DEDICATION	iii
CERTIFICATE	v
DECLARATION BY THE CANDIDATE	vii
COPYRIGHT TRANSFER CERTIFICATE	ix
Acknowledgment	xi
Table of Contents	xiii
List of Figures	xvii
List of Tables	xxiii
Preface	xxv
Chapter 1 Introduction and Literature Review	1
1.1 INTRODUCTION	
1.2 LITERATURE SURVEY	5
1.2.1 Synthesis of polymer nanocomposites (PNC)	5
1.2.2 Electrical Characterizations	7
1.2.3 Mechanical properties	
1.2.4 Thermal conductivity	20
1.3 Problem Formulation	23
1.4 Organization of Thesis	25
Chapter 2 Material Description and Sample Preparation	
2.1 Material used	
2.1.1 Host material	
2.1.2 Filler material	
2.1.3 Coupling Agent	29
2.1.4 Curing agent	
2.2 Sample Preparation	
2.2.1 Synthesis of pure epoxy samples	
2.2.2 Synthesis of nanocomposites with untreated nanofillers	
2.2.3 Synthesis of Nanocomposites with surface-treated nanoparticles	32
2.3 Dispersion of nanofillers	
2.4 Summary	39
Chapter 3 Experimental Techniques for Material Characterization	
3.1 Thermal Characterization	41
3.1.1 Thermo gravimetric analysis (TGA)	41
3.1.2 Differential scanning calorimetry (DSC)	42

## TABLE OF CONTENTS

3.1.	3 Thermal conductivity measurements	44
3.2	Electrical Characterization	45
3.2.	1 AC dielectric strength measurement	45
3.2.	2 DC conductivity	47
3.2.	3 Dielectric Spectroscopy	51
3.3	Chemical Characterization	56
3.3.	1 Fourier Transform Infrared Spectroscopy (FTIR)	56
3.4	Structural Characterization	58
3.4.	1 X-Ray Diffraction (XRD) Analysis	58
3.5	Summary	60
Chapter	Exploring the Interphase and its Impact on Electro-Thermal Properties	61
4.1	Introduction	61
4.2	Experimental	62
4.2.	1 Sample Preparation and Dispersion Analysis	62
4.2.	2 X-Ray Diffraction (XRD) Analysis	64
4.2.	3 Dielectric Properties Measurements	66
4.2.	4 Thermogravimetric analysis (TGA)	69
4.2.	5 Differential scanning calorimetry (DSC)	70
4.3	GENESIS OF INTERPHASE AND ITS RELATIONSHIP WITH MATERIAL PROPERTIES	71
4.4	Summary	83
Chapter	5 Estimating Relative Permittivity and Size of Interphase	
51		85
5.1	Introduction	85 85
5.2	Introduction Methodology	85 85 85
5.2 5.2	Introduction Methodology 1 Building model geometry and selection of unit cell	85 85 85 86
5.2 5.2 5.2. 5.2.	IntroductionMethodology1Building model geometry and selection of unit cell2Applying physics and boundary conditions	85 85 85 86 88
5.2 5.2 5.2. 5.2. 5.2.	<ul> <li>Introduction</li> <li>Methodology</li> <li>Building model geometry and selection of unit cell</li> <li>Applying physics and boundary conditions</li> <li>Assignment of material properties</li> </ul>	85 85 86 88 88
5.2 5.2 5.2. 5.2. 5.2. 5.2.	IntroductionMethodology1Building model geometry and selection of unit cell2Applying physics and boundary conditions3Assignment of material properties4Calculation of effective permittivity	85 85 86 88 88 89 89
5.2 5.2 5.2. 5.2. 5.2. 5.2. 5.2.	IntroductionMethodology1Building model geometry and selection of unit cell2Applying physics and boundary conditions3Assignment of material properties4Calculation of effective permittivityValidation of Finite Element Analysis	85 85 86 88 89 89 92
5.2 5.2 5.2. 5.2. 5.2. 5.2. 5.3 5.4	Introduction         Methodology         1       Building model geometry and selection of unit cell         2       Applying physics and boundary conditions         3       Assignment of material properties         4       Calculation of effective permittivity         Validation of Finite Element Analysis         Determination of Interphase Permittivity using Bisection Method Algorithm	85 85 86 88 89 89 92 96
5.2 5.2 5.2. 5.2. 5.2. 5.3 5.4 5.4.	Introduction         Methodology         1       Building model geometry and selection of unit cell         2       Applying physics and boundary conditions         3       Assignment of material properties         4       Calculation of effective permittivity         Validation of Finite Element Analysis         Determination of Interphase Permittivity using Bisection Method Algorithm         1       Bisection method	85 85 86 88 89 89 92 96 96
5.2 5.2 5.2. 5.2. 5.2. 5.3 5.4 5.4 5.4.	IntroductionMethodology1Building model geometry and selection of unit cell2Applying physics and boundary conditions3Assignment of material properties4Calculation of effective permittivityValidation of Finite Element AnalysisDetermination of Interphase Permittivity using Bisection Method Algorithm1Bisection method2Application of bisection method for estimation of interphase permittivity	85 85 86 88 89 92 96 96 97
5.2 5.2 5.2. 5.2. 5.2. 5.3 5.4 5.4 5.4 5.4. 5.5	IntroductionMethodology1Building model geometry and selection of unit cell2Applying physics and boundary conditions3Assignment of material properties4Calculation of effective permittivityValidation of Finite Element Analysis1Determination of Interphase Permittivity using Bisection Method Algorithm2Application of bisection method for estimation of interphase permittivityDiscussion on important findings	85 85 86 88 89 92 96 96 97 101
5.2 5.2. 5.2. 5.2. 5.2. 5.3 5.4 5.4 5.4 5.4 5.5 5.6	Introduction         Methodology         1       Building model geometry and selection of unit cell         2       Applying physics and boundary conditions         3       Assignment of material properties         4       Calculation of effective permittivity         4       Calculation of effective permittivity using Bisection Method Algorithm         1       Bisection method         2       Application of bisection method for estimation of interphase permittivity         1       Discussion on important findings         Summary       Summary	85 85 86 88 89 92 96 96 97 101 106
5.2 5.2. 5.2. 5.2. 5.3 5.4 5.4 5.4 5.4 5.5 5.6 Chapter	Introduction         Methodology         1       Building model geometry and selection of unit cell         2       Applying physics and boundary conditions         3       Assignment of material properties         4       Calculation of effective permittivity         5       Determination of Interphase Permittivity using Bisection Method Algorithm         1       Bisection method         2       Application of bisection method for estimation of interphase permittivity         1       Discussion on important findings         2       Summary         5       Estimating electrical and thermal conductivity of interphase	85 85 86 88 89 92 96 97 101 106 107
5.2 5.2. 5.2. 5.2. 5.2. 5.3 5.4 5.4 5.4 5.4 5.5 5.6 Chapter 6.1	Introduction         Methodology         1       Building model geometry and selection of unit cell         2       Applying physics and boundary conditions         3       Assignment of material properties         4       Calculation of effective permittivity         Validation of Finite Element Analysis         Determination of Interphase Permittivity using Bisection Method Algorithm         1       Bisection method         2       Application of bisection method for estimation of interphase permittivity         0       Summary         5       Estimating electrical and thermal conductivity of interphase	85 85 86 88 89 92 96 96 97 101 106 107 107
5.2 5.2. 5.2. 5.2. 5.2. 5.3 5.4 5.4 5.4 5.4 5.5 5.6 Chapter 6.1 6.2	Introduction         Methodology         Building model geometry and selection of unit cell         Applying physics and boundary conditions         Assignment of material properties         Calculation of effective permittivity         Validation of Finite Element Analysis         Determination of Interphase Permittivity using Bisection Method Algorithm         Bisection method         Application of bisection method for estimation of interphase permittivity         Summary         Estimating electrical and thermal conductivity of interphase         Introduction         Estimation of dc conductivity of interphase	85 85 86 88 89 92 96 97 101 106 107 107 108

6.2.	1	Methodology	108
6.3	Esti	imation of thermal conductivity of interphase	115
6.3.	1	Methodology	115
6.4	Res	ult and Discussion	128
6.5	Sun	nmary	132
Chapter and ther	7 Ir mal p	nterphase and its effect on optimizing filler concentrations for improve properties	d dielectric 133
7.1	Intr	oduction	133
7.2	Me	thodology	133
7.2.	1	Estimation of effective electrical conductivity	134
7.2.	2	Estimation of effective thermal conductivity	135
7.2.	3	Experimental validation	136
7.2.	4	Optimizing filler concentrations and role of interphase	137
7.3	Sun	nmary	139
Chapter	8 C	Conclusion and Future Scope	141
8.1	Sun	nmary of Important Findings	141
8.2	Futi	ure Scope	143
Referenc	es		145
A. App	endi	x: Publication in referred and peer-reviewed Journals	155

## LIST OF FIGURES

Figure 1.1	(a) Porcelain insulator, (b) glass insulator, (c) polymer insulator2
Figure 1.2	Insulator strings in transmission line2
Figure 1.3	Schematic showing various applications of polymeric insulation in
electrical p	ower components
Figure 1.4	Schematic showing the effect of particle size on interfacial region
Figure 1.5	Basic process for degradation of insulation due to partial discharge 14
Figure 1.6	Mechanism illustrating erosion behavior in (a) neat polymer, (b) micro
composites	, and (c) nanocomposites 17
Figure 2.1	Chemical structure of uncured epoxy
Figure 2.2	Epoxy resin (LY556) and hardener (HY951) supplied from Huntsman 28
Figure 2.3	Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> ) nanopowder supplied from Sigma Aldrich 29
Figure 2.4	Chemical structure of coupling agent
Figure 2.5	3-Glycidoxypropyltrimethoxysilane (GPS) supplied from Sigma Aldrich 30
Figure 2.6	Chemical structure of hardener
Figure 2.7	Schematic diagram for synthesis of epoxy alumina nanocomposite
Figure 2.8	Apparatus used for synthesis of epoxy alumina nanocomposite (a)
Weighing	machine, (b) Ultra-sonicator (c) Magnetic stirrer with hot plate, and (d)
Vacuum pu	ump
Figure 2.9	ZEISS SEM apparatus at CIF, IIT (BHU)

Figure 2.10 Schematic showing particle vol.% within sampling square of different
length
Figure 2.11 Filler particles of 50 nm diameter and with a concentration of 1 vol.% (a)
uniformly distributed (b) agglomerated
Figure 2.12 Variance ( $\sigma$ 2) vs. window length (L) for dispersion in Figures 2.11 38
Figure 3.1 TGA-50 (Shimadzu) apparatus at CIF, IIT (BHU) 42
Figure 3.2 DSC-60 Plus (Shimadzu) apparatus at CIF, IIT (BHU)
Figure 3.3 TPS sensor sandwiched between samples
Figure 3.4 Schematic for the measurement of short term AC dielectric strength 46
Figure 3.5 Experimental setup for the measurement of AC dielectric strength
Figure 3.6 Three electrodes arrangement for measurement of DC conductivity 48
Figure 3.7 Schematics of three-electrode system for measurement of DC conductivity
Figure 3.8 Experimental Setup for the measurement of DC conductivity
Figure 3.9 Schematics of a typical polarization-depolarization current waveform 50
Figure 3.10 Polarization phenomena as a function of frequency
Figure 3.11 Experimental setup of Dielectric Spectroscopy
Figure 3.12 Dielectric sample and electrode assembly
Figure 3.13 Schematics of dielectric spectroscopic measurements
Figure 3.14 FTIR (Nicolet IS5 model) apparatus at CIF, IIT (BHU) 58

Figure 3.15 XRD (Rigaku smart lab 9kW) apparatus at CIF, IIT (BHU)60
Figure 4.1 SEM images of nanocomposites (a) with untreated nanofillers (b) with
surface treated nanofillers
Figure 4.2 Digitized images indicating center coordinates of nanoparticles (a) with
untreated nanofillers (b) with surface treated nanofillers
Figure 4.3 XRD pattern of: (a) epoxy (b) alumina nanoparticle (c) epoxy alumina
nanocomposites
Figure 4.4 Weibull probability plot for the short-term AC dielectric strength of epoxy
and nanocomposites
Figure 4.5 Polarization current at an applied electric field of 2 kV/mm
Figure 4.6 Complex relative permittivity (a) real part (εr') (b) imaginary part (εr") 68
Figure 4.7 TGA plots for epoxy and nanocomposites
Figure 4.8 DSC graph of Nanocomposites
Figure 4.9 Flow diagram on curing process of epoxy resin
Figure 4.10 FTIR spectra (a) uncured epoxy (b) hardener (c) cured epoxy74
Figure 4.11 Chemical structure and reactive functional groups of GPS
Figure 4.12 Schematic diagram to illustrate surface functionalization of alumina
nanoparticles
Figure 4.13 FTIR spectra of (a) as received nanofillers (b) GPS (c) surface treated
nanofillers

Figure 4.14 Electric potential and field distribution with needle-plane geometry (a)
electric potential (b) electric field (c) electric field around needle tip (magnified view)81
Figure 4.15 Time to failure (in Hrs.) during voltage endurance test
Figure 4.16 Barrier effect (a) pure epoxy (b) nanocomposites with untreated
nanofillers (c) nanocomposites with surface treated nanofillers
Figure 5.1 Flow diagram for performing numerical simulation using FEM 86
Figure 5.2 Highlighted region in a simple cubic unit cell (a) nanoparticle (b) interphase
(c) base polymer
Figure 5.3 Plots from simulation studies (a) electric field intensity (E), (b)
displacement field (D)
Figure 5.4 Capacitor with two different dielectric materials
Figure 5.5 Electric field distribution in two layer dielectric system
Figure 5.6 Bisection method converge at $f(x) = 0$
Figure 5.7 Flowchart to calculate permittivity of the interphase 100
Figure 5.8 Estimated interphase permittivity and interphase thickness required get the
solution converged
Figure 5.9 Relative permittivity of nanocomposite and interphase at power frequency
50 Hz corresponding to interphase thickness 104
Figure 5.10 Interphase permittivity obtained thorough the simulation model and
measured permittivity of nanocomposites sample (a) interphase thickness of 50 nm (b)
interphase thickness of 100 nm 104

Figure 5.11 Interphase (a) highlighted region in unit cell (b) computed interphase
volume fraction for different interphase thicknesses
Figure 6.1 Flow diagram for performing finite element analysis
Figure 6.2 Randomly distributed multi-particle model
Figure 6.3 Flowchart to illustrate building of model geometry
Figure 6.4 Potential, electric field and current density distribution with the
nanodielectrics
Figure 6.5 Flowchart to estimate the dc conductivity of the interphase
Figure 6.6 Neat epoxy and nanocomposite samples for thermal conductivity
measurement
Figure 6.7 TPS 500 instrument in mechanical engineering department IIT (BHU) 117
Figure 6.8 TPS sensor sandwiched between samples
Figure 6.9 Model geometry considered for FEA and analytical study (a) 3-D view (b)
2-D view
Figure 6.10 Heat transfer through different parts of the model
Figure 6.11 Flowchart to estimate the thermal conductivity of the interphase 127
Figure 6.12 Thermal conductivity of nanocomposite sample (measured value) and
simulated value for a two-phase model
Figure 6.13 Phonon scattering phenomena in a polymer
Figure 6.14 Phonon transport phenomena through aligned polymers chains in
interphase

Figure 7.1	Epoxy matrix containing filler nanoparticles	34
Figure 7.2	Computed effective DC conductivity	35
Figure 7.3	Computed effective thermal conductivity	36
Figure 7.4	Interphase volume fraction vs. filler concentrations characteristics	at
different in	terphase thicknesses1	39

## LIST OF TABLES

Table 1.1	Polymer insulation weight advantage over porcelain insulation (Courtesy-
Hubbell Po	ower Systems)
Table 1.2	Comparison between porcelain and polymer for 10Miles, 345 kV, 250
Strings of I	nsulators (Courtesy- Hubbell Power Systems)
Table 2.1	Quantification of particle dispersion in Figure 2.11
Table 4.1	Quantification of nano-filler dispersion in nanocomposites
Table 4.2	Weibull parameters ( $\alpha$ and $\beta$ )
Table 4.3	Measured DC conductivity at an applied electric field of 2 kV/mm
Table 4.4	Measured relative permittivity and loss tangent (tanb) at 50Hz69
Table 4.5	Degradation temperature of pure epoxy and nanocomposites
Table 4.6	Glass transition temperature (Tg) data of pure epoxy and Nanocomposites 71
Table 5.1	List of symbols or notations associated with unit cell
Table 5.2	Comparison of analytical and numerically computed values
Table 5.3	List of variables used in the flowchart
Table 6.1	Experimental values of thermal conductivity of specimens
Table 6.2	Material properties of different constituents in the numerical model 120
Table 7.1	Effective dc conductivity and thermal conductivity of nanocomposites
obtained fro	om experimental and simulation studies137