis, 2004). The advent of nanotechnology leading to the availability and commercialization of nanoparticles, polymer nanocomposite with better
dielectric and electrical insulation properties has become a promising area of functional materials for dielectrics and electrical insulation applications.

Researchers’ findings on nano-sized particle (nanoparticle) filled dielectrics show significant improvement in the property of the material even at low filler concentration compared to a higher amount of micron-sized fillers. Though the promise of further improvements of dielectric materials is an interesting field of study, until now nanofillers have not been considered for commercial outdoor insulation. Hence, this has become the objective of this thesis.

1.1.1 Polymeric Composite Insulators for High Voltage

Since the introduction of polymeric composite insulators by General electrical in 1957, the use of polymeric insulators has increased dramatically at the cost of conventional ceramic insulators. Electrical companies have started using polymeric insulators at distribution voltages, at low voltage transmission and now up to 765 kV AC and 500 kV DC. The insulators are classified according to the way that they are used, for example, post and suspension types. The suspension type is most common, supporting an energized conductor from an overhead structure, such as a tower. Post insulators are commonly used in distribution lines and substations.

The composite suspension insulator, as illustrated in Figure 1.1, consists of three components; namely, a fibreglass core, an end attachment hardware (end fittings) connected to the core, and a protective housing with weather sheds for the core. The core provides the mechanical function of the insulator. The hardware allows the insulator to be attached to an overhead tower and to an energized conductor. The core by itself is inappropriate for outdoor use, as, moisture and voltage cause electrical tracking on the core which results in mechanical failure. Therefore, housing is moulded onto the
core, to protect the core from electrical tracking, and the design of the housing provides the electrical strength under wet and polluted conditions.

![Composite Suspension Insulator](image)

**Figure 1.1 Components of a composite suspension insulator**

For outdoor insulation, two materials are commonly used for the housing: Ethylene Propylene Diene Monomer (EPDM) rubber and Silicone Rubber (SR). Although both materials are used, SR is preferred due to its characteristic hydrophobicity and its good performance in polluted environments. This study is concerned only with the SR housing material and its ability of performing in polluted environments.

### 1.1.2 Polymer Nanocomposite Insulators

Polymer nanocomposites are defined as polymers in which small amounts of nano-meter size fillers are homogeneously dispersed by only several weight percentages (Tanaka et al, 2004). Addition of just a few weight percent of the nano-fillers has profound impact on the physical, chemical, mechanical and electrical properties of polymers. Such change is often favourable for engineering purpose. This nanocomposite technology has emerged from the field of engineering plastics, and potentially expanded its
application to structural materials, coatings, and packaging to medical, biomedical products, electronic and photonic devices. Recently, these ‘hi-tech’ materials with excellent properties have begun to attract researchers in the field of dielectrics and electrical insulation. Since new properties are brought about from the interactions of nanofillers with polymer matrices, mesoscopic properties are expected to come out, which would be interesting to both scientists and engineers. Improved characteristics are expected as dielectrics and electrical insulation. Several interesting results indicate that foreseeable future has been revealed, and some of which are described on materials and processing in the paper together with basic concepts and future direction.

1.2. FOCUS OF THE RESEARCH

The use of composite insulators has radically increased over recent years as a substitute for traditional ceramic insulators. The inclusion of fillers improves electrical, thermal and mechanical properties of the polymer. Extensive research has been done concerning micro fillers in silicone (SR) housings. The fillers used for these materials are micron-sized particles with particle sizes ranging from 1-50 µm. In the recent years, a great deal of attention has been paid to the application of nanofillers in the field of electrical insulating materials. Most researchers agree that uniform mixing and particle dispersion are critical in the development of nanocomposites useful for outdoor insulation. With nanocomposites, the electrical properties of the materials can be improved, if the nanoparticles are well dispersed. The focus of this research work is to develop SR based nanocomposite for outdoor insulation.
1.2.1 Selection of Materials

Many research works have been published on polymers like Epoxy, EPDM, Silicone Rubber (SR) etc. are electrical application. In practice, SR is widely used in outdoor insulations due to its good performance under polluted environment. SR, which is an extraordinarily versatile, convenient, and unique synthetic elastomer, offers professionals with many options for creative and innovative design and engineering [Tuncer et al 2000]. SR in general has very high chemical and thermal stabilities. The bonds of the silicone chains are stronger than the bonds of other polymers like ethylene propylene rubber or epoxy. This property of SR gives stability against heat and UV radiation and also helps to withstand water, silicone grease, salt and dust. Contemporary silicone rubber is used generally as outer insulation.

Recent research has shown the enhancement in the physical and mechanical properties of the SR nanocomposites. Significant changes in AC conductivity, dielectric constant, dielectric loss and arc resistance have been noted on various research works carried out in SR filled with nano sized Al₂O₃ and TiO₂. SR nanocomposites offer improved resistance to tracking and corona degradation, when compared to conventional fillers. These findings suggest that SR can be effectively employed to combine nano metric ceramic fillers to achieve improved electric and dielectric properties.

This research focuses on the electrical properties of SR combined with various filler materials like Aluminium Oxide, Titanium dioxide, Barium Titanate, Zinc Oxide, Magnesium Oxide and CaCu₅Ti₄O₁₂(CCTO) at low filler concentration.
1.2.2 Preparation of sample and Characterization

Proper processing techniques have to be adopted to ensure uniform dispersion of the nanoparticles in the polymer matrix. In the current study, nanocomposites are prepared using a combination of two different processing techniques – Mastication and Compression moulding. These processing techniques are preferred in the current study because, they are easy to use at the laboratory scale and in industrial applications.

1.2.3 Testing and Analysis of Samples

The dispersion of fillers in the SR composites has been investigated by examining the sample cross-sections under a scanning electron microscope. The composition and the dispersion of the fillers are verified by X – Ray Diffraction studies. The dielectric properties of the materials are studied by measuring ac conductivity, dielectric constant, dielectric loss and dielectric strength as per the standards. The measurement arc of resistance helps to understand the effect of the addition of the filler material in increasing surface resistance to high voltage arc. Further, mechanical and thermal analyses are carried on every sample.

1.3 IMPORTANCE OF THE RESEARCH

This research is significant in four aspects

First, the growing electric power industry demands the need to upgrade insulation system of the high power apparatus to improve the reliability of the apparatus.

Secondly, the application of polymeric materials associated with high dielectric constant and high breakdown strength have been dramatically increased in the recent years.
Third, the high dielectric permittivity composite materials have been considered to be potential candidates for integration into electronic devices. Owing to the continuous development towards the miniaturization of electronics, newer dielectric materials are sought which would enable to achieve high energy density for capacitor applications.

Fourth, recent research works on polymers filled with nanofillers help to overcome the disadvantages of the polymers and prove to be a promising trend to meet out the increasing demand of the industry with respect to electrical insulation of high power devices and high energy density capacitor for integrated circuits.

1.4. LITERATURE SURVEY

Many research works have been made on applications of polymeric insulators over ceramic insulators. There are so many research articles on the influence of nanofillers on the dielectric properties of polymer matrix. Literatures relevant to this are reviewed.

1.4.1 Studies on polymeric composite insulators

Cherney (1991) in the paper on Porcelain insulation maintenance with SR have studied that the properties of adhesion to porcelain insulators, water repellency, tracking and/or erosion and their ability to suppress leakage current are important characteristics of RTV SR coating systems. It is reported that these properties vary considerably with coatings and are dependent on the formulation of the coating system. Coatings which do not adhere well to porcelain are not useful as a maintenance tool. Likewise, coatings which show tracking or excessive erosion are also not useful as a maintenance tool, as they likely will have a short life. SR coating systems perform by the fact that they are able to suppress leakage current. This
enables insulation systems to attain increased flashover performance by about 30% over uncoated insulations.

The history and bibliography of polymeric insulators for outdoor applications have been given by James Hall (1993). In this paper, it is suggested that an accelerated aging test method is needed to characterize degradation modes and predict expected life, based on site specific environmental conditions. Since polymeric materials are dynamic and interact with their environment, they are also affected during contamination testing. Because of the contamination the flashovers during testing affect the surface, test repeatability is not achieved. A flashover or withstand test method is needed and that will not impact test repeatability. Again, it is reported that polymeric insulators perform much better than the ceramic insulators in the polluted environment.

Flashover mechanism of SR insulators used for outdoor insulation has been studied by George G. Karady & Brown (1998) and found that both the sea and industrial pollution produce a uniform contamination layer on silicon insulator surface. Using the X – Ray mapping technique, it is demonstrated that the surface recovery produces a thin, not continuous silicon layer on the surface and which permits the migration of water to the contaminant and the salt to the droplets. The wetting produces a high resistive layer scattered by conductive droplets.

Tiebin Zhao & Allen (1996) have documented the ageing of the polymeric materials used for high voltage outdoor insulation using the ageing and diagnostic tests outlined. The field aged materials, demonstrated slight changes in the diagnostic tests, because these materials have been formulated to minimize the ageing effects. It is a real challenge to interpret the data of the ageing and diagnostic tests. However, accelerated laboratory ageing tests are utilized to compare the relative performance of the materials and insulator
design under identical test conditions. The performance should be evaluated by various ageing tests.

Cherney (1996) has analyzed the use of non-ceramic insulators and reported that at distribution voltages, confidence in non-ceramic insulators is high so that, many utilities purchase only non-ceramic type insulators. In other utility owned and operated equipment (transformers and their bushings, surge protective devices, etc.), the industry has rapidly converted from porcelain to non-ceramic wherever the opportunity has presented itself.

Vaillancourt et al (1998), in the study on detection of line insulator defects by electric field measurement has reported that a composite insulator electric field distribution can be measured easily and conveniently with the new tester and repeatable results can be consistently obtained. In the high voltage laboratory, simulated conductive defects as short as 8 cm long, and real conductive defects down to 16 cm long have been successfully detected.

Liang Xidong et al (1999) from China has reported the development of composite insulators and the usage of insulators on AC 35 kV to 500 kV systems. In China, composite insulators are used in all contamination areas, especially in moderate and heavy pollution conditions. Because of this, only SR composite insulators are used. Consequently, pollution flashover accidents have been avoided efficiently and maintenance cost of the lines has dramatically been lowered.

Cherney (1999), in the paper on RTV Silicone Rubber Coatings for outdoor Insulators, has presented a review of Room Temperature Vulcanized (RTV) silicone rubber High Voltage Insulator Coatings (HVIC). These coatings are designed to replace greasing and water washing of insulators. The paper focuses on the important characteristics of these coatings and on
the rigorous attention that is required in their application in order to ensure good performance.

Phillips (1999) has reported that water drops on the sheath surfaces of SR can produce corona. They found that the magnitude of surface E-fields is necessary to result in the onset of water drop corona and is a function of both drop size and surface hydrophobicity. Water drop corona results in temporary changes in the hydrophobic properties of SR material. The loss of hydrophobicity, due to water drops, is proportional to the magnitude of the applied E-field.

Reuben Hackam (1999) in his review paper has explained the tremendous growth in the applications of non-ceramic composite insulators and it is due to their advantages over the traditional ceramic and glass insulators. These include light weight, higher mechanical strength to weight ratio, resistance to vandalism, better performance in the presence of heavy pollution in wet conditions, and comparable or better withstand voltage than porcelain or glass insulators. However, they suffer from erosion and tracking in the presence of severe contamination and sustained moisture. This leads to the development of dry band arcing and that too under certain circumstances could lead to failure of polymer insulators.

The performance experience of HV composite polymeric insulators in outdoor service, testing methods, aging, the ranking of the materials, the role of fillers, the role of low molecular weight components present in the insulators, the mechanisms responsible for the loss and recovery of hydrophobicity, detection of faults, effects of exposure to rain, hydrocarbons, stationary air and wind, various methods to optimize the electrical performance and a relatively new method for evaluating the performance status of polymeric insulators are also explained.
Silicone rubber cylindrical samples with known differences in material composition have been aged due to voltage stress, ac and dc, in a coastal environment for a period of 32 months and tested with high electrical stress to accelerate the aging and the creepage distances are 30% and 60% of what normally is used at this location for ceramic insulators (Gustavsson 2001). The electrical performance is quantified by counting the number of peak leakage current values.

Ehsani et al (2005) has investigated the effect of different aging conditions on the surface properties and tracking resistance of silicone rubber, EPDM, blend of silicone and EPDM, and silicone modified polymer. The hydrophobicity of polymers is found to decrease with UV aging and is attributed to the formation of polar groups (such as carbonyl groups) and loss of hydrophobic groups (such as methyl groups) on surface of polymers. The results of the contact angle measurement show that the water repellency of polymers decreases with water salinity. This study shows that the silicone-modified polymer is more hydrophobic than other samples under various conditions, and the tracking resistance of silicone rubber decreases with saline water aging. It is also shown that UV aging decreases the tracking resistance of EPDM possibly as a result of loss of hydrophobicity at the surface of EPDM.

Zhang et al (2011) have done a study on aging characteristics of silicone rubber insulator sheds. The groups such as Si-O-Si and Si-(CH$_3$)$_2$ of the first shed at high voltage side in the same insulator are broken most seriously. Hence, so the shed has aged more seriously than that in others positions. Along with the increase of service time, the fracture degree of the main groups and the aging of the insulator under the same voltage level increase gradually. As for the insulator strings under different environments,
the effect of contamination level on the FTIR characteristics of the shed is less than that of operating years.

Moussavi et al (2012) have presented the simulation results of electric field and potential distributions along the surface of silicon rubber polymer insulators of 20 kV under clean and various contamination conditions. The two conditions are investigated by using FEM. Finally, a conductive layer on the insulator surface has been used in order to simulate the environmental pollution. The main observations are the increased voltage, field values and the transition to a resistive potential distribution, when the values of the pollution conductivity are high. In both cases of pollution conductivity, the values of the electric field strength exceed those of the non polluted insulator. A further conclusion is that a deposition of a pollutant with higher conductivity creates higher field values and may thus cause easier flashover.

The above studies show that polymeric composite insulators are more advantageous than the ceramic fillers with respect to pollution behaviour and maintenance. However, the real challenge comes from the ageing of the polymers and its tendency to get affected by the UV rays.

1.4.2 Influence of nanofillers in polymer matrix

Lewis (1994) has suggested that a major field of study in the future development of dielectrics will concern their properties, when relatively few molecules are involved. Such smallness arises naturally at interfaces of nanometric thickness and will occur also, when dielectrics are employed in the nano-technical devices of the future. The transverse and lateral properties of interfaces, including the effects of molecular ordering, are considered. It is suggested that the advent of scanning tunneling and atomic force microscopies provide a significant opportunity for nanometric dielectric
studies. An important feature, suggested for future exploitation, is the cross-coupling in interfaces of force fields arising from electrical, mechanical, chemical and entropic potential gradients. This paper has drawn the role of nanometric interfacial processes in the initiation of electrical breakdown in insulating materials.

Dongguang Wei et al (2002) have selected three different nanosized material systems based on their physical and chemical properties. The mixing experiments of the selected nanopowders are performed using a variety of environmentally friendly dry powder processing devices and the Rapid Expansion of Supercritical CO2 Suspensions (RESS process). They are compared with solvent-based methods coupled with ultrasonic agitation. The results indicate that only some of the imaging techniques are capable of determining the quality of nanoparticle mixing, depending on the physical and chemical properties of the nanopowders.

Lewis (2004) has explained that the behaviour of dielectric particles, as they shrink in size through micrometric to nanometric scales, will be increasingly dominated by the properties of their interfaces with the environment. The various interatomic and intermolecular forces that determine the structure of these interfaces are reviewed with special emphasis on their electrical nature. A number of situations in which passive and dynamic dielectric properties traceable to nano-metric interfacial are considered. It is also demonstrated that such interfaces are Nanometric Electro Mechanical (NEM) systems which act collectively to explain piezoelectricity in macroscopic systems. Interfaces are naturally nanometric entities and must have a major role in the future development of nanotechnology. Their ubiquitous employment in living systems is noted and comparison suggests synergistic opportunities.
Frechette et al (2004) have presented the scope, potential and development of the material. The broad field of nanotechnology is outlined along three major axes of growth. These are presented with an emphasis on molecularly tailored materials. Basic principles regarding the nano structuration of solid bulk materials are explained with the aim of delineating the problem area pertaining to materials with an amorphous phase. It is put forward that new and improved dielectrics with insulating capabilities and electro technical potential would be found among the nanostructured ceramics and tailored polymer nano-composites. The presence of an amorphous phase in the nanodielectric composition brings challenges and requirements with regards to the development of new nanostructuration concepts, assembling and processing methodologies.

Cao et al (2004), in their paper on the future of nanodielectrics in the electrical power industry, have summarized the development, applications and time scale in the development of nanodielectrics. The incorporation of nanoparticles will make combined progressive electrical, mechanical and thermal improvements in important engineering fields, resulting in many interesting applications such as enamel insulation, electrical grading and EMI shielding in a cost effective manner. It is identified that with proper material processing developments, nanocomposites based on preformed mineral or synthetic anisotropic fillers will have unique anisotropic properties suitable for applications such as electrical discharge resistant machine insulation.

Roy et al (2005) have explained that the incorporation of nanoparticles into thermosetting resins is seen to impart desirable dielectric properties, when compared with conventional (micron-sized particulates) composites. Although the improvements are accompanied by the mitigation of internal charge in the materials, the nature of the interfacial region is shown to
be pivotal in determining the dielectric behaviour. In particular, it is shown that the conditions and enhanced area of the interface change the bonding that may give rise to an interaction zone, which affects the interfacial polarization through the formation of local conductivity.

Santanu Singha & Joy Thomas (2006), in their paper on Polymer composite/nanocomposite processing and its effect on the electrical properties have reported that the processing methods will significantly contribute to variations in the dielectric properties of nanocomposites due to the variations in the distributions of the particles in the polymer matrix. It is recommended that whenever dielectric properties of nanocomposites are evaluated, apart from looking at the cross section micrographs, it is probably better to cross-check some of the basic dielectric properties with micro composite samples of the same matrix having same concentration and type of filler.

Frêchette et al (2006) have presented a brief overview on the emergence of this new field tagged as now “Nanodielectrics”. Measurements and properties are found to depend greatly on the material synthesis particularities and reproducibility and phenomenology is very much sensitive to recipes and quality of the end-products. If there is magic, it is very much varying with content and morphology, and there is a serious need for quality control of the developed materials. Nanofiller must be added to micro composites, if one wants to obtain solid dielectrics with electro technical superior performance as compared to conventionally filled polymeric matrix. They indicate that there is a strong need for quality control of the “nanodielectrics” and accrued documented knowledge links the nanostructural morphology and the macroscopic observables.

Juh Tzeng Lue (2007) has reviewed several methods to prepare nanoparticles including insulators, semiconductors, carbon nanotubes, metals and magnetic ferrofluids. Aligned and random aligned carbon nanotubes
grown on copper based iron alloys, respectively, by radio frequency induced self-bias hot-filament method and by microwave enhanced plasma are specially illustrated in the paper. Temperature dependence on the field emission of CNTs is successfully expressed by semiconductor thermionic emission theory. The physical properties of nanomaterials, comprising structure, electrical and magnetic characters, linear optical and nonlinear optical properties subjecting to classical size and quantum size effects are succinctly described. Nano-ferro fluids are illustrated to behave the unusual quantum phase transition. The dielectric constants of metallic nano-particles are measured within the microwave frequency ranges. Nanofabrication for tackling nanodevices is portrayed. It is impossible to meticulously display every detail of this newly developed complex system in this scenario review.

Takahiro Imai et al (2006) in their study demonstrated that nano-filler dispersion is effective in improving insulation properties of epoxy-based insulating materials. Moreover, the nano-filler/micro-filler combination system not only verifies that nanocomposite materials are practical insulating materials in terms of thermal expansion but also provides synergy effects on improvement of insulation properties of nanocomposite insulating materials.

A complex oxalate precursor, CaCu$_3$(TiO$_4$)$_4$(C$_2$O$_4$)$_6$9H$_2$O, (CCT-OX), is synthesized and the precipitate obtained is confirmed to be monophase by the wet chemical analyses, X-ray diffraction, FTIR absorption and TG/DTA analyses(Thomas et al 2009). The thermal decomposition of this oxalate precursor has led to the formation of phase-pure calcium copper titanate, CaCu$_3$Ti$_4$O$_{12}$, (CCTO) at $\geq$680°C. The powders so obtained has excellent sinterability resulting in high density ceramics which exhibit giant dielectric constants up to 40000 (1 kHz) at 25°C, accompanied by low dielectric losses <0.07.
Polizos et al (2010) BT and MMT nanoparticles are covalently bonded in solution, forming hybrid nanofillers with BT cores bearing chemically attached MMT layers. These hybrid nanomaterials are subsequently dispersed in epoxy resin, yielding nanocomposites that exhibit good dispersions even at high filler loadings. This approach has led to a unique spatial configuration of the nanofillers that consists of BT spherical nanoparticles surrounded by covalently-bonded layered MMT platelets. With respect to the dielectric performance viewpoint, the unique filler structure, resulted from the covalent bonding of BT and MMT, is found to synergistically combine the good properties of the two individual inorganic phases, i.e., the high permittivity of the BT and the good interfacial properties of the reactive MMT. The resulting nanocomposites demonstrate good electrical properties under low and high electric fields.

Raetzke & Kindersberger et al (2010), have explained the role of Interphase on the Resistance to High-voltage arcing, on Tracking and Erosion. Two kinds of silicone/SiO2 nanocomposites are tested with respect to their resistance to high-voltage arcing and their resistance to tracking and erosion. The resistance to high-voltage arcing and the resistance to tracking and erosion are found to be strongly improved for the materials depending on the type of filler.

BaTiO3 crystallites with various particle sizes from 25 to 500 nm are prepared by a solvothermal method (Mao et al 2010). The BaTiO3 particles are of pure perovskite phase, uniform and well dispersed, as proved by means of x-ray powder diffraction and SEM. The composites are prepared with BaTiO3 nanoparticles of various sizes as active phase and polymer PVDF as matrix. A two-step mixing method is adopted to obtain the BaTiO3/PVDF two-phase composites of homogenous dispersion. The polarization-electric field hysteresis loops confirm the ferro electricity of the nanocomposites. The
size dependences of the remnant polarization and dielectric constant in the BaTiO$_3$/PVDF nanocomposite are measured for various particle sizes from 25 to 500 nm. The dielectric constant of the composite with BaTiO$_3$ nanoparticles over 250 nm remains almost constant, while it increases with decreasing particle sizes and reaches a maximum value at a BaTiO$_3$ particle size around 80–100 nm. The dielectric constant decreases with further decrease in particle sizes down to 50 nm and then increases from 50 to 25 nm, showing a minimum at 50 nm. The ferroelectric nanocomposites prepared in this work with enhanced switchable spontaneous polarization, high dielectric constant and relatively low dielectric loss will find many applications in such devices as electromechanical energy transducers, sensor and actuators, and high-energy density capacitors, which are useful for energy conversion and storage.

Su et al (2011), have reported a simple and rapid synthesis method of MgO nanocubes via DC arc discharge method without metal catalysts, in which mixed air/Ar gases are buffer gases. The results indicate that the synthesized MgO nanocubes are all face centered-cubic structure, and enclosed by \{100\} facets. The edge lengths mainly range from 60 nm to 100 nm. Most nanocubes interface with adjacent nanocubes in production, which can be divided into three types: point contacts, line contacts and face contacts, which contribute to lowering the total surface energy. Compared with the PL emission band of commercial MgO powders, as-synthesized MgO nanocubes show more intensive luminescence bands, which is ascribed to various structural defects, the nanosize effect and surface states of MgO nanocubes.

Kaviyarasu, K & Prem Anand Devarajan (2011), have developed a facile method to prepare high quality MgO nanocrystals. It is safer, easier to perform, and more cost effective than the chemical vapour deposition route. The XRD data indicate that MgO nanoparticles exhibit lesser defective
crystalline internal perfection. The structural perfection and the growth features of the synthesized crystals are studied. The quality of the nanocrystals is visualized by observing the surface morphology using SEM studies. The dielectric studies on the nanocrystals reveal that dielectric constant decreases slowly with increase in frequency but attains saturation for higher frequencies. Owing to all these properties, the synthesized nanocrystals could be promising materials for modern materials design.

Latif et al (2012) in their study, the dielectric behaviour of the polar Polyvinyl Alcohol /ZnO nanocomposite films has been investigated. The results show that the dopant composition has great influence on the magnitude of dielectric properties. The results also show that the composite polymer films have both electric and electronic properties. The composite polymer films exhibit the combination of intrinsic dielectric anisotropy as a result of the competition of free charges and electronic polarization corresponded to CPVA matrix. Relaxation times become shorter as the composition of ZnO nanoparticles concentration is increased and it indicates high availability of free charges.

Das et al (2013) have developed a practical and greener ‘NOSE’ protocol for the clean synthesis of both aliphatic and aromatic amides utilizing nano-MgO as an efficient, reusable and cheap catalyst. Simple experimental condition, varied substrate compatibility, high yields of the products, chemo selectivity, and non-hygroscopic nature of catalyst give new alternative over conventional ones for amide synthesis.

The study shows that the addition nanofillers in the place of conventional fillers is advantageous particularly with respect to higher surface area to volume fraction. The interaction at the interface between the nanofillers and the polymer matrix is the dominant feature in determining the
characteristics of the composite. The invention of novel methods to synthesis nanofillers is an added advantage to develop polymer nanocomposites.

1.4.3 Studies on the dielectric property of Polymer nanocomposites.

Rao et al (2000) have proposed the Effective-Medium Theory (EMT) and it has been used to predict the effective dielectric constant of the polymer–ceramic nanocomposite. EMT model includes a fitting factor ‘n’ that accounts for the morphology of ceramic particles. The prediction results have error less than 10% compared to experimental data.

Zilg et al (2003) have studied the electrical properties of nanostructured materials obtained from EVA and PP as base materials and organophilic layered silicates as nanofillers show interesting modification of electrical properties that may affect positively insulation system design and performance on short term and long term basis. The increase of conductivity and the good behaviour of DC electric strength might open interesting perspectives for electrical applications of the investigated materials. The way of obtaining nanocomposites described in this paper is worth of consideration for additional research efforts.

The mechanical and thermal properties of thermosetting polyimides nanocomposites are investigated further to understanding of the structure-property relationships of nanoparticles and polymeric systems (Irwin et al 2003). It is found that the surface modified, nanofilled polyimide films have shown increased elongation and strength to failure as compared to unfilled materials. The increased scratch hardness is observed in nanofilled films related to micron-filled films and thermal conductivity of coated nanofilled polyimide films is also enhanced, when compared to micron-sized filled polyimide films and unfilled films.
Montanari et al (2004) have studied that nanostructuration of Ethylene Vinly Acetate and Polypropylene by modified organophilic layered silicates can give rise to interesting modification of electrical properties that may affect positively insulation system design and performance on short term and long term basis. The decrease of trapped space charge at fields close to design stress, the increase of conductivity and the good behaviour of dc breakdown voltage might open interesting perspectives for electrical applications of the investigated materials and indicate that the way of obtaining nanocomposites described in this paper is worth consideration for additional research efforts.

Kozako et al (2004) have presented the Surface Degradation of Polyamide Nanocomposites Caused by Partial Discharges (PD). It is reported that the surface roughness caused by PDs is far smaller in specimens with nanofillers than those either without nanofillers, or those containing microfillers. Even the specimen with 2 wt% nanofillers is found to have sufficiently improved resistance to PDs.

Fuse et al (2005) have examined the complex permittivity, conductivity, and dielectric strength of polyamide-6/mica nanocomposites. Analysis of the complex permittivity shows that molecular motion is restricted in nanocomposites, which indicates a strong interaction between the resin and filler. The conduction current decreases with the addition of nanofillers. It is reported that four mechanisms, reinforcement of mica/resin interfaces, increase in the transport distance of carriers by zigzag structures, formation of nanometric spherulites, and carrier trapping by the charged mica nanofillers seem to be responsible. The dielectric strength is nearly independent of nanofillers content.

Tanaka (2005) in his review paper explains that polymer nanocomposites are the 21\textsuperscript{st} century engineering materials with wide range of
markets such as transportation, electrical and electronics, food packaging, and building industries. They are particularly attractive as advanced dielectrics and electrical insulation. Experimental data obtained thus far on the nano dielectrics are reviewed mainly for electrical properties and analyzed on the basis of the multi-core model.

Roy et al (2005) have analyzed the influence of physical and chemical linkage on the properties of nanocomposites. The results for breakdown strength and endurance clearly show that the biggest impact is the size of the filler. All the nanoscale fillers have significantly better breakdown strength and endurance than the base resin.

Huang et al (2007) have studied that the dielectric properties like the dielectric permittivity and loss tangent of PE/Al nanocomposites are dependent not only on the Al nanofiller concentration but also on the measuring frequency. The significant differences of the dielectric behaviours are found in the extra-low frequency range of 0.1–10 Hz. It is reported that, higher the nanofiller loading level, the larger the total effective area of the interfaces between the polymer matrix and the fillers, and the thinner the insulating spacers separating Al nanoparticles, which results in the significant increment of the interfacial space-charge polarization.

Tagami et al (2008) have investigated the effects of curing agent and clay dispersion method on the dielectric properties of epoxy/clay nanocomposites. The experimental results indicate that the curing agent gives the strongest effect on the properties of epoxy/clay NC. Permittivity and conductivity are higher in the amine cured samples than in the acid anhydride-cured samples. The space charge distribution measurement, show accumulation of negative heterocharge and is observed near the anode in the amine-cured samples, while positive homocharge is seen near the anode in the acid anhydride cured samples. UV absorption, PL, and PLE measurements
proved the band gap or the energy difference between localized electronic state and extended state is 3.4 eV for the amine-cured samples and 4.0 eV for the acid anhydride-cured samples.

The characteristics of dielectric permittivity and tan delta in epoxy nanocomposites with Al₂O₃ and TiO₂ nano-fillers over a frequency range of 1 MHz - 1 GHz are found to be different from the expected trends seen in polymer microcomposites (Santahmu et al 2008a). The incorporation of nano-fillers to an epoxy matrix reduces the permittivity of the nanocomposites for specific filler percentages, when compared to that of unfilled epoxy and such phenomena is never observed in epoxy microcomposites earlier. At the same time, it is found that the effective permittivity increases with increasing filler concentration.

For Al₂O₃-epoxy nanocomposites, tan delta at all the filler concentrations are less than or equal to the unfilled epoxy value over the frequency range studied. But in TiO₂- epoxy nanocomposites, although the tan delta values do not deviate much with respect to the value for unfilled epoxy, there are variations with respect to the frequency. In summary, it is the epoxy-filler interface which determines the behaviours of the effective permittivity and tan delta values in epoxy nanocomposites and a complete understanding of the interfacial phenomena is of utmost importance to fully understand not only these two dielectric parameters, but also several other important electrical properties.

Santanu Singha et al (2008b), report that epoxy nanocomposite systems with inorganic oxide fillers display some advantageous dielectric behaviour at low nanofillers loadings. The permittivity and tan delta values in the nanocomposites are found to be lower than that of microcomposites as well as unfilled systems (for few filler loadings). At the same time, a marginal reduction in the epoxy dc volume resistivity is also observed by incorporating
a small amount of nano-filler into the base material. Although the AC
Dielectric Strength in nanocomposites is lower than those of unfilled epoxy
systems, when compared to microcomposites, the type of filler seems to
influence the results. A dual layer model reported for the mechanical
properties in polymer nanocomposites is found to be suitable in explaining the
observations of the dielectric properties in epoxy nanocomposites at low filler
concentrations.

Murakami et al. (2008) have investigated the volume resistivity, space charge behaviour, and breakdown strength of MgO/LDPE
nanocomposite materials under DC voltage applications. From the result, it is
clear that the addition of MgO nano-filler is suitable for the dc insulating
material. It is found that the volume resistivity of LDPE is increased by
addition of MgO nano-filler. Under high electric field (85 kV/mm more over),
the packet-like charge appears in LDPE, whereas the appearance of packet-
like charge is suppressed by addition of MgO nano-filler. The charge mobility
and amount of injected charge are decreased by addition of MgO nano-filler.
The dc breakdown strength of LDPE using McKeown type electrode is
increased by addition of MgO nano-filler. The dc breakdown strength using
needle-plane electrode of the film with MgO nano-filler is also higher compared to that without MgO nano-filler

Maity et al. (2008a) have identified that the use of nano-sized
particles rather than platelets as fillers improves ability of the composites to
resist surface degradation. The improvement, therefore, seems to be directly
linked to the surface to volume ratio of the filler material. Further, pre-
processing the particles before use makes the composites more resistant. It is
observed that heating the particles to 200°C was greatly beneficial. It is
further shown that functionalizing the nanoparticles with GPS before
composite preparation is beneficial.
Santanu et al (2009), have examined the epoxy-ZnO nanocomposite to validate few of the earlier observations obtained for the dielectric properties of epoxy nanocomposite systems with TiO$_2$ and Al$_2$O$_3$ fillers to characterize and understand the dielectric properties of this system. Results of this study corroborate some of the interesting dielectric characteristics observed earlier and confirm the fact that at lower filler loadings, the changes in the morphology of the nanocomposite material have large influence on their dielectric properties. The changes occur in the morphology of the nanocomposite material occur due to the formation of interface regions caused by nanoparticle-epoxy interactions. Apart from the effect of morphology, the influence of the ZnO filler is also observed (at lower filler loadings) as recorded from the results of permittivity/tan$\delta$ characteristics at high frequencies over the frequency range of $10^6$-$10^9$ Hz. The influence of nanofillers shows a steep reduction in the dc resistivity and ac dielectric strength at low filler concentration. In another interesting observation, between 5% and 20% filler concentration, nanocomposites show higher values of dc resistivity and ac dielectric strength than the microcomposites. In conclusion, results seem to show that nanocomposites do possess very unique properties and some of the characteristics are better than microcomposites.

Comparative studies of surface degradation of neat epoxy, nanocomposite and microcomposites are undertaken by Maity et al (2008b). It is clearly seen that neat epoxy specimens are most vulnerable to degradation by surface discharges. Microparticles help in reinforcing the bulk epoxy material to a certain extent. However, the resistance to surface degradation is considerably improved, if even a small volume fraction (0.5%) of nanoparticles is used instead of microparticles. It is possible that use of TiO$_2$ fillers instead of Al$_2$O$_3$ may be more advantageous, but it could be that size of the nanoparticles is the more dominant factor rather than the material.
Patsidis et al (2008) has investigated the dielectric response of polymer matrix – ceramic BaTiO$_3$ composites, in a wide frequency and temperature range. Relaxation phenomena are found to be present in all the examined systems. From the slower to the faster one, the recorded processes are attributed to interfacial polarization or MWS effect, glass to rubber transition of the amorphous polymer matrix and local motions of polar side groups of the macromolecular chains. Finally, the functionality of the filler arising from the thermally activated disorder to order transition, offers a ‘switch’ type polarization response to the composites with low or moderate BaTiO$_3$ content in the vicinity of the Critical Temperature (T$_c$).

Abraham et al (2009) have studied that the mechanical properties of polycrystalline Barium Sodium Niobate (BNN) ceramic powder with particle size less than 100 nm have been synthesized using conventional ceramic technique. The morphology and tensile behaviour of BNN-PS composites are also studied in detail. The most fascinating property of the composites is the relatively good dispersion of the filler particles in the matrix. The particle dispersion and particle-matrix reinforcement play vital roles for both tensile and elongation properties of the composites. Young’s modulus and tensile strength of polystyrene show an increment by the incorporation of BNN filler. Elongation at break value of the composites is same as that of neat PS showing the good reinforcement between the filler and the matrix and the stress transfer at the filler-polymer interface is effectively possible by the efficient dispersion and good adherence of the filler to polymer.

Thomas et al (2010) prepared composites of CCTO /PVDF with CCTO content ranging from 0% to 55% by volume. They observed that the flexibility of the composite could be retained, when the ceramic loading is up to 30 vol. %. Again, the effective dielectric constant and dielectric loss increase with increase in the volume fraction of CCTO at all frequencies.
under study. Dielectric constant as high as 95 at 100 Hz is achieved. Though the dielectric constant increases with increasing temperature, the rise in dielectric constant with rise in temperature is not significant at frequencies from 10 kHz to 1 MHz. They suggest that among the various models used for rationalizing the dielectric behaviour, experimental dielectric constant at higher volume fractions regime is comparable with those obtained with the models like EMT (\(n = 0.11\)) and Yamada (\(n = 9.3\)). The difference between the experimental data and the predicted value is less than 10%.

Jun-Wei Zhu et al (2010) has reported that the relative permittivity and ac conductivity of the PI/TiO\(_2\) nanocomposite films increase with increasing nano-TiO\(_2\) particle concentration. The breakdown strengths of the PI/TiO\(_2\) nanocomposite films decrease with increasing nano-TiO\(_2\) particle concentration and increasing corona aging time. The space charge density and the electric field distortion decrease significantly in the nanocomposite films with 10 wt % nano-TiO\(_2\) particles loading. The accumulation of space charge near the cathode weakens with increasing the concentration of the nano-TiO\(_2\) particles under the same corona aging time 10 h. The depth of new traps of the PI/TiO\(_2\) nanocomposite films is much shallower than the one of pure PI films under the same aging time. The corona resistance of the PI/TiO\(_2\) nanocomposite films is improved by increasing the concentration of the nano-TiO\(_2\) particles. The relation of space charge distribution with the concentration of the nano-TiO\(_2\) particles and the aging time are explored.

Thomas et al (2010b) have fabricated high dielectric permittivity polyvinylidene fluoride (PVDF)/Ca\(_2\)Cu\(_3\)Ti\(_4\)O\(_{12}\) (CCTO) nanocrystal composite films, and their study show, that the dielectric permittivity of PVDF increases with increase in CCTO content. The PVDF+CCTO-30% nanocomposite showed higher dielectric permittivity than that of pure PVDF and the other composites under study. The relaxation processes associated with these
composites are attributed to the interfacial polarization or MWS effect. Though there is an improvement in the dielectric permittivity, the decrease in dielectric breakdown may limit its use for high voltage applications.

Tomer et al (2010) have reported that Epoxy/inorganic nanocomposite systems display some advantageous dielectric behaviours at low nanofiller loadings. Studies of the resulted nanocomposites have recorded changes in the cross linking density, the glass transition, and the interfacial polymer dynamics, which are subsequently correlated with the respective dielectric responses. The addition of high permittivity BT fillers has resulted in increased permittivity and loss values, compared to the respective unfilled systems, whereas addition of lower permittivity MMT does not have a marked effect. It is observed that for all nano composites, a significant change in the local environment of the polymer is found after the incorporation of nanofillers. A reduction in the epoxy dc volume resistivity is also observed upon nanofiller incorporation and, more notably, although the dc dielectric strengths of all nanocomposites are lower than those of unfilled epoxy systems, there are distinct benefits in their recoverable energy density values. Specifically, Barium Titanate nanofillers have resulted in increased recoverable energy densities, while no advantages are found for MMT fillers. This demonstrates that high permittivity fillers are indeed crucial in enhancing the energy storage capabilities of low permittivity polymers, such as epoxies.

A new organic/inorganic Meso Porous Silica (MPSA) is used to develop new high performance bismaleimide/ diallylbisphenol resin matrix composites with improved mechanical and dielectric properties as well as thermal resistance (Hu et al, 2011). The addition of MPSA to DBA/BDM resin does not change the curing profile of DBA/BDM resin, but varies the curing mechanism, leading to different cross linked networks, and thus, affects the integrated performance of cured composites. Apparently, the
content of MPSA exhibits a great influence on the integrated performance of cured composites. The outstanding integrated performance of MPSA/DBA/BDM composites with suitable content of MPSA shows a great potentiality to be used as high performance insulators for applications needing harsh requirements in thermal, mechanical and dielectric properties.

Haldar et al (2013) have studied the Dielectric Properties of Polyaniline–Montmorillonite Clay Hybrids prepared by mechanical-grinding method. The dielectric constant has shown very high values at low frequency (102 Hz) followed by a sharp dispersion at a high frequency. Parameters like grain-boundary resistance and capacitance and conductivity – relaxation time are evaluated in the light of Maxwell-Wagner two layered model. AC conductivity is independent of frequency in the range 0.1–1 kHz showing a subsequent tendency to rise (1–25 kHz range) due to trapped charges at grain-boundary interfaces. DC conductivity values are lower than the PANI homopolymer.

The dielectric property epoxy resin composites have been studied in different filler contents, at different frequencies as well (Peng et al 2013). The dispersing methods including high speed stirring and three-roller mill have some advantages in the technological parameter adjustment. With regard to the detailed dielectric property, it exhibit that the dielectric constant of MWCNTs/epoxy resin composites has decreased gradually with the increasing of frequency (103–106 Hz) at fixed filler content. Then, as the content of MWCNTs increasing, dielectric constant rises in the early stage and drops later on. It is reported that the dielectric constant improved on account of the polarization enhancing which due to the interfacial areas increases with adding the filler contents originally.

Ke Yu et al 2013 have prepared homogeneous ceramics-polymer nanocomposites consisting of surface treated Barium Titanate particles as
fillers and PVDF polymer as matrix. The dielectric responses and energy storage properties of the nanocomposites are investigated and it is found that the nanocomposites exhibit enhanced dielectric permittivity in agreement with the Maxwell-Wagner model and reduced loss tangent. Both the frequency and temperature dependencies of the dielectric permittivity and loss tangent of the nanocomposites are measured and the results suggest that the introduced BT phase and interface areas contribute to the improvement of the dielectric responses of the nanocomposites. In addition, the XRD patterns indicate that the incorporation of ceramic fillers decreases the crystallite size and increases the crystallinity of the polymer matrix. The DSC result shows the shift of the crystallization temperature of the polymer matrix. Furthermore, the dielectric displacement and energy density of the nanocomposites are significantly enhanced due to the introduced ceramic phase, improved polymer matrix, and increased interface areas. The results of this work suggest that the incorporation of ceramic fillers has positive influences on the nanocomposites: the ceramic phase, interface areas, and the improvement of the polarization of the polymer matrix contribute to the enhancement of the dielectric responses and energy storage properties.

Effect of filler concentration on dielectric properties of RTV silicone rubber / TiO$_2$ Nanocomposite has been studied by Madidi (2013). In this study, it is observed that a better dispersion can improve the electrical properties of the nanocomposite. The introduction of TiO$_2$ increases the permittivity of the polymer composite mainly due to the influence of filler permittivity. The highest relative permittivity in the nanocomposites with TiO2 is observed at the highest filler concentration of 20%. An increase in the nanofillers concentration in RTV-SR composite has resulted in an increase in the number of nanoparticles and thus to an increase in the effective permittivity. As a result, increasing the nanofiller concentration in the RTV silicone rubber increases its permittivity.
All these studies prove that polymer nanocomposites have more advantages than the conventional micro sized fillers.

1.4.4 Studies on Silicone Rubber Nanocomposites

A Study on the insulation properties of RTV silicone rubber SiO$_2$ nanocomposites by Cai Dengke (2004) shows an improved performance to RTV SR in the mechanical and thermal stability. It is also suggested that SiO$_2$ prepared by sol – gel method is more suitable for dispersion with respect to RTV SR coatings.

Inorganic fillers added to silicone rubber dielectrics, enhance their properties to make them useful materials for outdoor high voltage insulation applications (Cherney, 2005). Fillers such as barium titanate contribute to increasing the relative permittivity of silicone composites and when used as a housing material for outdoor insulators, the surface stress is significantly reduced, while other fillers, such as antimony doped zinc oxide, contribute to electrical conductivity achieving a similar result thereby preventing partial discharge, corona discharge or dry band arcing on the surface of the insulation. Other fillers such as silica and aluminum trihydrate improve the thermal conductivity of the composites and increase their resistance to erosion and that results from the heat produced in dry band arcing.

Nano-silica and micro-silica have been added to silicone rubber and an inclined plane setup is used to test samples tracking and erosion resistance (Meyer et al 2006). The analysis of the results indicate that the RTV silicone rubber filled with nano-silica has, in comparison with micro-silica filled RTV SR, higher tracking and erosion resistance, lower roughness and slightly lower hydrophobicity, at the concentrations tested. In comparison with micro-silica, the addition of nano-silica into RTV SR has caused a reduction of the surface roughness and is an indication that less contamination
accumulation is expected, when the material is exposed to outdoor environments.

El-Hag et al (2006) in their study on the Erosion Resistance of Nano-filled Silicone Rubber have found that the weight loss assessments using IPT test results confirm that the nano-filled SR composites depict significant resistance to erosion compared to micro-filled SR. Further, it is reported that no significant improvement in terms of thermal conductivity is found between nano filled and unfilled SR. As far as the surface behaviour, the formation of silica like layer helps to resist the further degradation of SR in nanofilled samples due to the nature of the strong bonding between nano particles and rubber. However, this surface behaviour is only a characteristic of nano filled composites by virtue of their size, distribution and interface formation.

Ramirez et al (2008a) have shown that the surfactant greatly improves the dispersion of nano-sized particles, yielding nanocomposites that are more homogeneous, with improved resistance to heat ablation. The surfactant appears to be beneficial to the dispersion, as long as the surface covered by the surfactant is lower than the BET surface area of the fillers. Fumed silica is shown to impart greater heat ablation resistance than either natural silica or alumina. There is no big difference in the erosion resistance of natural silica- or alumina-filled compositions. The ablation observed on nano silica-filled specimens suggests that the silica accumulated at the surface forms a heat-resistant barrier preventing further erosion of the underlying silicone rubber. This phenomenon is not observed in the alumina filled specimens. The application of inorganic nanofiller and microfiller with commercial surfactant to silicone rubber imparts improved erosion resistance to dry band arcing to the composite (Isaias Ramirez et al. 2009). This improved resistance is demonstrated by laser ablation, incline plane, and salt
fog tests. It has shown that the surfactant is essential for this improvement otherwise, no improvement is evident.

Ramirez et al (2009a) have shown that silanol groups play an important role in the properties of nanofilled silicone composites. The influence of the concentration of silanol groups on erosion resistance and thermal stability was demonstrated. The thermal stability of the nanocomposite is weakened as the number of silanol groups on the silica surface is reduced through thermal treatment. The resistance to ablation under laser heating is compared using 14 and 28 pph of surfactant, and a lower eroded mass is observed at the higher surfactant concentration. The results obtained demonstrate that modest (14 – 28 pph) surfactant concentrations do not affect the tensile properties and the hardness of the filled samples significantly. However, excessive amounts of surfactant (100 pph) have a negative impact on the mechanical properties.

Silicone rubbers composed of diverse vinyl content silicone gums blending are prepared and their mechanical properties are studied by Qiang Xu et al (2010). The results show that the silicone rubber from gums with diverse vinyl content blending, has higher tensile modulus and higher tearing strength than that the single 0.16% vinyl molar content. For gums with less vinyl content blending with 0.30%, the Tg increases with the increment of vinyl content of silicone gums. And the rubber composed of less vinyl content gums blending with more vinyl content gums has better flexibility at low temperature. The storage modulus and loss modulus decrease with the increment of temperature. The 0.04% vinyl content gums blending with the 0.3% vinyl content gums have larger storage modulus than that from single 0.16% vinyl content gums.

Erosion resistance performance of the unfilled and nano-alumina filled composites have been compared using an inclined plane tracking and
erosion resistance test (Venkatesulu et al, 2010a). From the obtained results, it can be stated that 4% by wt nano alumina composite erosion performance is equivalent to the 30% by wt ATH microcomposite which is again a function of the filler distribution. Physical studies on the degraded areas reveal that thermal degradation due to discharges on the nanocomposite leads to the formation of a unique honey comb type structure, whereas a lump type of structure is observed on the microcomposite, which can be attributed to the better bonding between the filler and the SR matrix. The superior erosion performance of the nanocomposite is attributed to its better thermal stability.

The analysis of all the results reinforces the idea that the nanoparticles interact with the host polymer and thereby play a role in the final erosion performance of the SR nanocomposite. The ratio of the r.m.s to average leakage current appears to be a good indicator of the degradation state as well as the performance of the sample. Use of lower loadings of filler as in the case of the nanocomposite can lead to better flexibility, ease of processing during the product manufacturing and at the same time better electrical performance.

Joseph Vimal Vas et al (2010) have studied the influence of DC voltages on silicone rubber nanocomposites and it is reported that polymeric silicone rubber insulators perform better under negative DC, when compared to positive dc. Loading the silicone rubber insulator with fillers can improve the performance in the case of negative dc. Moderate filler loading of micron fillers, is not able to achieve properties similar to unfilled samples in the case of positive DC and hence, higher filler loadings are required to get performance comparable to the unfilled samples. Low concentration of nano fillers performs better than large loadings of ATH even under positive dc conditions. Hence, they prove that the addition of nano fillers is more advantageous and a small percentage loading can give appreciable results.
when compared to high micro filler levels, without compromising on the flexibility of the sample. The increase in eroded mass in positive dc can be attributed to increase in surface conductivity due to the electrolysis and subsequent larger leakage current values leading to higher energy dissipation on samples.

Venkatesulu & Thomas (2010b) have studied that the corona aging of nanosilica filled silicone rubber with various filler loadings of 0 %, 1 %, 2% and 3 % by weight is conducted for 25 h and 50 h. Relative corona performance has been studied in terms of the surface roughness, crack width, loss of hydrophobicity and chemical modifications. Results indicate that corona can significantly damage the polymer insulators in the long run. The corona performance has been improved significantly with the filler loading. The amount of the material eroded reduces with filler loading. This supports the fact that nanofillers influence significantly the physical degradation in terms of reduced surface erosion, less surface roughness and improved hydrophobicity. The possible reasons for the better performance of the nanocomposites are better polymer holding capability of the nanofiller, increase in barrier resistance and other interfacial effects introduced by the nanofillers. The improved performance of nanocomposite can significantly contribute to the long term reliable performance of the polymeric outdoor insulators.

Nakamura et al (2013) have dealt with the effects of addition of nano-scale silica filler on erosion and tracking resistance, arcing resistance, flame resistance, hydrophobicity, mechanical and electrical property of silicone rubber. As a result, it is elucidated that the addition of small amount of nano-silica filler is able to increase erosion and tracking resistance, arcing resistance, and flame resistance.
Madidi et al (2013) have reported that the addition of semiconducting materials with high dielectric constants, like TiO$_2$ (ε~80), to Silicone Rubber (SR) can improve its dielectric properties and electrical conductivity. The presence of these inorganic fillers allows the homogenization and distribution of the insulator electric field, thus, considerably reduces electrical stress. In this paper, a RTV SR/TiO$_2$ nanocomposite was synthesized and characterized. The influence of the filler concentration (up to 20 wt% TiO$_2$) on the dielectric behaviour of the nanocomposite over a frequency range of (40 Hz to 2 MHz) is discussed. The results show that the surfactant Triton-X-100 improves the dispersion of the nanoparticles. Furthermore, it is found that the real relative permittivity ($\varepsilon_r$), as well as the imaginary relative permittivity ($\varepsilon''$), increases as the nanofiller concentration increases.

The above literatures help to understand that the SR nanocomposites offer improved dielectric properties, and show improvements in mechanical and thermal properties. With respect to aging and erosion resistance, SR nanocomposites are more advantageous over pure SR and micro filled SR.

1.5. LACUNAE IDENTIFIED FROM LITERATURE SURVEY

Many research works have been published on the dielectric properties of the epoxy, polyethylene and polyvinyl fluoride nanocomposites. However, very few literatures are available on the dielectric properties of SR nanocomposites. The review of literature reveals that the SR nanocomposites are prepared by chemical processing, but, physical process like mastication is not discussed. In this context, this research aims at covering up this gap by preparing the samples using mastication, which is the simplest way of adding nanofillers to the SR matrix. Further, in order to have a better understanding of the influence of the nanofillers on the dielectric behaviour of SR matrix, it
is proposed to prepare six composites with different compositions and to study their dielectric characteristics.

1.6. OBJECTIVES OF THE RESEARCH

Outdoor composite polymeric insulators are emerging as promising and reliable candidates for the transmission and distribution of electrical power. Composite polymeric insulators offer attractive advantages like light weight (high strength to weight ratio), good vandalism resistance as well as easy transportation and installation. Polymer nanocomposites with a high dielectric constant have attracted much attention because of their flexibility and their ability to be easily fabricated into various shapes. Recently, various polymer nanocomposites are given much attention as new materials with superior properties in many fields. In this research, SR nanocomposites are given much importance and studied in detail.

The specific objectives of this research are:

- To develop silicone rubber based nanocomposites using nanofillers like Al₂O₃, TiO₂, BaTiO₃, MgO, ZnO and CCTO as a suitable substitute for the conventional insulating materials.

- To study the features of SR nanocomposites using scanning electron microscopy and X – Ray diffractometry.

- To analyze the performance of SR nanocomposites with respect to its dielectric, insulating, thermal and mechanical properties by investigating the influence of the filler materials, filler concentration and frequency.

- To identify a suitable nanocomposite material, for outdoor insulation as an outcome of this work and to carry out the
surface degradation analysis on the selected composite under high voltage stress to confirm its efficacy as a better insulating material for outdoor applications.

1.7. OUTLINE OF THE THESIS

The thesis is organized as follows. A detailed review on the literatures regarding the researches, which have been carried out related to this research, is presented. The primary objectives of the thesis are also discussed in depth in the first chapter.

The selection of materials and processing of rubber are expressed in the second chapter. The mastication process for the preparation of rubber nanocomposites is explained in detail here. The structural morphology and the composition of the samples are also presented in detail with the help of SEM images and XRD pattern.

The third chapter is about the study of electrical properties of the SR nanocomposites. Here, various electrical properties like AC conductivity, relative permittivity, loss tangent, dielectric strength and arc resistance are measured. The frequency dependence of AC conductivity, relative permittivity and loss tangent are analyzed in this chapter. The influence of the filler material and the filler concentration on the AC conductivity, relative permittivity, loss tangent, dielectric strength and arc resistance are also investigated in detail here.
Polymer Nanocomposites for Outdoor Applications

Selection of Materials

Polymer
Silicone

Nanofillers
Al₂O₃ BaTi CCT Mg TiO Zn

Processed by Mastication and
Characterized by XRD and SEM

Tested for the

Electrical Properties Thermal Studies Mechanical

Selection of Suitable Nanocomposite for outdoor

Efficacy of the Material further confirmed by Surface Degradation

Figure 1.2 Schematic diagram of Thesis Organization
The fourth chapter gives attention to the thermal characteristics of the SR nanocomposites. TG/DT measurements are carried out and the behaviour of different samples is compared here.

The mechanical studies like hardness and ultimate tensile strength of every sample are measured in the fifth chapter and the results are discussed.

The sixth chapter elaborates the surface degradation analysis of SR – CCTO nanocomposite. SR – CCTO nanocomposite shows a better improvement in the above properties studied. The experimental set up for surface degradation and measurement procedure are explained in this chapter. The analysis of the degraded surface was done with the help of AFM and FTIR studies.

Finally, conclusions, contributions of this research, future work directions and suggestions are presented in the seventh chapter. The findings from this research are also discussed.

The schematic diagram of thesis organization is shown in figure 1.2

1.8. SUMMARY

Polymer insulating materials are widely applied to power apparatuses and cables. Traditionally, additive agents and fillers are often used for improving insulating and mechanical properties. Recently, nanocomposite material is attracting many researchers’ attention in the field of dielectric and electrical insulation. A nanocomposite polymer is composed of nano-filler, of which diameter is as small as a few tens to a few hundreds of
nanometers, and a polymer as a matrix. The sectional area of the interface between the filler and the matrix is enormously large compared to that of conventional microcomposite materials, some improvements of insulating performance are expected to be realized by using such technology.

In the present work, silicone rubber based nanocomposites using Al₂O₃, TiO₂, BaTiO₃, MgO, ZnO and CCTO nanofillers are prepared for various weight percentages of the nanofillers. The dispersion of the nanofillers and the composition of the material are studied with the help of SEM images and XRD pattern respectively. The influences of the nanofillers, filler concentration and frequency on the dielectric properties of the material are discussed in detail. The results obtained are compared with pure SR. The effect of nanofillers on the thermal and mechanical properties of the SR matrix is also studied.

In this research, surface degradation analysis is carried out on SR – CCTO nanocomposites and they give better insulating performance than other composites. Based on the studies, it is found that SR – CCTO nanocomposites are suitable for outdoor insulation applications. This may help the industry to find a suitable remedy for the conventional composites and pave way to future researchers to carry out future work in this area.