

Chapter 1

INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Electrical insulation is an indispensable component of any electrically powered device. The performance of all electrical equipment is highly dependent on the quality of its electrical insulation. In recent years, there has been a significant increase in the demand for electrical energy. To meet ever-increasing energy demand, the electrical power infrastructure has been subjected to high levels of stresses. Electrical insulation is the backbone of all high-voltage transmission systems that transport bulk electrical power over long distances. Only naturally occurring materials (rubber, mica, cotton, paper, etc.) were used as insulating materials until 1925 [1]. Various insulating materials have grown in popularity over time. Due to their high resistance to discharge, mechanical strength, and thermal stability, ceramic and glass insulators (Figures 1.1, 1.2) have long been preferred materials for high voltage insulators. Ceramic and glass insulators have a number of disadvantages, including poor performance in contaminated environments, vulnerability to vandalism, and increased installation costs [1], [2]. Polymer insulators were introduced for the first time in 1959 as a viable alternative to ceramic and glass insulators. Polymers are known for their good dielectric properties, light weight, and ease of production [1], [2]. Tables 1.1 and 1.2 clearly indicate how polymers outperform porcelain insulators in terms of weight and cost savings while meeting all other technical specifications. Today electrical power industry utilizes a wide variety of polymeric materials (Figure 1.3). Epoxy resin, polyethylene, polypropylene, polyvinyl

chloride, polymethyl methacrylate, polycarbonate, polyamide, polyimide, and silicon rubber are commonly used polymeric electrical insulating materials.

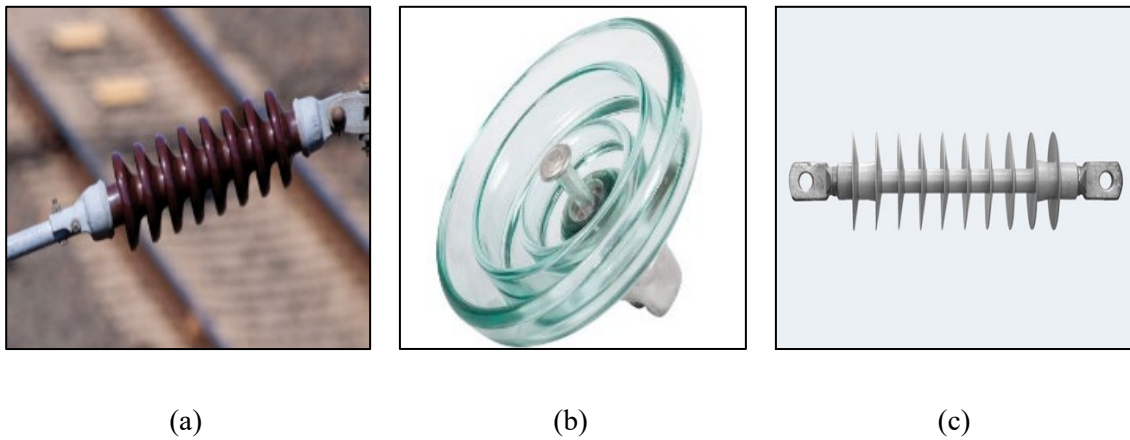


Figure 1.1 (a) Porcelain insulator, (b) glass insulator, (c) polymer insulator

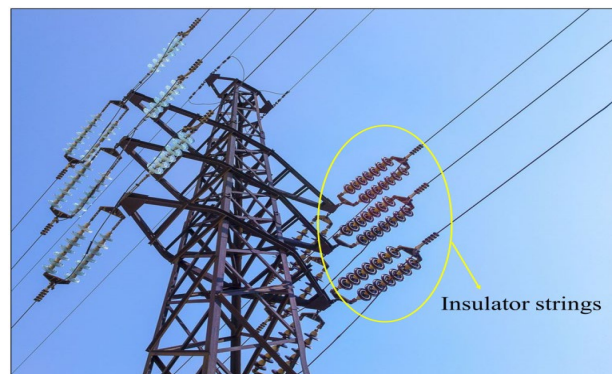


Figure 1.2 Insulator strings in transmission line

Table 1.1 Polymer insulation weight advantage over porcelain insulation (Courtesy- Hubbell Power Systems)

Product	Type	Voltage (kV)	Porcelain Weight (lbs)	Polymer Weight (lbs)	Percent Weight Reduction
Insulator	Distribution	15	9.5	2.4	74.7 %
Arrester	Distribution	15	6.0	3.8	36.7 %
Post Insulator	Transmission	69	82.5	27.2	67.0 %
Suspension Insulator	Transmission	138	119.0	8.0	93.2 %
Intermediate Arrester	Substation	69	124.0	28.0	77.4 %
Station arrester	Substation	138	280.0	98.9	64.7 %

Table 1.2 Comparison between porcelain and polymer for 10Miles, 345 kV, 250 Strings of Insulators (Courtesy- Hubbell Power Systems)

Sr. No.	Operations	Porcelain	Polymer	Saving	
1	Storage space at receiving point	580 sq. ft.	100 sq. ft.	480 sq. ft.	\$ 60.00
2	Off-load, re-load at receiving point	10 man-hrs	2 man-hrs	8 man-hrs	\$120.00
3	Breakage - off-loading, storage, reload	1 percent	0 percent	1 percent	\$517.50
4	Truck - receiving point to tower sites	1.00/cwt	50/cwt	\$589.50	\$589.50
5	Off load at tower site	5 man-hrs	1 man-hr	4 man-hrs	\$60.00
6	Unpack at tower site	50 crates/hour, 25 man-hrs	50 insulators/hour , 5 man-hrs	20 man-hrs	\$300.00
7	Breakage - off-loading through string assembly & cleaning	1 percent	0 percent	1 percent	\$517.50
8	Assemble strings, attach blocks	40 man-hrs	8 man-hrs	32 man-hrs	\$480.00
9	Clean insulators	10 min./string	3 min./string	29 man-hrs	\$435.00
10	Lift string into place (2 men)	5 min./string	2 min./string	25 man-hrs	\$375.00
11	Install & connect to tower (2 men)	5 min./string	2 min./string	25 man-hrs	\$375.00
12	Breakage - lifting & installation	0.5 percent	0 percent	0.5 percent	\$258.75
13	Clean up packaging materials at jobsite	6 man-hrs	1.5 man-hrs	4.5 man-hrs	\$67.50

High-voltage direct current (HVDC) and High Voltage Alternating Current (HVAC) systems are two of the most prevalent applications for polymeric insulation. HVDC (0-1100 kV) is utilized in both energy-related (cable, capacitor, line insulators, bushings, converter, etc.) and non-energy-related applications (X-ray machines, electron microscopy, etc.). Polymeric materials displayed good dielectric performance in HVAC systems. Their broad use in HVDC systems, on the other hand, is constrained due to the accumulation of space charges. Space charge is a significant contributor to electric field

distortion and the acceleration of aging. Apart from the space charge, polymers have a narrow service temperature range, inadequate stiffness, and low thermal stability. In order to improve the thermo-mechanical properties of polymers, a predetermined percentage of inorganic oxide fillers are introduced into the host polymers. When the desired features of individual constituents are combined, composites are expected to exhibit material properties that are distinct and superior to those of their constituents. In contrast, composites formed with conventional micro-sized fillers are seen to improve thermo-mechanical properties at the expense of deteriorating electrical properties. Additionally, the production of composites using micron-sized fillers requires a high loading to provide a marginal improvement in the desired property. The advent of polymer nanocomposites (PNCs) has created new avenues of exploration. The sections that follow provide a thorough survey of the literature on polymer nanocomposites research and development.

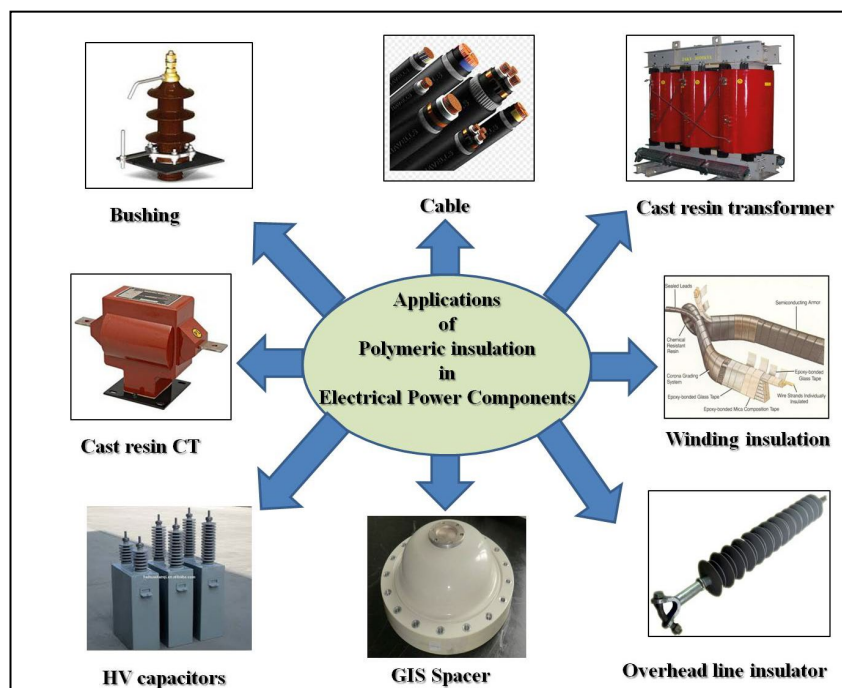


Figure 1.3 Schematic showing various applications of polymeric insulation in electrical power components

1.2 LITERATURE SURVEY

Polymer nanocomposites (PNCs) are a novel class of materials in which a small quantity of nanofillers (with size less than 100 nm at least in one dimension) is homogeneously dispersed in the polymer matrix. Polymers incorporated with a small quantity of nanofillers undergo a dramatic change in material characteristics as a result of the enormous increase in the interfacial region. Figure 1.4 demonstrates how a reduction in particle size leads to a massive increase in the interfacial area. Following Lewis' pioneering work [3], the field of nanocomposites has seen an upsurge of research activity. The following sub-sections cover the substantial literature survey focused on the synthesis and characterization of dielectric polymer nanocomposites.

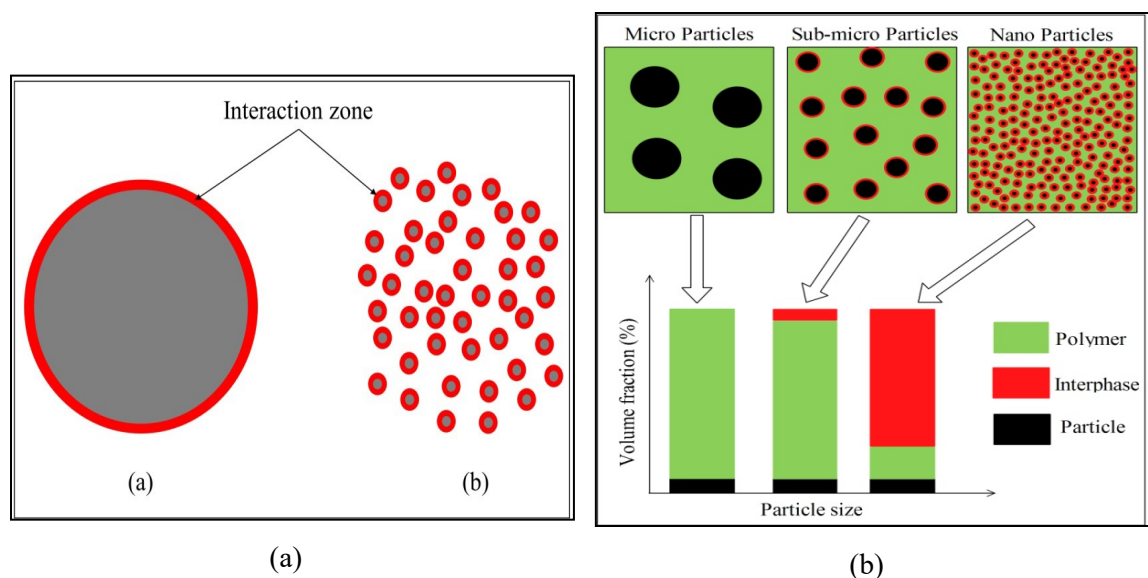


Figure 1.4 Schematic showing the effect of particle size on interfacial region

1.2.1 Synthesis of polymer nanocomposites (PNC)

There are several difficulties associated with the synthesis of nanocomposites (NCs). Nanoparticles tend to agglomerate due to their high specific surface area and hydrophilic nature. It is critical to achieve a homogeneous dispersion of nanoparticles

within the polymer matrix to exploit the potential of PNCs. Furthermore, inherent inorganic oxide fillers are incompatible with organic polymers. Thus, inorganic fillers are surface-functionalized with a suitable surfactant to enhance their dispersion and bind them with the host polymer. The surfactant acts as a chemical bridge between the particle surface and the base polymer. Effective coupling occurs when the surfactant's head interacts with the surface of the particle, and the functional group at the surfactant's tail forms a bond with the base polymer during curing. The chemical process through which typical nanofillers are surface-functionalized has been reported in published studies [4]–[6].

Numerous techniques for synthesizing PNCs have evolved over the years. The intercalation method, in-situ polymerization, melt blending, and sol-gel methods are all frequently used techniques for the synthesis of NCs [4]–[8]. The method of intercalation is used to create polymer-layered silicate nanocomposites. This procedure entails swelling the layered silicate in a suitable solvent and then combining it with the soluble polymer. Permeation of the monomer solution into the silicate galleries is permitted. After the solvent is removed and the polymerization process is completed, silicate layers sandwich the polymer to create a multi-layered structure. The technique of in-situ polymerization is primarily used to fabricate thermoset polymer nanocomposites. This method begins by directly incorporating nanoparticles into monomers. After filler particles have been evenly distributed throughout the polymer matrix, a curing agent is added to initiate the polymerization process. Ultrasonication is another viable method for the fabrication of thermoset polymer-based nanocomposites. Ultrasonication is a process that uses sound energy to disperse agglomerates through cavitation and expansion. Nanofillers are incorporated directly into polymers or via a solvent. After removing the solvent from the mixture, the curing process is initiated. For the

processing of thermoplastic nanocomposites, the melt blending technique is used. Melt blending is the process of dispersing reinforcement in molten polymer to create composites. Metal oxide-based nanostructures, such as fibers, thin films, and fine powders, are synthesized using the sol-gel technique. The metal hydroxide solution is generated by hydrolysis of the metal precursor. As a result of the condensation process, three-dimensional gels are formed. Finally, the gel is heated to form various nanostructures, including high-density thin films, xerogels, and aerogels.

The consistency of nanofiller dispersion in the host polymer has a significant effect on the property shift in PNCs. For a qualitative evaluation of filler dispersion, imaging techniques such as field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (*HRTEM*), and atomic force microscopy (AFM) may be used. Quantitative analysis of filler dispersion in the polymer matrix is required for accurate interpretation of the effects of various control parameters (e.g., processing techniques, filler concentrations, filler size, filler agglomeration, and interfacial interaction) on material properties [9]–[14].

1.2.2 Electrical Characterizations

1.2.2.1 Dielectric strength

The dielectric strength of electrically insulating material is one of the most critical electrical properties to determine. PNCs have already shown promise in a variety of scientific and engineering applications. Therefore, it is critical to investigate the breakdown characteristics of PNCs in order to determine their suitability as electrical insulators.

The AC breakdown characteristics of epoxy-based composites with SiO₂ and Al₂O₃ nano-fillers have been detailed in [15]. In comparison to neat epoxy, nano-filled

epoxy displayed lower breakdown strength. Another study on the short-term dielectric strength of epoxy/TiO₂ was carried out by Nelson et al. [16]. Short-term breakdown strength measurements were carried out under DC conditions with a ramp rate of 500 V/sec. They observed a decrease in the breakdown strength of micro composites with an increase in filler loading. However, the addition of nanoparticles resulted in a dielectric strength that was comparable to that of pure epoxy. Roy et al. [17] observed improvement in DC breakdown strength of polyethylene/SiO₂ nanocomposites if nanofillers were surface-functionalized before use. Imai et al. [18] noticed a slight decrease in the breakdown strength of layered silicate and TiO₂-nanocomposites with respect to neat polymer. Li et al. [19] describe the breakdown strength of alumina-filled nanocomposites, unfilled epoxy, nano-micro-composites, and micro composites. The highest breakdown strength was observed in alumina-filled nanocomposites, and the breakdown strength of unfilled epoxy was found to be greater than in nano-micro-composites and micro composites. Shin et al. [20] measured the breakdown strength of epoxy/SiO₂ nanocomposites with different filler loadings ranging from 0.2 to 1.4 wt% and at different temperatures. Under all experimental conditions, they found an increase in the breakdown strength of nano-filled epoxy. Huang et al. [21] compared the merits of pure epoxy versus epoxy/silica nanocomposites in terms of breakdown strength (formed with and without surface-treated nanoparticles). Nanocomposites demonstrated a lower breakdown strength than pure epoxy when fillers were not surface-functionalized before usage. However, when nanocomposites were synthesized with surface-treated silica, their breakdown strength was greater than that of pure epoxy. Montanari et al. [22] investigated the breakdown properties of nanostructured epoxy-silicate insulating materials. According to their findings, the breakdown strength (i.e., Weibull scale parameter) of neat epoxy and its nanocomposites did not vary

significantly. Nonetheless, adding nanofiller to the base resin improved the Weibull shape parameters, suggesting less scatter in failure data. Ma et al. [23] investigated the breakdown strength of LDPE/TiO₂ nanocomposites with as-received, and AEAPS coated nanoparticles. The space charge and breakdown characteristics of polyethylene/silica nanocomposites were investigated by Lau et al. [24]. At various concentrations of untreated and treated nano-silica (i.e., 0 wt. %, 2 wt. %, 5 wt. %, and 10 wt. %), space charge and breakdown strength measurements were carried out. With increasing nanofiller loading, the authors observed a consistent decrease in breakdown strength. In addition, measurements of space charge in nanocomposites revealed homo polar charge formations. However, this charge was not visible in the unfilled PE. Furthermore, as the filler content increased, the magnitude of the homo-polar charge increased. Field distortion and concomitant material degradation were cited as reasons for a decrease in breakdown strength as filler content was increased. Mi et al. [25] investigated the effect of morphology and trap characteristics on DC conductivity and electrical breakdown strength in MgO/LDPE nanocomposites with varied nanofiller loadings. DC conductivity is found to be dependent on both shallow and deep traps. The density of shallow traps increases as the nanofiller loading increases, resulting in increased shallow trap-controlled hopping conductivity, whereas deep traps increase at first due to the development of isolated interfacial regions and eventually decrease due to interfacial region overlapping. Both the morphology and the depth of the traps are observed to have an effect on the DC electrical breakdown strength. Kurimoto et al. [26] analysed the impulse and AC breakdown characteristics of epoxy/TiO₂ NCs using a centrifugation technique to control the dispersion state. The breakdown strengths of nanocomposites containing micrometric agglomerates are found to be lower than those of pure epoxy resin. When agglomerates larger than 0.5 μm are removed, the

breakdown strength of the nanocomposites is found to be greater than that of the unfilled epoxy.

1.2.2.2 Complex permittivity

Dielectric permittivity is a constant proportionality that describes the relationship between the electric flux density and the electric field intensity. When a time-varying electric field is applied across a dielectric material, permittivity becomes a complex number. The real part of the relative permittivity (dielectric constant) represents the amount of energy stored in the material by the external field. On the other hand, imaginary relative permittivity describes the dielectric losses associated with the polarization and orientation of electrical dipoles. Electrical insulation in power apparatuses should be made of dielectric materials with high dielectric strength and, preferably, a low dielectric constant. Nonetheless, the choice of the dielectric constant must be prudent in order to maintain an acceptable level of uniformity in the electric field distribution, particularly in heterogeneous structures. It is desirable to have high dielectric strength in conjunction with a high dielectric constant in order to minimize the physical size of energy storage devices. Low loss tangent is a desirable property for all dielectric materials, regardless of their intended use.

Dielectric spectroscopy is widely used in material research for a variety of purposes, including deciphering the molecular structure of dielectric materials, correlating dielectric spectra with constituent interfaces in heterogeneous materials, monitoring the condition of in-service apparatus, and determining the dielectric response to varying ambient conditions. Nelson and Fothergill [27] performed dielectric spectroscopy on epoxy composites (filled with nano and micro-sized TiO_2) and concluded that dielectric response is dependent on filler size rather than filler materials. The effect of absorbed water on the dielectric properties of silica-filled epoxy

nanocomposites was studied by Zou et al. [28], [29]. Nanocomposites absorb slightly more water than unfilled epoxy, with the excess water condensing on the nanoparticles' surfaces. Zou et al. [28] developed a water shell model to characterize dielectric relaxation processes at low frequencies when nanocomposites are exposed to a humid environment. This is consistent with the results of other theoretical models [30]–[32]. Kyle et al. [33] used dielectric spectroscopic measurements to demonstrate that adding nano-silica to epoxy-silica nanocomposites increased the dielectric constant and decreased the dielectric loss. Ciuprina et al. [34] describe the dielectric spectroscopy of LDPE nanocomposites filled with SiO_2 , TiO_2 , and Al_2O_3 nanoparticles. Nanocomposites (with filler loadings up to 5 wt. %) had lower permittivity and loss tangent than neat polymers. Huang et al. [35] observed a monotonous increase in permittivity with an increase in filler loading (up to filler concentrations of 24 wt.%) in polyethylene-alumina nanocomposites. Sun et al. [36] describe the dielectric properties of epoxy loaded with silica nanoparticles. At low frequencies, nanocomposites display higher dielectric permittivity and loss factor than micro-composites. It was speculated that the contaminants from the sol-gel prepared nano-sized silica could have increased the ionic conductivity, and that led to the higher dielectric loss in nanocomposites. Frechette et al. [37] reported a decrease in real permittivity of the polymer with the addition of nanofillers (up to 2 wt. %). The permittivity increased beyond the value of the base material when the filler loading was increased. This is in line with the experimental findings of Andritsch et al. [38] for epoxy nanocomposites (with MgO and Al_2O_3 nano-fillers). The effect of water on the permittivity of nanodielectrics is studied in [39]. As the filler particle size got to be dynamically smaller, polarization properties changed, particularly with the presence of water. This is often genuine at lower frequencies where the molecular polarization of water overwhelms. The dielectric

properties of epoxy-based nanocomposites with TiO₂ and ZnO as filler materials were investigated by Singha and Thomas [40]. In the frequency range of 400 Hz to 1 MHz, they found an increase in permittivity with increased filler loading. Dielectric spectroscopic measurements on epoxy alumina nanocomposites by Maity et al. [41] show relatively lower real and imaginary parts of complex relative permittivity in nanocomposites than in neat epoxy. This peculiar behavior of NCs was attributed to the barrier effect of nano-fillers on charge transport. In addition, they observed a low-frequency dispersion (LFD) phenomenon at different temperatures (25 °C, 50 °C, 70 °C, and 90 °C). A theoretical treatment of the LFD phenomenon in terms of cooperative intra-cluster and inter-cluster charge transport is well documented in [42]. LFD phenomena were only observed in the humid atmosphere and at elevated temperatures in dielectric spectroscopic measurements performed by Patel et al. [43]. Li et al. [44] performed dielectric properties measurements on epoxy-TiO₂ nanocomposites and proposed a potential barrier model to explain their experimental findings. At a filler loading of 1 wt.%, they observed that nanocomposites have a lower dielectric constant than neat epoxy. In the low-frequency field, their measurements at room temperature revealed classical LFD and quasi-DC conduction. Mori et al. [45] conducted terahertz absorption spectroscopy to examine the intermolecular interaction between filler and polymer matrix in epoxy-based nanocomposites with and without co-addition of micro-sized fillers. When both micro-sized MgO and nano-sized SiO₂ were applied to epoxy resin, optical absorption spectra in the frequency range of 0.5 to 5 THz showed much greater absorption than predicted based on the fillers' absorption coefficient. The presence of intermolecular interaction between the filler and the polymer is responsible for the change in absorption spectra. The temperature dependent dielectric response of the LDPE/TiO₂ nanodielectric with 5 wt.% TiO₂ nanoparticles is reported in [46]. The

role of the nanofiller polymer interface in this dielectric response is discussed in light of dielectric spectroscopy results obtained at temperatures between 300 and 350°K and frequencies ranging from 10^{-2} - 10^6 Hz. Three thermally activated relaxation processes in nanodielectric were highlighted in comparison to the unfilled polymer. All of these relaxations are caused primarily by the dielectric response of the polymer-nanofiller interface region, which dominates the nanodielectric's dielectric behaviour. Rahim et al. [47] explored the role of filler calcination in the structure and dielectric properties of nanocomposites composed of polyethylene and zirconia (ZrO_2). Calcination temperatures of 600 and 900°C were used to modify the surface chemistry and structure of ZrO_2 . Additionally, calcination allowed for re-organization of the ZrO_2 nano-powder's structure. Experiments with these materials demonstrate that nanocomposites containing calcined ZrO_2 have a lower permittivity and a higher DC breakdown strength than equivalent nanocomposites containing uncalcined ZrO_2 .

1.2.2.3 Progressive erosion (Partial discharge, treeing, and tracking)

The electrode shapes in a realistic insulation system are incredibly complex. Owing to micro defects such as surface irregularity at the conductor-dielectric interface, air pockets, and conducting particles within the dielectric materials, a macroscopic uniform electric field may not be uniform at microscopic dimensions. These defects contribute to the intensification of localized stress. Partial discharge (PD) occurs at these defects as a result of local field enhancement. During PD, the bombardment and irradiation of electron ions induce a permanent change in the chemical structure of dielectric materials and the creation of eroded channels along the dielectric volume. Since the eroded channels resemble a network of tree branches, this gradual erosion mechanism is known as electrical treeing. The basic process for degradation of insulation due to partial

discharges is shown in Figure 1.5. To extend the life of electrical equipment, it is critical to produce dielectric materials with high resistance to electrical discharges.

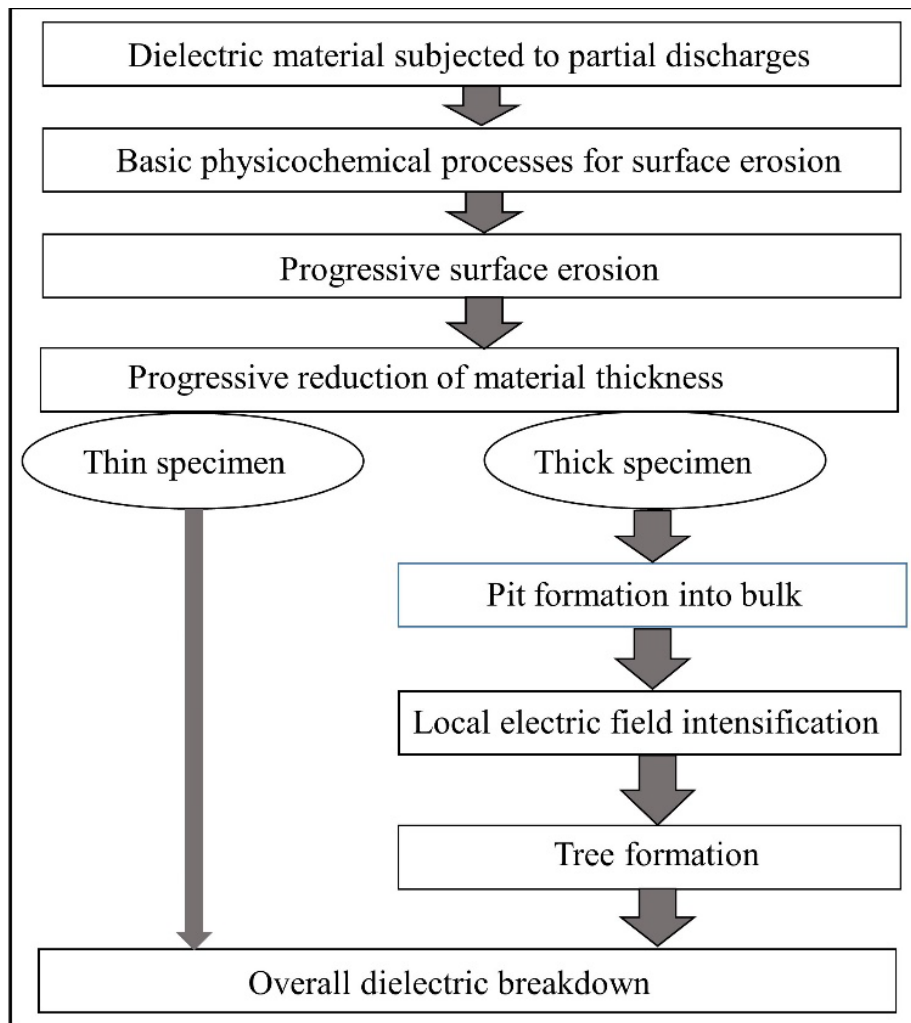


Figure 1.5 Basic process for degradation of insulation due to partial discharge

Several studies have been undertaken in recent years to assess the discharge resistance characteristics of polymer nanocomposites. The partial discharge endurance of epoxy/silica nanocomposites was investigated by Henk et al. [48]. Nanocomposites display significantly higher discharge endurance than neat epoxy. Tanaka [49] observed higher PD resistance in polyamide-based nanocomposites with respect to neat polymer. Another research group perceived a change in the surface roughness due to surface discharge [50]. However, this change was relatively lower in nanocomposites than in pure polymers. Raetzke et al. [51] found improvement in resistance to high-voltage

arcng in nanocomposites formed with hydrophilic precipitated silica fillers. Tanaka et al. [52] agreed that the PD erosion performance of epoxy could be improved by the addition of nanofillers. Fabiani et al. [53] observed improved discharge resistance characteristics at larger concentrations of nanofillers (i.e., 25 wt.%), and it was suggested that the barrier formed by nanofiller to PD slowed down pit growth and erosion of the specimen surface. A comprehensive study on degradation to surface discharges of epoxy, filled with micro-sized and nano-sized Al_2O_3 and TiO_2 fillers is reported in [6], [54]. Using experimental data (on laser surface profilometer (LSP), atomic force microscopy (AFM), and scanning electron microscopy (SEM), the authors substantiated an improved discharge resistance behavior of nanocomposites even at low filler content (i.e., 0.5 vol. %). Furthermore, in nanocomposites made with pre-processed alumina nanoparticles, the discharge resistance characteristic was improved even further. Pre-processing techniques include heating and functionalization of particles using 3-glycidoxypropyltrimethoxy-silane (GPS). Heating the nanoparticles before use was found to be advantageous because it freed up hydroxyl groups on their surfaces, allowing hydrogen bonding with the polymer to occur. Chen et al. [55] reported higher tree initiation times in nanocomposites with respect to microcomposites. Raetzke et al. [56] investigated the tree initiation activity of epoxy and epoxy nanocomposite (with 5 wt.% nanoclay layered silicate) at 600 Hz and applied voltages ranging from 2 to 14 kV. In contrast to the neat epoxy resin, the epoxy/nanoclay composite showed a one-order-of-magnitude increase in the V-t characteristics of tree initiation. The suppression of fatigue by injected electrons with nanoscale filler particles or interfaces between nanoscale filler particles and polymer matrices was credited with extending tree initiation. Improvements in partial discharge resistance, thermal and mechanical properties of polyimide nanocomposites were stated by Irwin et al. [57].

Alapati and Thomas [58] studied treeing and associated PD characteristics in LDPE alumina nanocomposites. They observed an increase in tree inception voltage and retarded tree growth in nanocomposites with respect to that in unfilled LDPE. Through SEM studies, they demonstrated an increase in lamellae packing in LDPE nanocomposites. Further, PD measurements indicated a significantly lower PD pulse/cycle during tree growth in LDPE nanocomposites than in unfilled LDPE. Pandey and Gupta [59] used the electroluminescence (EL) technique to investigate electrical treeing phenomena in epoxy alumina nanocomposites. Numerous experiments were conducted in their studies to determine a correlation between space charge and material degradation. The results of an in-depth analysis of EL signatures revealed a positive correlation between space charge and tree initiation. The presence of nanofiller in base resin inhibits tree initiation and axial progression, as confirmed by EL data and microscopic images. The effect of temperature on tree propagation and the phase resolved partial discharge (PRPD) pattern in an epoxy/silica nanocomposite are discussed in [60]. At elevated temperatures, the nanoparticle effect on trees is thought to be more likely than at room temperature. When the tree began to propagate, the PRPD pattern became turtle-wing-like regardless of the nanoparticle concentration or temperature. Chandrasekar et al. [61] investigated the growth of electrical trees on silica-nanostructured XLPE specimens, while also recording the time behavior of partial discharges. Clustering analysis of PD signals using the time-frequency decomposition (T-F map) reveals the existence of distinct signal clusters that evolve over time until breakdown occurs. Major research groups' findings indicate that nano-filled polymers are substantially more resistant to discharges than neat polymers and micro-filled polymers. Figure 1.6 illustrates graphically how nanocomposites outperform pure polymers and microcomposites in terms of discharge resistance.

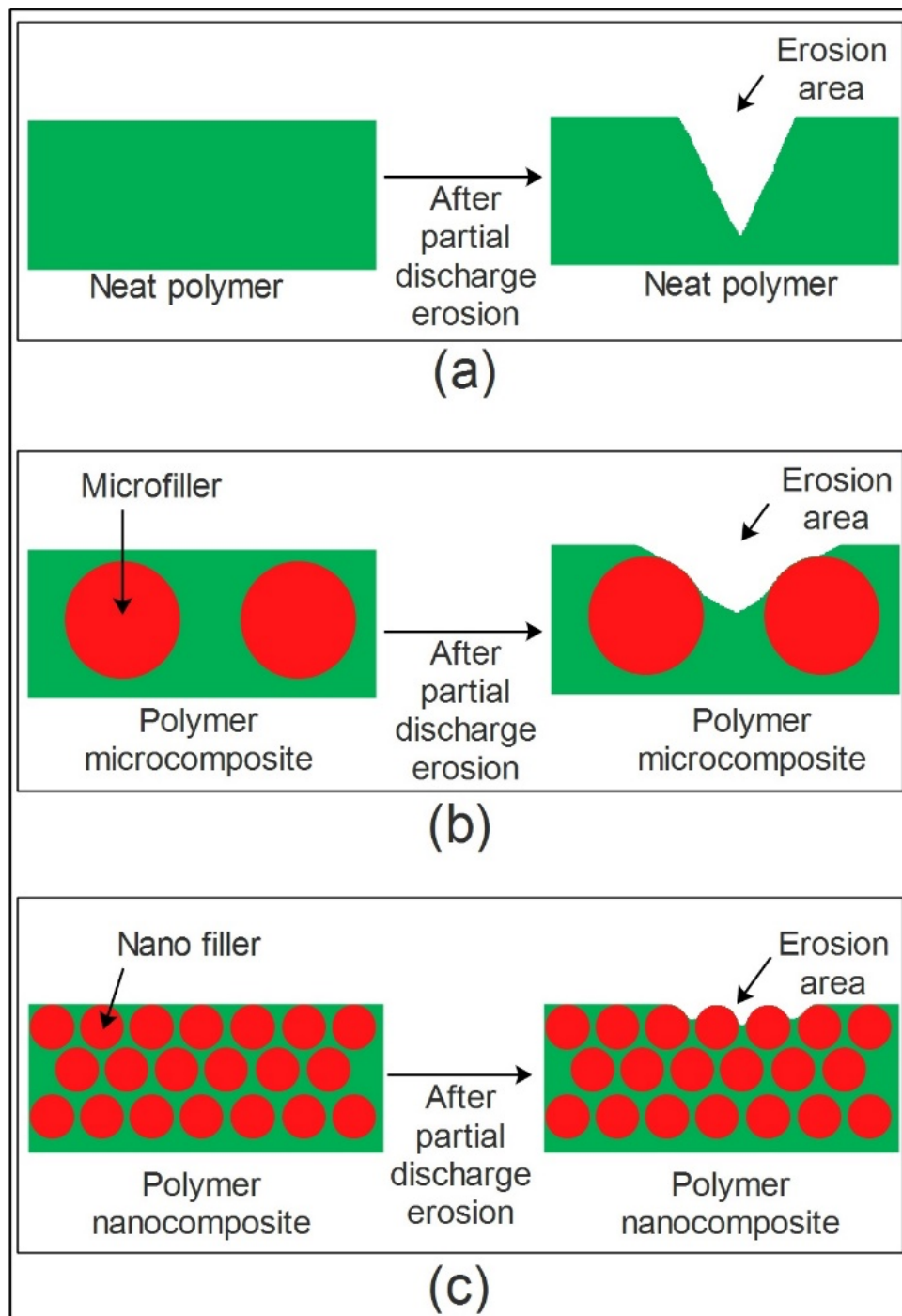


Figure 1.6 Mechanism illustrating erosion behavior in (a) neat polymer, (b) micro composites, and (c) nanocomposites

Tracking (another form of progressive erosion) is of particular interest to outdoor insulators working in polluted environments. Tracking is a surface erosion phenomenon caused by spark channels and dry band arcing. Numerous experiments have been performed to boost the tracking resistance of polymers by using micro and

nanoscale reinforcements [62]–[64]. The erosion resistance of silicone nanocomposite insulation was investigated by Ramirez et al. [62]. It was established that by using a surfactant in the optimum amount, erosion resistance could be increased. Excess surfactant degrades the material's properties. They demonstrated by TGA measurements that nanofumed silica imparts a higher degree of heat resistance to silicone than natural nanosilica or nano alumina. They asserted that silanol group concentrations are critical in improving the properties of silicone nanocomposites and that reducing the silanol group concentration during heat treatment had detrimental effects on erosion resistance. Venkatesulu et al. [63] investigated the erosion activity of silicone rubber nanocomposites at various nano-alumina concentrations. They found equivalence between the erosion characteristics of nanocomposites containing 4 wt.% nano alumina and microcomposites containing 30 wt.% ATH through an inclined plane (IP) test and other characterizations (SEM, EDAX, FTIR, and TGA). Ladeira et al. [64] compared the tracking resistance of HDPE/TiO₂ nanocomposites before and after UV aging to that of unfilled HDPE. While tracking resistance decreased with UV aging, nanocomposites exhibited greater stability and a lower loss of tracking resistance than unfilled HDPE.

1.2.3 Mechanical properties

In operation, dielectric materials are subjected to various mechanical loads, including axial, radial, compressive, bending, and vibration. Internal stresses are also created by external loads such as conductor thermal expansion and electromagnetic forces (static, harmonic, and transient). The cost-effective design of power apparatus and systems puts a premium on developing high-performance materials capable of withstanding increased electromechanical stresses. As a result, mechanical strength is another critical factor to consider when choosing a dielectric material for electrical power components. The mechanical properties of polymeric insulating materials often fall short of those of

ceramics. Therefore, polymers are often mixed with one or more materials to improve mechanical properties (tensile strength, bending strength, compressive strength, shear strength, torsion strength, fracture resilience, creep strength, and fatigue strength).

The design of a composite frame to improve mechanical strength is not new; for example, mud walls are reinforced with clay and straw. The latest and well-known examples of composite products with enhanced mechanical properties are vulcanized rubber compounds reinforced with fibers in carbon black tires. Numerous studies suggest that adding various forms of micro and nanofillers enhances the mechanical properties of the polymer. Park et al. [65] examined the impact of incorporating micro and nanofillers on a base polymer's mechanical and electrical properties. They used DGEBA epoxy resin as the base material, Me-THPA (methyl-1, 2, 3, 6-tetrahydrophthalic anhydride) as the curing agent, silica (particle size of 3 μm) as a microfiller, and layered silicate as a nanofiller. It was observed that as the micro-silica filler content increased, the tensile and flexural strengths increased dramatically, and these properties were further improved by the addition of 0.3 wt. % nano-layered silicates. However, as micro-silica filler increased in micro composites, the ac breakdown strength decreased. Diao et al. [66] investigated the influence of SiO_2 nanoparticles on the mechanical properties of isotactic polypropylene (IPP) and ethylene-octene polyolefin copolymer (POE), as well as the impact of SiO_2 nanoparticle surface alteration on mechanical properties. They observed that nanocomposites comprised of surface-treated nanoparticles possessed increased tensile strength. Chen et al. [67] investigated the effect of boron nitride nanotubes (BNNTs) on the shear strength of polymeric materials (epoxy and poly-methyl methacrylate). The shear strengths of epoxy BNNT composites and poly-methyl methacrylate BNNT composites were estimated to be 323 MPa and 219 MPa, respectively. The BNNT is thought to form a

much stronger bond with epoxy, resulting in improved load transfer characteristics for the BNNT epoxy composites. Duan et al. [68] studied the compressive and tensile strengths of polyacrylamide (PAM) using hexagonal boron nitride (h-BN) nanosheets. In contrast to PAM, the compressive and tensile strengths of the PAM/h-BN nanocomposite have been increased. The effect of clay on the fracture and tensile strength of epoxy was investigated by Wang et al. [69]. They observed that the epoxy/clay nanocomposite had a higher fracture and tensile strength than pure epoxy. This improvement could be attributed to the establishment of an interpenetrating network (IPN) structure within the confines of the epoxy material. Significant research has been conducted in recent years on nanocomposites containing carbon nanomaterials (CNMs) such as carbon nanotubes and graphene.

1.2.4 Thermal conductivity

Heat is generated in electrical equipment by various types of losses, including resistive losses in the winding, magnetic losses in the core, polarization and conduction losses in the insulation, and friction losses in moving parts. Thermal management in electrical equipment has become challenging as a result of compact designs and increased power density. Temperature rise caused by inadequate thermal design decreases the equipment's load-bearing capability and its service life. To avoid winding hotspots and progressive degradation of dielectric properties under thermal stress, it is beneficial to use dielectric materials with enhanced thermal conductivity. Polymeric materials are well-known for their exceptional insulating properties but low thermal conductivity (i.e., from 0.1 to 0.2 Wm⁻¹K⁻¹). Numerous experiments have been performed in the past to enhance polymers' thermal conductivity. This segment highlights studies on the enhancement of thermal conductivity in pure polymers and polymer-based composites.

Shen et al. [70] utilized a two-stage heating and mechanical stretching technique to fabricate polyethylene nanofibers. The thermal conductivity of polyethylene nanofiber was determined to be $104 \text{ Wm}^{-1}\text{K}^{-1}$ at a draw ratio of 400 while maintaining a 50–500 nm fiber diameter. The authors attributed the improvement to polymer chain restructuring via stretching. Canetta et al. [71] synthesized amorphous polystyrene nanofibers via electro-spinning. The thermal conductivity of polystyrene nanofibers ranges between 6.6 and $14.4 \text{ Wm}^{-1}\text{K}^{-1}$. The authors hypothesized that the enhanced thermal conductivity could be a result of molecular chain alignment. Using the extrusion and drawing technique, Xu et al. [72] fabricated polyethylene film with thermal conductivity of $62 \text{ Wm}^{-1}\text{K}^{-1}$. Kusunose et al. [73] investigated the thermal conductivity of epoxy resins reinforced with silicon nitride (Si_3N_4) nanowires. At a silicon nitride content of 60 wt.%, the composite had a thermal conductivity of $9.2 \text{ Wm}^{-1}\text{K}^{-1}$. It was asserted that nanowires, as a one-dimensional filler, create a thermally conductive path at high filler concentrations, thereby increasing the thermal conductivity of epoxy-based composites. The effect of filler size on the thermal conductivity of polymer composites was investigated by Wu et al. [74]. They used polyetherimide as the base polymer and graphite nanoplatelets ranging in size from $1 \mu\text{m}$ to $15 \mu\text{m}$ as the filler. They observed that composites made with $15 \mu\text{m}$ fillers had significantly higher thermal conductivity values than composites made with $1 \mu\text{m}$ fillers. According to the authors, as the size of the filler increases, the thermal interfacial resistance decreases significantly. Li et al. [75] investigated the effect of micro and nanoscale boron nitride on the thermal conductivity of a polyimide composite. The thermal conductivity of a polyimide composite with a micro-sized filler was greater than that of a polyimide composite with a nano-sized filler, owing to the ease with which a micro-sized filler could form a thermally conductive path. Additionally, it was

reported that combining micro and nano-sized boron nitride fillers at a weight ratio of 7:3 resulted in higher thermal conductivity values than composites synthesized solely with nano or micro-sized fillers. Fu et al. [76] studied the impact of filler surface treatment on the thermal conductivity of epoxy alumina nanocomposites. It was realized that nanocomposites formed with silane-treated nanofillers have higher thermal conductivity than those formed with untreated nanofillers. Teng et al. [77] investigated the thermal conductivity of epoxy composites containing hybrid fillers. They combined aluminum nitride and multi-walled carbon nanotubes to create the filler. The findings revealed that the thermal conductivity of an epoxy composite containing 1 wt.% multi-walled carbon nanotubes and 25 wt.% AlN is comparable to that of an epoxy composite containing 50 wt.% AlN. Choi et al. [78] studied the thermal conductivity of epoxy-based composites using Al₂O₃ and AlN hybrid fillers. They reported thermal conductivity of 3.402 Wm⁻¹K⁻¹ at a filler content of 58.4 wt.% and an Al₂O₃: AlN weight ratio of 7:3. Yuan et al. [79] investigated the effect of a hybrid filler on the thermal conductivity of an electrically insulating polymer composite. As a base material, they used phenolic formaldehyde resin (PF), followed by boron nitride (BN) flakes and tetrapod-shaped zinc oxide (T-ZnO) whiskers as fillers. The thermal conductivity of the composite was determined to be 1.96 Wm⁻¹K⁻¹, which was 6.8 times that of neat phenolic formaldehyde resin. The electrical insulation properties of the above composites were maintained up to 30 wt. % filler concentrations of T-ZnO; However, beyond that concentration, the electrical insulation properties of the PE composite deteriorated. Zhou [80] examined the effect of various coupling agents on the thermal conductivity of epoxy-aluminum composites. It was observed that the composites formed with surface functionalized fillers have higher thermal conductivity than composites formed with untreated fillers. Gulotty et al. [81] investigated the effect

of surface treatment on the thermal conductivity of single-wall and multi-wall carbon nanotube (CNT) polymer composites. They used carboxylic acid as a surfactant in both single and multi-wall carbon nanotubes. The results indicated that surface functionalization of multi-wall carbon nanotube composites resulted in an increase in thermal conductivity. On the other hand, surface functionalization of single-wall carbon nanotubes resulted in a decrease in the thermal conductivity of the composite. Additionally, they documented an increase in the electrical conductivity of carbon nanotube reinforced polymers. Thus, carbon nanotubes as a filler material are not recommended for increasing the thermal conductivity of insulating polymers. Pettes et al. [82] observed improved thermal conduction with three-dimensional graphene foam. Zeng et al. [83] investigated the thermal conductivity of epoxy-based composites formed with boron nitride nanosheets. They determined a thermal conductivity of $2.85 \text{ Wm}^{-1}\text{K}^{-1}$ for a 9.29 wt.% filler content. According to Zeng et al. [83], thermal conductivity was increased due to the formation of hierarchical three-dimensional structures in the epoxy matrix by the BN nanosheet and low thermal interfacial resistance.

1.3 PROBLEM FORMULATION

Historically, composite polymeric materials have demonstrated modified physical properties as a result of the blending of two constituent phases. When it comes to micro composites, conventional two-phase mixture principles appear to be sufficient to explain their response to external input. Interestingly, as the filler size is reduced to the nanometre range, nanocomposites reveal unforeseen changes in their physical properties. As a corollary, the mixing rule of two constituent phases is not applicable to nanocomposites. According to the findings of the literature review conducted in the preceding sections, polymers reinforced with nanometer-sized fillers exhibit material

properties that are distinct from those of their conventional counterparts (i.e., pure polymers and polymer composites created with micron-sized fillers). So it is plausible to relate changes in the physical properties of nanocomposites to a large number of interfaces. Additionally, it is hypothesized that the interaction of the filler and the polymer matrix at interfaces will result in a third phase (known as the interphase). The interphase may have properties that are distinct from those of the filler and host polymer. Due to the fact that interphases tend to influence the eventual properties of the nanocomposite materials, the characterization of these nanometric regions becomes unquestionably important. The state of the art falls well short of offering a mechanistic description of the interphase formation and its experimental manifestations. Further, quantitative analysis of interphase in conjunction with qualitative analysis is crucial for tailoring material properties of polymer nanocomposites. Despite much research on PNCs, we are still a long way from having a thorough understanding of interphase, including its origin, material features, and size. It is the goal of this thesis to conduct a thorough investigation of interphase in terms of its genesis, size, and associated dielectric and thermal properties. Present work is being conducted on epoxy and epoxy-based composites because they are the commonly used insulating materials for a variety of electrical applications, including bushings, GIS spacers, generator ground wall insulation systems, cast resin transformers, and printed circuit boards. Apart from dielectric attributes, investigating thermal characteristics is crucial for the careful design of epoxy-based electrical insulation systems. Thus, the primary objectives of this thesis are as follows:

- ❖ Investigate interphase formation and its role in property shift epoxy alumina nanocomposites.

- ❖ Develop a computational model and propose a method for quantifying the interphase size in epoxy alumina nanocomposites.
- ❖ Determine dielectric properties (viz. permittivity and dc conductivity) of interphase in epoxy alumina nanocomposites.
- ❖ Introduce a numerical model to determine the effective thermal conductivity of the epoxy alumina nanocomposites.
- ❖ Devise a methodology for determining the thermal conductivity of interphase in epoxy alumina nanocomposites.
- ❖ Identify optimal filler content for improved electro-thermal properties of epoxy alumina nanocomposites.

1.4 ORGANIZATION OF THESIS

The thesis is organized as follows:

Chapter 1- Provides an overview of state of the art in polymer nanocomposites.

Additionally, this chapter discusses the thesis's purpose and the rationale that led to problem formulation.

Chapter 2- Delves into the technical aspects of material synthesis, including the analysis of surface functionalization of nanofillers using FTIR spectroscopy, qualitative assessments of filler dispersion using FESEM, and quantitative analysis of nano filler dispersion. Additionally, this chapter establishes a protocol for the synthesis of nanocomposites with homogeneous nanofillers dispersion.

Chapter 3- Describes in detail various characterization strategies used in the current research.

Chapter 1

Chapter 4- Outlines a comprehensive analysis to understand interphase formation in epoxy alumina nanocomposites and its effect on the material properties and long-term performance of nanocomposites.

Chapter 5- Explores the dielectric permittivity and size of interphase in epoxy alumina nanocomposites.

Chapter 6- Estimates the dc conductivity and the thermal conductivity of interphase in epoxy alumina nanocomposites.

Chapter 7- Aims at finding the optimal filler content for largest improvement electro-thermal properties of epoxy alumina nanocomposites.

Chapter 8- Presents the consolidated findings of this research and future outlook.