

FABRICATION AND ELECTROMECHANICAL STUDIES OF KNN-POLYMER 0-3 COMPOSITES

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(Under the Faculty of Science)

By
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Under the Guidance of
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DECLARATION

I hereby declare that the work presented in the thesis entitled “**FABRICATION AND ELECTROMECHANICAL STUDIES OF KNN-POLYMER 0-3 COMPOSITES**” is based on the original work done by me under the guidance of Dr. Nijesh K. James, Assistant Professor, PG & Research Department of Physics, St. Joseph’s College (Autonomous), Devagiri, Kozhikode and has not been included in any other thesis submitted previously for the award of any degree. The contents of the thesis have undergone a plagiarism check using iThenticate software at C.H.M.K. Library, University of Calicut, and the similarity index was found within the permissible limit. I also declare that the thesis is free from AI-generated content.

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Dedicated to my Family and Teachers.



TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

LIST OF SYMBOLS

ABSTRACT

PREFACE

	Page No
Chapter 1: INTRODUCTION	1-16
1.1. Brief introduction to piezoelectricity and history of piezoelectrics	3
1.2 Definition of terms and symbols- Piezoelectric material parameters	4
1.2.1 Piezoelectric charge coefficient	4
1.2.2 Piezoelectric voltage coefficient	5
1.2.3 Dielectric constant	5
1.3 Piezoelectric materials	6
1.3.1 Ceramics	6
1.3.2 Polymers	8
1.3.3 Composites	10
1.4 Applications of piezoelectric materials	12
REFERENCES	13-16
Chapter 2: MATERIALS AND METHODS	17-33
2.1 Material selection	19
2.1.1 Environmental impact of lead-based materials	19
2.1.2 Emergence of lead-free piezoelectric materials	20
2.2 Preparation techniques: Ceramics	22
2.2.1 Conventional solid state reaction method	22
2.2.2 Sol-Gel method	23
2.2.3 Molten salt synthesis method	23
2.3.4 Hydrothermal synthesis route	24
2.3 Electroding	25
2.4 Poling	26

2.5 Characterization technique	28
2.5.1 Piezoelectric measurements	28
2.5.2 Dielectric property measurements	28
2.5.3 Structural and morphological characterization	29
2.5.4 Conclusion	29
REFERENCES	30-32
OBJECTIVES	33
Chapter 3: PREPARATION AND CHARACTERIZATION OF KNN FILLERS	35-47
3.1 Introduction to KNN fillers	37
3.1.1 Properties of KNN	38
3.2 Preparation methods for KNN ceramics	38
3.2.1 Solid state reaction method	39
3.2.2 Templated grain growth method	40
3.3 Results and Discussions	41
3.3.1 X-ray diffraction	41
3.3.2 Lotgering orientation factor (LOF)	43
3.3.3 Scanning electron microscopy	44
3.3.4 Electrical characterization	45
3.4 Conclusion	46
REFERENCES	47
Chapter 4: KNN-EPOXY COMPOSITES	49-59
4.1 Introduction	51
4.2 Materials and methods	52
4.2.1 Preparation of KNN-epoxy composites	52
4.3 Results and Discussions	53
4.4 Conclusion	57
REFERENCES	57-59
Chapter 5: KNN-NR COMPOSITES	61-76
5.1 Introduction	63
5.2 Materials and methods	65
5.2.1 Materials	65

5.2.2 Compounding: KNN-NR composite preparation	67
5.2.3 Characterization of KNN-NR composites	68
5.3 Results and Discussions	68
5.4 Conclusion	74
REFERENCES	75-76
Chapter 6. KNN-NYLON 11 COMPOSITES	77-100
6.1. Introduction	79
6.2. Chemical structure of nylon 11	81
6.3 Processing and fabrication of KNN-nylon 11 composites	82 86
6.4 Results and Discussions	86
6.4.1 Microstructure	
6.4.2 Electrical properties	87
6.4.3 Moisture absorption	96
6.5 Conclusion	97
REFERENCES	98-100
Chapter 7. PERFORMANCE ANALYSIS	101-118
7.1 Introduction	103
7.2 Arduino Uno	106
7.3 Circuit configuration	107
7.4 Microcontroller code for piezoelectric response analysis	108
7.5 Voltage output under mechanical excitation	109
7.5.1 Performance analysis of KNN ceramics	109
7.5.2 Performance analysis of KNN-polymer composites	112

7.6 Conclusion	116
REFERENCES	117-118
Chapter 8: SUMMARY AND FUTURE SCOPE	119-125
Chapter 9: RECOMMENDATIONS	127-130

LIST OF FIGURES

Figure No.	Title of Figures	Page No.
Chapter 1: INTRODUCTION		
1.1	Pictorial representation of direct and inverse piezoelectric effect	3
1.2	Perovskite with ABX_3 structure	7
1.3	Historical milestones in the development of piezoelectric materials	9
1.4	Schematic Diagram of Piezocomposites with various types of connectivity	11
Chapter 2: MATERIALS AND METHODS		
2.1	Dipole orientation in the direction of applied field	26
2.2	In-house direct poling setup	27
Chapter 3: PREPARATION AND CHARACTERIZATION OF KNN FILLERS		
3.1	Room temperature XRD pattern of (a) BNN precursor (b) NN template (c) KNN prepared by SSR and (d) KNN prepared by TGG	42
3.2	Peak splitting observed at about 45.5° for (a) KNN prepared by SSR (b) KNN prepared by TGG.	42
3.3	SEM micrographs of NN templates	44
3.4	SEM micrographs of KNN fillers prepared via solid state reaction method	44
3.5	SEM micrographs of KNN fillers prepared via templated grain growth method	44
3.6	Bar chart on piezoelectric response of KNN ceramics prepared through SSR and TGG	46
Chapter 4: KNN-EPOXY COMPOSITES		
4.1	Variations of dielectric constant of the composite as a function of TGG KNN volume percent in Epoxy matrix fitted using Yamada model	54
4.2	Variations of piezoelectric charge constant (d_{33}) of the composite fitted using Yamada model	55
4.3	Variations of piezoelectric voltage coefficient (g_{33}) of the	56

	composite as a function of KNN volume percent in epoxy matrix.	
Chapter 5: KNN-NR COMPOSITES		
5.1	Schematic of molecular chain structure of NR and effect of vulcanization to form cross linking	64
5.2	Photograph of ISNR Grade 20 natural rubber before processing	66
5.3	Vulcanized KNN-NR sheet (composite)	66
5.4	FESEM micrograph of 30% KNN-NR composite	69
5.5	Variation of d_{33} of KNN-NR composites	69
5.6	Variation of dielectric constant of KNN-NR composite	71
5.7	Variation of g_{33} of KNN-NR composites	72
5.8	Tensile strength of KNN-NR composites	73
5.9	Young's modulus of KNN-NR composites	74
Chapter 6: KNN-NYLON 11 COMPOSITES		
6.1	Brabender	83
6.2	Hydraulic press (hot press)	84
6.3	KNN-nylon 11 composite sheets and pellets	85
6.4	FESEM micrograph of 30 volume percent of KNN in nylon 11 matrix	86
6.5	FESEM micrograph showing the primary particles	87
6.6	The dielectric properties of the composites as a function of KNN volume percent.	88
6.7	Variation of dielectric loss with volume percent of KNN-nylon 11 composites at different frequencies.	89
6.8	Variation of electrical resistivity of KNN-nylon 11 composites with volume percent of KNN at different frequencies.	90
6.9	Variation of d_{33} with KNN volume percent	91
6.10	Variation of g_{33} with KNN volume percent	92
6.11	Polarization hysteresis loop for 10% KNN-nylon 11 composites	93

6.12	Polarization hysteresis loop for 20% KNN-nylon 11 composites	93
6.13	Polarization hysteresis loop for 30% KNN-nylon 11 composites	94
6.14	Polarization hysteresis loop for 40% KNN-nylon 11 composites	94
6.15	Polarization hysteresis loop for 50% KNN-nylon 11 composites	95
6.16	Moisture absorption behaviour of KNN-Nylon 11 composites	97
Chapter 7: Performance Analysis		
7.1	Pictorial representation of circuit	107
7.2	Performance analysis of SSR KNN	110
7.3	Performance analysis of TGG-KNN	111
7.4	Performance analysis of KNN-Epoxy composite	113
7.5	Performance analysis of KNN-NR composite	114
7.6	Performance analysis of KNN-nylon11 composites	115

LIST OF TABLES

Table No.	Title of Table	Page No.
Chapter 1: INTRODUCTION		
1.1	Overview of applications of piezoelectric materials	13
Chapter 2: MATERIALS AND METHODS		
2.1	Comparison of key lead-free piezoelectric ceramic systems, their structures, major properties and typical applications	21
2.2	Comparison of common synthesis methods for lead-free piezoelectric ceramics	25
Chapter 3: PREPARATION AND CHARACTERIZATION OF KNN FILLERS		
3.1	Properties of KNN fillers	38
Chapter 5: KNN-NR COMPOSITES		
5.1	Cure Characteristics of KNN-NR composites	67
Chapter 6: KNN-NYLON 11 COMPOSITES		
6.1	Nylon 11 structure	81
6.2	P-E loop characteristics of KNN-nylon11 composites	96
Chapter 7: PERFORMANCE ANALYSIS		
7.1	Connection pins	108
7.2	Comparative piezoelectric response of KNN-polymer composites	116

LIST OF TABLES

Table No.	Title of Table	Page No.
Chapter 1: INTRODUCTION		
1.1	Overview of applications of piezoelectric materials	13
Chapter 2: MATERIALS AND METHODS		
2.1	Comparison of key lead-free piezoelectric ceramic systems, their structures, major properties and typical applications	21
2.2	Comparison of common synthesis methods for lead-free piezoelectric ceramics	25
Chapter 3: PREPARATION AND CHARACTERIZATION OF KNN FILLERS		
3.1	Properties of KNN fillers	38
Chapter 5: KNN-NR COMPOSITES		
5.1	Cure Characteristics of KNN-NR composites	67
Chapter 6: KNN-NYLON 11 COMPOSITES		
6.1	Nylon 11 structure	81
6.2	P-E loop characteristics of KNN-nylon11 composites	96
Chapter 7: PERFORMANCE ANALYSIS		
7.1	Connection pins	108
7.2	Comparative piezoelectric response of KNN-polymer composites	116

LIST OF ABBREVIATIONS

DC	Direct current
PZT	Lead zirconium titanate
KNN	Potassium sodium niobate
BNT	Bismuth sodium titanate
PVDF	Polyvinylidene fluoride
PVDF-TrFE	Polyvinylidene fluoride-trifluoroethylene
BT	Barium titanate
e-waste	Electronic waste
WHO	World Health Organization
RoHS	Restriction Of Hazardous Substances
WEEE	Waste Electrical And Electronic Equipment
MPB	Morphotropic phase boundary
MEMS	Micro-electro-mechanical systems
SAW	Surface acoustic wave devices
pH	Potential of hydrogen
SSR	Solid state reaction
MMS	Molten salt synthesis
PDMS	Polydimethylsiloxane
XRD	X-Ray diffraction
SEM	Scanning electron microscopy
FESEM	Field emission scanning electron microscopy
JCPDS	Joint Committee On Powder Diffraction Standards
TGG	Templated grain growth method
LOF	Lotgering orientation factor
SSR-KNN	KNN prepared via solid state reaction method
TGG-KNN	KNN prepared via templated grain growth method
NR	Natural rubber

ISNR	Indian Standard Natural Rubber
ZnO	Zinc oxide
MBTS	Mercaptobenzothiazole Disulfide
TMTD	Tetramethylthiuram Disulfide
UTM	Universal testing machine
PA	Polyamide
P-E	Polarization-Electric field
LED	Light emitting diode
ADC	Analog to digital converter
SDG	Sustainable development goals

LIST OF SYMBOLS

D	Dielectric displacement
S	Mechanical strain
S^E	Compliance for constant electric field
ε^T	Permittivity under stress T
d_{ij}	Piezoelectric charge coefficient
g_{ij}	Piezoelectric voltage coefficient
ε₀	Permittivity of free space
ε_r	Relative dielectric constant
Tan δ	Dielectric loss tangent
λ	Wavelength
θ	Theta (Bragg angle)
F	Degree of orientation
n	Inverse of depolarization factor
φ	Volume fraction of ceramic
α	Poling ratio

FABRICATION AND ELECTROMECHANICAL STUDIES OF KNN-POLYMER 0-3 COMPOSITES

ABSTRACT

The growing demand for environmentally benign and flexible functional materials has accelerated research on lead-free piezoelectric systems for sensing and energy harvesting applications. In this context, the present thesis investigates the development, characterization, and performance evaluation of lead-free potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$, KNN) based ceramic-polymer composites, with particular emphasis on their piezoelectric and dielectric behaviour for sensor applications. The work aims to address the limitations of ceramics such as brittleness, by integrating them with suitable polymer matrices to achieve enhanced mechanical flexibility without compromising its functional performance.

Initially, phase-pure KNN fillers were synthesized using the conventional solid-state reaction method and templated grain growth method. The structural characteristics were examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM), confirming the formation of the perovskite phase with well-developed grain morphology. The dielectric and piezoelectric properties of the prepared KNN fillers were systematically evaluated to establish a baseline for composite development. Subsequently, 0–3 type KNN-based piezoelectric composites were fabricated using different polymer matrices such as, epoxy, natural rubber and nylon11, to tailor the electromechanical response. The influence of KNN filler volume fraction on microstructure, dielectric constant and piezoelectric properties were analysed. The results demonstrated enhanced electromechanical coupling and stable dielectric behaviour, highlighting the suitability of KNN–polymer composites for flexible sensor applications. A comparative performance analysis of the developed composite systems was carried out to evaluate their sensing efficiency under mechanical excitation. The composites show significant potential for integration into sensor and energy harvesting devices, and the results indicate their capability to deliver reliable functional performance under practical operating conditions. Finally, directions for further investigation have been suggested based on the outcomes of the present work.

Keywords: Lead-free piezoelectrics, Potassium sodium niobate (KNN), 0-3 Ceramic-polymer composite, Electromechanical properties, Flexible energy harvesters.



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FABRICATION AND ELECTROMECHANICAL STUDIES OF KNN-POLYMER 0-3 COMPOSITES

സംഗ്രഹം

ആധുനിക സാങ്കേതിക വിദ്യകളുടെ കണ്ടുപിടുത്തം പരിസ്ഥിതി സൗഹൃദം ആയിരിക്കണം. അതുകൊണ്ട് തന്നെ ശാസ്ത്ര ലോകം അത്തരത്തിലുള്ള കണ്ടെത്തലുകൾക്കാണ് പ്രധാനമായും മുൻഗണന നൽകുന്നത്. ഊർജ്ജാൽപാദനത്തിൽ ഗണ്യമായ വർധനവുണ്ടാക്കുന്നതിനായി ലെഡ് രഹിത ഗവേഷണങ്ങൾക്ക് വേഗതയേറിയത് എടുത്തുപറയേണ്ടകാര്യമാണ്. ഈ പശ്ചാത്തലത്തിൽ ലെഡ് രഹിത പൊട്ടാസ്യം സോഡിയം നിയോബേറ്റ് അടിസ്ഥാനപ്പെടുത്തിയ സെറാമിക് പോളിമർ കോമ്പോസിറ്റുകളുടെ വികസനത്തെയും സ്വഭാവ സവിശേഷതകളെയും പ്രകടനത്തെയും ആണ് ഈ തീസീസിലൂടെ പരിശോധിക്കുന്നത്. KNN ന്റെ പീസോ ഇലക്ട്രിക്, ഡൈ ഇലക്ട്രിക് സവിശേഷതകൾക്ക് പ്രാമുഖ്യം നൽകിക്കൊണ്ട് പുതിയ സെൻസറുകൾ വികസിപ്പിക്കാൻ ശ്രമിച്ചിട്ടുണ്ട്. Brittle സ്വഭാവമുള്ള പീസോ ഇലക്ട്രിക് സെറാമിക്സുകളുടെ പരിമിതി മറികടക്കുന്നതിനായി മികച്ച മാർഗ്ഗങ്ങൾ കണ്ടെത്തുക കൂടിയാണിവിടെ. പ്രവർത്തന മികവിൽ യാതൊരു വിധത്തിലുള്ള വിട്ടുവീഴ്ചയും നടത്താതെ അനുയോജ്യമായ പോളിമർ മാട്രിക്സുമായി ബന്ധിപ്പിച്ച് മെച്ചപ്പെട്ട യാന്ത്രിക ശേഷി കൈവരിക്കുക എന്നതും ഈ പഠനത്തിന്റെ ലക്ഷ്യമാണ്. ആദ്യഘട്ടത്തിൽ രണ്ട് രീതികൾ അനുവർത്തിച്ചുകൊണ്ടാണ് KNN ഫില്ലറുകൾ സിന്തസൈസ് ചെയ്തത്. പരമ്പരാഗത സോളിഡ് സ്റ്റേറ്റ് റിയാക്ഷൻ രീതിയും ടെംപ്ലേറ്റഡ് ഗ്രെയിൻ ഗ്രോത്ത് രീതിയും ഇതിനായി ഉപയോഗിച്ചു. ഇവയുടെ ഘടനാപരമായ സവിശേഷതകൾ വിശദമായി പരിശോധിച്ചു. സ്കാനിംഗ് ഇലക്ട്രോൺ മൈക്രോസ്കോപ്പി എക്സറെ ഡിഫ്രാക്ഷൻ, എന്നിവയും പരിശോധിച്ചവയിൽ ഉൾപ്പെടും. ഈ പരിശോധനയിലൂടെ ഗ്രെയിൻ ഘടനയോട് കൂടിയ പെറോസ്കൈറ്റ് ഘട്ടത്തിന്റെ രൂപീകരണം സ്ഥിരീകരിക്കാൻ സാധിച്ചു. തുടർന്ന് കോമ്പോസിറ്റ് വികസനത്തിന് അടിസ്ഥാനമായി തയ്യാറാക്കിയ KNN ഫില്ലറുകളുടെ ഡൈ ഇലക്ട്രിക് പീസോ ഇലക്ട്രിക് ഗുണങ്ങൾ വിലയിരുത്തി.

തുടർന്ന്, ഇലക്ട്രോ മെക്കാനിക്കൽ പ്രതികരണം നിയന്ത്രിക്കുന്നതിനായി എപ്പോക്സി നാച്ചുറൽ റബ്ബർ, നൈലോൺ,-11 എന്നീ പോളി മാട്രിസുകൾ ഉപയോഗിച്ച് 0-3 തരത്തിലുള്ള KNN ആധാരമായ പീസോ ഇലക്ട്രിക് കോംപോസിറ്റുകൾ നിർമ്മിച്ചു.

KNN ഫില്ലറിന്റെ വോൾട്ടം ഫ്രാക്ഷൻ കോംപോസിറ്റുകളുടെ സൂക്ഷ്മഘടന, ഡൈഇലക്ട്രിക് സ്ഥിരാങ്കം, പീസോഇലക്ട്രിക് ഗുണങ്ങൾ എന്നിവയിൽ ചെലുത്തുന്ന സ്വാധീനം വിശദമായി വിശകലനം ചെയ്തു. ഫലങ്ങൾ മെച്ചപ്പെട്ട ഇലക്ട്രോമെക്കാനിക്കൽ കപ്സിംഗും സ്ഥിരതയുള്ള ഡൈഇലക്ട്രിക് സ്വഭാവവും പ്രകടിപ്പിച്ചതിലൂടെ, KNN-പോളിമർ കോംപോസിറ്റുകൾ സെൻസർ പ്രയോഗങ്ങൾക്ക് അനുയോജ്യമാണെന്ന് വ്യക്തമാക്കുന്നു.

യാന്ത്രിക ഉത്തേജനത്തിന് വിധേയമാക്കിയപ്പോൾ വികസിപ്പിച്ച വിവിധ കോംപോസിറ്റ് സംവിധാനങ്ങളുടെ സെൻസിംഗ് കാര്യക്ഷമത താരതമ്യേന വിലയിരുത്തി. ഒടുവിൽ, ഈ പഠനത്തിൽ നിന്നുള്ള കണ്ടെത്തലുകളുടെ അടിസ്ഥാനത്തിൽ ഭാവിയിലെ ഗവേഷണങ്ങൾക്ക് ആവശ്യമായ ദിശകൾ നിർദ്ദേശിച്ചിരിക്കുന്നു.

പ്രധാന പദങ്ങൾ: ലെഡ്-ഫ്രീ പീസോ ഇലക്ട്രിക്, പൊട്ടാസിയം സോഡിയം നിയോബേറ്റ് (KNN), 0-3 സെറാമിക്-പോളിമർ കോംപോസിറ്റ്, ഇലക്ട്രോ മെക്കാനിക്കൽ പ്രോപ്രട്ടീസ്, ഫ്ലൂക്സിബിൾ എന്നർജി ഹാർവെസ്റ്റേഴ്സ്

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PREFACE

The rapid advancement of modern electronic and energy technologies has intensified the demand for functional materials that are efficient, sustainable, and environmentally benign. Among such materials, piezoelectric systems play a pivotal role in sensors, actuators, transducers, and energy harvesting devices. Conventional lead-based piezoelectric materials, though widely used, pose serious environmental and health concerns, thereby motivating extensive research into lead-free alternatives with comparable or superior performance.

In this context, alkali niobate-based ceramics, particularly potassium sodium niobate (KNN), have emerged as promising lead-free piezoelectric materials owing to their favourable electromechanical properties and high Curie temperature. However, the inherent brittleness of ceramic materials limits their application in flexible and wearable devices. Polymer–ceramic composites offer an effective solution by combining the functional advantages of piezoelectric ceramics with the mechanical flexibility, lightweight nature, and ease of processing of polymer matrices. In such composites, the polymer matrix provides mechanical compliance and durability, while the ceramic phase contributes functional electrical properties. By carefully selecting polymer systems and optimizing filler content and dispersion, it is possible to tailor the dielectric, piezoelectric, and mechanical properties of the composite materials.

The present thesis focusses on the preparation, structural, dielectric, and piezoelectric characterization of lead-free piezoelectric ceramics and fabrication of polymer–ceramic composite. Different polymer systems exhibit distinct dielectric responses, mechanical behaviour, and interfacial interactions with ceramic fillers. Therefore, the choice of polymer matrix plays a crucial role in determining the overall performance of polymer–ceramic composites. Investigating multiple polymer systems allows a comprehensive understanding of how polymer characteristics influence composite behaviour, particularly in terms of dielectric response, piezoelectric efficiency, and energy harvesting capability.

This thesis entitled “Fabrication and Electromechanical Properties of KNN-Polymer 0-3 Composites” is organized into eight chapters. Each chapter highlights different aspects of the work, including introduction, materials and methods, ceramic synthesis procedures, fabrication of composite systems, performance analysis and conclusions. A brief outline of each chapter is provided below.

Chapter 1 provides the foundation of the work. The Phenomenon of piezoelectricity and piezoelectric material parameters were explained. A brief description for different piezoelectric materials like, ceramics, polymers and composites were given and the history of development of each was explained. This chapter summarizes the background and significance of the study and motivation for the research.

Chapter 2 provides a general description of material selection along with the various preparation and characterization methods. The piezoelectric material for the research was selected by analysing the drawbacks of lead based ceramics. The second half of this chapter discusses about the various preparation techniques employed in the preparation of piezoelectric ceramics like solid state reaction method, sol-gel method, molten salt synthesis method etc. Also various structural and electrical characterization techniques employed for evaluating the prepared ceramics and composites are discussed.

Chapter 3 deals with the preparation and characterization of KNN ceramic samples. The influence of synthesis parameters on phase formation, crystal structure, and microstructure is systematically examined. Structural analysis using XRD and microstructural investigations using SEM are presented. The piezoelectric properties of the KNN ceramics are studied and the results are discussed.

Chapter 4 extends the study towards the development of KNN ceramics- polymer composite system with epoxy. The effect ceramic filler content on the structural, morphological, dielectric, and piezoelectric properties of the composites is investigated. Dielectric and piezoelectric studies are carried out to analyse filler dispersion and interfacial interactions between the ceramic fillers and polymer matrices.

Chapter 5 discusses the preparation and characterization of KNN–natural rubber (NR) composites. The structural, dielectric and piezoelectric properties of the composites are investigated as a function of ceramic filler content. The role of natural rubber in imparting flexibility and mechanical compliance to the composite system is discussed.

Chapter 6 focuses on the fabrication and detailed characterization of KNN–Nylon 11 polymer–ceramic composites. The influence of Nylon 11 matrix on filler dispersion,

interfacial bonding, dielectric behaviour, and piezoelectric response is analysed. The suitability of KNN–Nylon 11 composites for flexible and functional applications is evaluated.

Chapter 7 presents a comprehensive performance analysis of the developed KNN-based polymer–ceramic composites. The sensing performance, including output voltage and power generation under mechanical excitation, is examined. A comparative assessment of performance between KNN-epoxy, KNN–NR and KNN–Nylon 11 composites is provided to identify optimal material systems.

Chapter 8 summarizes the major findings and conclusions of the present work.

Chapter 9 highlights possible directions for future research, including enhancement of sensitivity, long-term stability, and integration of the composites into flexible and wearable sensor systems, are also outlined.

A comprehensive bibliography is provided at the end of each chapter.

Chapter 1

INTRODUCTION

1.1 Brief introduction to piezoelectricity and history of piezoelectrics

Piezoelectric materials are known for their ability to develop electric charge in response to applied mechanical stress and the phenomenon is known as piezoelectric effect. The discovery of this effect was made by J. and P. Curie in 1880 [1]. The observation they made was that, certain crystals like quartz, tourmaline, Rochelle salt, when subjected to mechanical stress produce electrical charge and this phenomenon they called as direct piezoelectric effect. Subsequent observations revealed that materials exhibiting direct piezoelectric effect must also behave conversely, i.e. materials strain or deform proportional to the applied electric field, which is known as the inverse piezoelectric effect [1, 2].

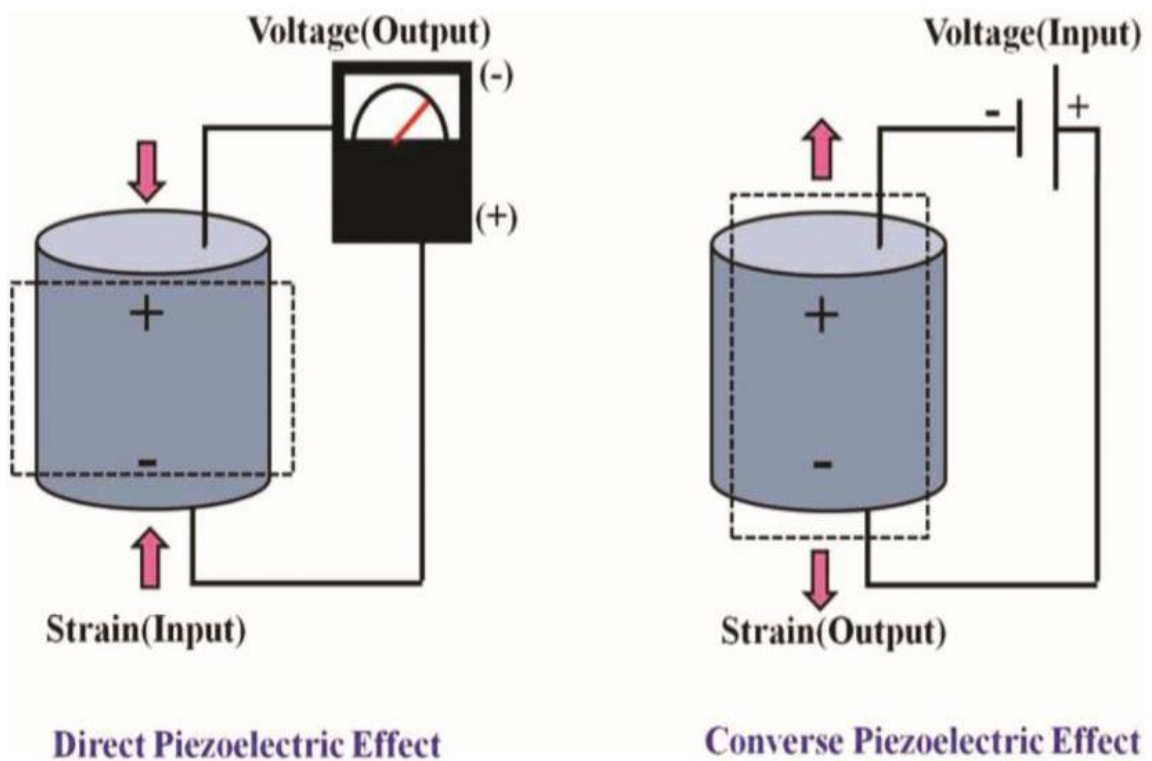


Figure 1.1: Pictorial representation of direct and inverse piezoelectric effect [3]

The phenomenon of piezoelectricity remained as a scientific curiosity until early 20th century, when practical applications of the effect began to emerge. The first significant use of piezoelectricity occurred during World War I. In 1917, French physicist Paul Langevin [4] used piezoelectric materials (quartz) to develop the first sonar device, which was used to detect submarines by measuring underwater sound waves. Throughout the early 1900s, the piezoelectric effect became the foundation for

other technologies, such as the quartz oscillator used in watches, clocks and the frequency controller in radios and other electronic device [4, 5].

1.2 Definition of terms and symbols – Piezoelectric Material Parameters

A pair of linear constitutive equations is used to describe the piezoelectric effect. The equations represent the piezoelectric phenomenon due to the relation between the elastic and electric variables. It is represented as follows [6]:

$$D = dT + \epsilon^T E \longrightarrow \text{Direct Piezoelectric effect} \quad (1.1)$$

$$S = S^E + dE \longrightarrow \text{Inverse Piezoelectric effect} \quad (1.2)$$

Where,

D: dielectric displacement

S: mechanical strain

S^E : compliance for constant dielectric field E

ϵ^T : permittivity under constant stress T

The superscripts in ϵ^T and S^E (T & E) denote the electrical and mechanical boundary conditions.

In addition, there are several important parameters used to characterize piezoelectric materials that define their electrical and mechanical behaviour [7].

1.2.1 Piezoelectric charge coefficient (d_{ij})

The piezoelectric charge coefficient d_{ij} , is defined as the strain induced in the material per unit of electric field or conversely, the electric charge generated per unit of applied mechanical stress. It measures the electromechanical coupling between mechanical and electrical properties of the piezoelectric material [7, 8]. This can be explained using the expression given in equation 1.3. The equation relates the magnitude of induced strain S due to an electric field for zero mechanical stress [9]. The units for d_{ij} are coulombs per Newton (C/N) for the direct piezoelectric effect and as meters per volt (m/V) for the inverse piezoelectric effect.

$$S = dE \quad (1.3)$$

There are different representations for piezoelectric charge coefficient d_{ij} . The most commonly used are d_{33} and d_{31} . The longitudinal piezoelectric effect is represented by d_{33} coefficient, where both the electric field and mechanical stress are applied in the same direction. In the contrary, the d_{31} coefficient corresponds to the transverse piezoelectric effect, where both the electric field and mechanical stress are applied in perpendicular directions [6].

1.2.2 Piezoelectric voltage coefficient (g_{ij})

The piezoelectric voltage coefficient g_{ij} , is defined as the electric field generated per unit of mechanical stress or conversely, the strain produced per unit of electric displacement. The efficiency of the material in converting mechanical energy to electrical energy is reflected from its g_{ij} value [6]. The units of the g_{ij} are expressed in terms of volt meter per Newton (V.m/N) or (m²/N). The g_{ij} of the material relates the induced electric field E to an external stress T as well as it relates the d_{ij} to dielectric constant at open circuit condition D= 0 as follows [1].

$$E = gT \quad (1.4)$$

$$g = \frac{d_{ij}}{\epsilon_0 \epsilon_r} \quad (1.5)$$

Where,

$\epsilon_r \longrightarrow$ relative dielectric constant

$\epsilon_0 \longrightarrow$ permittivity of free space

The representations of g_{ij} that are commonly used- g_{33} for longitudinal voltage coefficient and g_{31} for transverse voltage coefficient [10].

1.2.3 Dielectric constant (ϵ_{ij})

The relative dielectric constant, ϵ_r commonly referred to as the dielectric constant, is given by the ratio of the charge stored between two electrode plates separated by any material to the charge that would be stored under the same conditions if the plates were separated by vacuum [11].

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (1.6)$$

The parameters, d_{ij} , g_{ij} and ϵ_{ij} , collectively define the behaviour and performance of piezoelectric materials. Therefore, by optimizing these values, materials can be tailored for various technological applications such as energy harvesting, sensors, actuators, medical devices etc.

1.3 Piezoelectric Materials

1.3.1 Ceramics

Ceramics are generally composed of fine crystals which are further comprised of atoms with positive or negative electric charge. In most ceramics, these positive and negative charges are balanced, which results in zero net polarization [12]. However, due to inherent imbalance in the charge within the crystal lattice, a specific class of ceramics known as ferroelectric ceramics exhibit spontaneous polarization. This polarization does not require any external electric field, creating a permanent electric dipole moment naturally within each domain of the material. Though ferroelectric ceramics exhibit spontaneous polarization, the orientation of the polar axes is random across different domains immediately after firing [13, 14]. However, when high DC voltage is applied across the ceramics, the polar axes generated by spontaneous polarization are aligned in a uniform direction, which will be retained after the removal of the electric field. This process of aligning the polar axes through spontaneous polarization is called polarizing (poling) process. Piezoelectric ceramics are produced only when polarizing process is applied to ferroelectric ceramics [15]. The centre of the positive and negative electric charges in the piezoelectric ceramics are individually attracted or repelled, when subjected to external voltage, causing the ceramics to expand or contract [16, 17]. On the other hand, when pressure is applied to piezoelectric ceramics, it generates positive and negative electric charge opposing to the face of the piezoelectric ceramics. Therefore, piezoelectric ceramics are class of materials that utilizes polarization of ceramic crystals to enable the mutual conversion from electric energy to mechanical energy and vice versa [14].

a) Structure

Piezoelectric ceramics fall into perovskites materials which are characterized by the general formula ABX_3 , sharing the same crystal structure of calcium titanium oxide

(CaTiO_3). CaTiO_3 is a mineral which was first discovered in 1839 by Gustav Rose in the Ural Mountains of Russia and named after Russian mineralogist L. A. Perovski [18]. In the general formula ABX_3 , A and B represent positively charged ions (cations), while X is a negatively charged ion (anion). Also, atoms A are divalent and are typically larger than atoms B, which are tetravalent. Often perovskite materials are of wide variety due to the choice of anion X, which is commonly an oxide, but it can also be a halide, sulphide or nitride. An ideal perovskite structure is shown in figure 1.2, which can be visualized as a cube with large B-type cation at the centre, surrounded symmetrically by an octahedron of anions and A-type cations positioned at the cube's corners [19, 20].

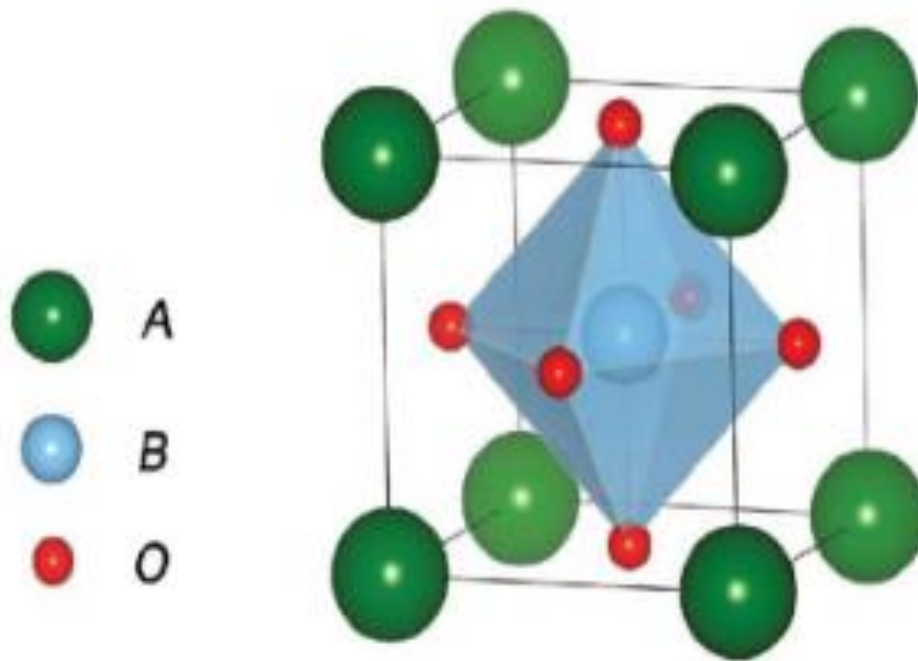


Figure 1.2: Perovskite with ABX_3 structure [21]

b) History

Among naturally occurring crystals, quartz and Rochelle salt were the earliest piezoelectric materials discovered that demonstrated direct piezoelectric effect. However, due to their relatively weak piezoelectric properties and structural limitations, these materials are limited in their practical applications [22]. In the mid of 20th century, with the discovery and development of synthetic piezoelectric ceramics, the field of piezoelectric materials took a significant leap forward. In 1942, researchers discovered that certain ferroelectric materials like barium titanate

(BaTiO₃), showed much stronger piezoelectric properties when exposed to appropriate electrical fields. This marked the beginning of the research and development of modern piezoelectric ceramics [23]. The introduction of lead zirconium titanate (PZT) in the 1950's further revolutionized the field. PZT and other lead-based ceramics emerged as the most widely used piezoelectric materials with its superior piezoelectric properties, like high electromechanical coupling coefficients and versatility in various applications [24, 25]. The tunability of PZT ceramics for specific applications allowed researchers to optimize it according to their requirements, making them a dominant material. Their engineered properties through modifications in composition and structure provided significant advantage over naturally occurring piezoelectric crystals [26, 27]. However, the dominance of lead-based ceramics, especially PZT, among piezoelectric materials raised serious environmental and health concerns, particularly with the increasing awareness of lead toxicity [27, 28]. As a result, the early 21st century saw a surge in research and development dedicated to lead-free alternatives. Historical milestones occurred in the development of piezoelectric materials are shown in figure 1.3. Ceramic materials such as potassium sodium niobate (KNN), bismuth sodium titanate (BNT) and other lead-free compositions became alternatives to lead based ceramics like PZT [29]. In conclusion, a continuous evolution from the discovery of natural piezoelectric crystals to the development of advanced synthetic ceramics, both lead-based and lead-free systems, can be observed. Advancements in the field of piezoelectric ceramics continue to play a vital role in modern technology, with future research focussing on sustainable and efficient materials for wide range of applications [25, 26].

1.3.2 Polymers

Piezoelectric ceramics are difficult to process and shape into required form due to its inherent brittleness, which limit their applications. On the other hand, polymers have become increasingly important due to their flexibility, lightweight nature and ease of processing. Some polymeric materials, similar to ceramics, exhibit piezoelectric properties by generating an electric charge in response to the applied mechanical stress. Such polymeric materials offer unique advantages such as mechanical flexibility and lower density, making them suitable for a variety of applications that require adaptable or flexible materials [30].

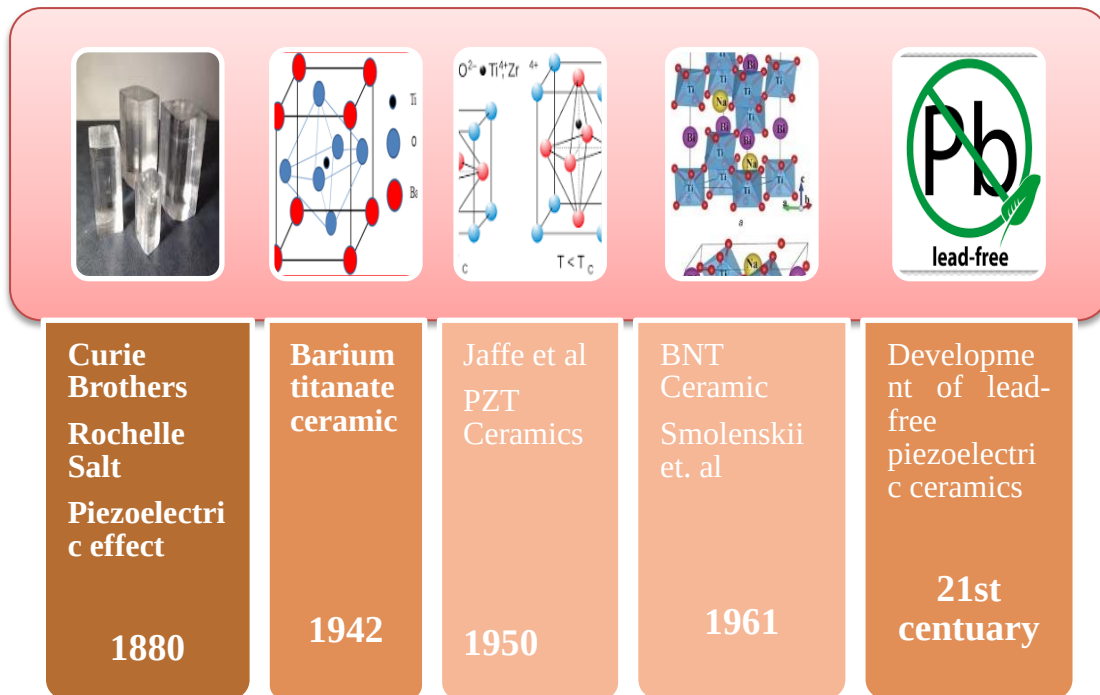


Figure 1.3: Historical milestones in the development of piezoelectric materials [20]

Compared to ceramics, properties of piezoelectric polymers are fundamentally different. In piezoelectric polymers, the orientation of molecular dipoles within polymeric chain results in piezoelectric effect [31, 32]. In its natural state the dipoles in a piezoelectric polymer are randomly aligned, resulting in no net piezoelectric effect. The piezoelectric behaviour of such polymers can be activated by subjecting them to mechanical stretching and poling, through which the dipoles can be aligned along the direction of the electric field, giving rise to piezoelectricity [33].

Piezoelectric polymers were discovered much later than piezoelectric crystals and ceramics. A ground breaking discovery was made by Kawai [34] in 1969, who observed piezoelectricity in polyvinylidene fluoride (PVDF). PVDF is a semi crystalline polymer. Kawai, in his work, demonstrated that under appropriate conditions of mechanical stretching and poling, PVDF could exhibit strong piezoelectric behaviour. This discovery paved the way for extensive research into the piezoelectric properties of polymers and its development. PVDF and copolymers of PVDF, for example- polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE), soon became the most widely studied and applied piezoelectric polymers due to their relatively high piezoelectric coefficients [35, 36]. Polymers like PVDF are flexible,

which makes them ideal for applications in sensors, actuators and wearable electronic devices [37]. In conclusion, the history of piezoelectric polymers after the discovery of PVDF has been one of rapid advancement [36].

1.3.3 Composites

Piezoelectric ceramic-polymer composites combine the desirable properties of both ceramics and composites, thus representing a unique class of materials. In this context, piezoelectric composites integrate the high piezoelectric performance of ceramics with the flexibility, low weight and processability of polymers. The development of ceramic-polymer piezocomposites has been a major focus of research due to their integrated properties which can be used for potential applications in flexible sensors, actuators, biomedical devices and energy harvesting systems [38].

Piezoelectric composites are classified based on the distribution and connectivity of ceramic-polymer phase. Connectivity of a two-phase piezoelectric composite is identified by two numbers. For example, if the polymeric phase is connected in all three-directions, then it is a 3-dimensional connectivity and if the ceramic phase is only in one-direction, then it has 1-dimensional connectivity [39, 40]. Hence the ceramic-polymer composite is designated as 1-3 composite. 10 different configurations can be used to express typical two-phase composite as shown in figure 1.4, depending on the physical connectivity of each phase. They are 0-0, 0-1, 0-2, 0-3, 1-1, 1-2, 1-3, 2-2, 2-3 and 3-3 – with the first number representing the connectivity of the active phase (ceramic phase) and the second number refers to the passive phase (polymer matrix) [39, 41, 42].

The most commonly studied configurations are the 0-3 and 1-3 connectivity types [43, 44]:

- 0-3 composites: In this configuration, ceramic particles (0-dimensional) are randomly dispersed within a polymer matrix (3-dimensional). Composite with 0-3 connectivity is relatively easy to fabricate and provides isotropic mechanical and electrical properties. However, compared to other configurations, the piezoelectric response of 0-3 composite is often lower, as the ceramic particles are not interconnected.

- 1-3 composites: In this configuration, one-dimensional ceramic fillers or rods are embedded in a three-dimensional polymer matrix. The alignment of the ceramic phase in one direction in 1-3 composite improves the piezoelectric response in that direction, making it more suitable for applications like hydrophones and transducers.

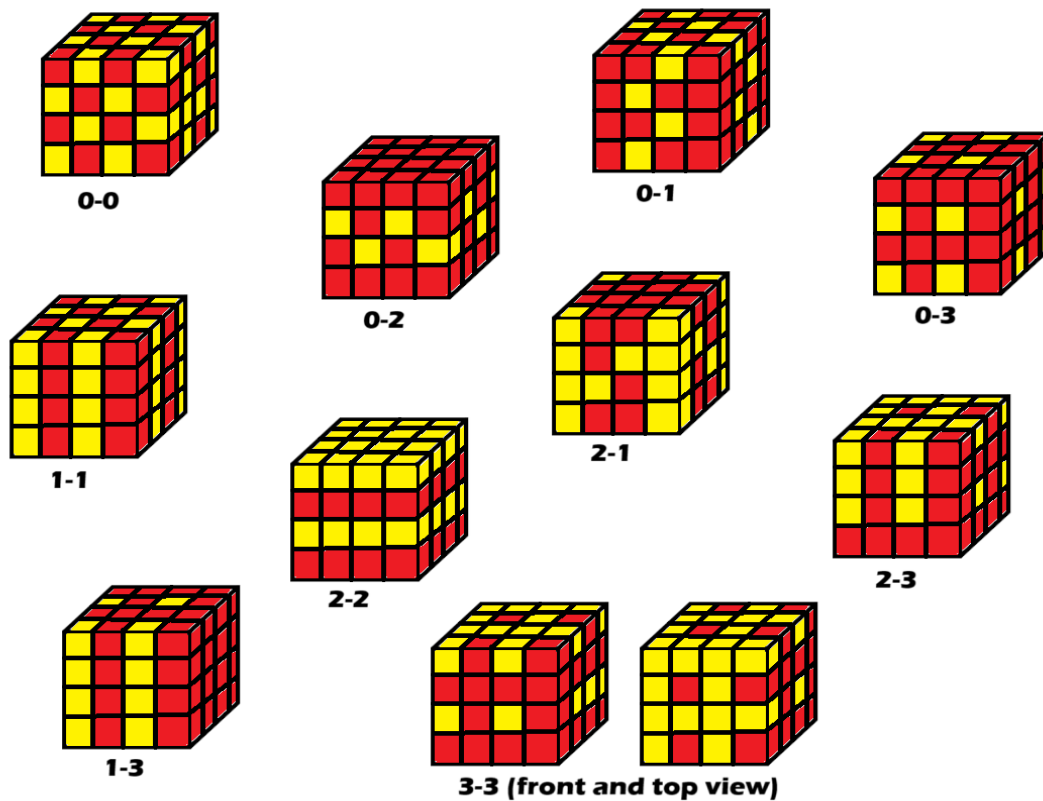


Figure 1.4: Schematic diagram of piezocomposites with various types of connectivity [41]

The concept of ceramic-polymer composite gained significant traction in the 1970's when researchers, notably Newnham et al. [41], introduced a connectivity classification system to describe the spatial distribution and interaction between the ceramic and polymer phases as discussed above. This framework of different configurations of composites enables designing of highly advanced composites in which ceramics contributes to high piezoelectric performance, while the polymer

matrix provides mechanical durability and better impedance matching. Throughout the 1980's and early 2000s, continuous advancements in composite fabrication techniques and material modelling have led to significant improvements in structural design and electromechanical performance of the composite system [43]. With growing environmental concerns over the toxicity of lead and lead-based materials, 21st century has seen researchers shifting their focus towards potassium sodium niobate (KNN), bismuth sodium titanate (BNT) and barium titanate (BT). These lead-free piezoelectric ceramics are often combined with biocompatible and biodegradable polymers for applications in biomedical devices [44]. Today, piezoelectric ceramic-polymer composites are at the forefront of innovation in self-powered electronics, wearable sensors, artificial skin, robotics and energy harvesting technologies. The transition from rigid bulk ceramics to stretchable, sustainable and multifunctional ceramic-polymer composites highlights their growing importance in next generation smart systems and environmentally conscious engineering solutions [42, 43].

1.4 Applications of piezoelectric materials

Piezoelectric materials offer a wide range of applications due to their unique ability to convert mechanical energy into electrical energy and vice versa. A concise overview of their major areas of applications is given in the table 1.1 [45].

Flexible sensors and actuators	Piezoelectric ceramic-polymer composites are both mechanically flexible and electrically active materials. The integration of ceramics into polymer matrix is particularly advantageous in wearable electronics and robotics for developing strain and pressure sensors. The developed composites can conform to complex, curved surface and maintain performance under mechanical deformation, making them ideal for applications where flexibility and durability are essential [46].
Biomedical devices	The ceramic polymer composites offers biocompatibility and flexibility, which makes them suitable for various biomedical applications, for

	example, they are employed in implantable medical devices, such as ultrasound transducers and artificial skin, where they can conform to soft tissues and provide reliable performance [47]. Additionally, these piezoelectric composites are engineered for converting mechanical energy from body movements into electrical energy by developing energy harvesting devices. This helps in potentially powering biomedical implants without the need for external power sources [48, 49].
Energy harvesting	In the realm of renewable energy technologies, piezoelectric ceramic-polymer composites are utilized in energy harvesting technologies for capturing mechanical vibrations, motion or pressure from the environment and convert them into electrical energy. Such energy harvesting devices can power small electronic devices or sensors, especially in remote or inaccessible locations where traditional power sources are impractical [46, 49].

Table 1.1: Overview of applications of piezoelectric materials

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Chapter 2

MATERIALS AND METHODS

2.1 Material Selection

2.1.1 Environmental Impact of Lead-Based Materials

Lead-based piezoelectric ceramic, such as lead zirconate titanate (PZT), has dominated industrial and research applications and is extensively used in sensors, actuators, transducers and energy harvesting devices due to its exceptional piezoelectric and dielectric properties [1]. However, lead (Pb), a well-known toxic heavy metal, poses significant risk to both human health and environment. Lead, due to its high toxicity and ability to accumulate in biological systems, can lead to neurological, renal and cardiovascular disorders [2]. Its presence in the environment poses risk to soil, air and water systems, and its disposal or recycling poses significant challenge during the electronic waste (e-waste) management. As per World Health Organization's (WHO) [3] classification of toxic chemicals, Pb finds its way in the top ten chemicals responsible for major public health concern. Consequently, the disposal of Pb containing devices has become a major environmental concern, especially those electronic devices which use lead-based ceramics. It is often seen that such devices end up in landfills or incinerating centres where toxic lead compounds get released into the environment. Additionally, lead ions, released from degraded components, are notoriously infamous for leaching into ground water resulting in its contamination of agricultural land [4].

It is needless to say that several international regulations have been put in place to mitigate these concerns, some of which are mentioned as under:

1. The Restriction of Hazardous Substances (RoHS) by European Union directive restricts the use of lead in electrical and electronic equipment to a maximum concentration of 0.1% by weight [5].
2. The Waste Electrical and Electronic Equipment (WEEE) directive promotes the recycling and recovery of e-waste, including lead-based components [6].
3. The E-Waste Management Rules (2016) in India outline similar restrictions and encourage the phasing out of hazardous substances like lead [7].

These and many other environmental and legislative checks have given much needed impetus towards the development of environmentally friendly, lead-free alternatives in piezoelectric applications at global level. A paradigm shift towards sustainable

materials is the need of the hour and is not only driven by regulatory compliance but also by the growing demand for green technology, specifically in the field of consumer electronics, biomedical devices and energy systems [8, 9]. Thus, development of lead-free piezoelectric materials has emerged as a critical research area to ensure both technological performance and environmental safety. This need of the hour to find better, sustainable and environment benign alternatives to lead-based piezoelectric ceramics forms the basis for the present study that focuses on the design, development and eventually, application of lead-free piezoelectric composites.

2.1.2 Emergence of Lead-Free Piezoelectric Materials

With focus toward finding sustainable and environmentally friendly alternatives, especially against lead-based materials which poses serious health hazards, there has been a global shift toward the development of lead-free piezoelectric materials. Potassium sodium niobate ($\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ or KNN), bismuth sodium titanate (BNT), barium titanate (BT) and their solid solutions have emerged as transformative alternatives to lead-based materials in the field of piezoelectric applications, demonstrating significant potential and promise in this domain. [10, 11].

- BaTiO₃- based materials

Barium titanate (BaTiO_3 or BT) is one of the earliest known piezoelectric ceramics. It is considered as the fundamental material in the development of lead-free piezoelectrics. Discovered in 1940s, BT was the first commercial piezoelectric ceramic and remains widely studied due to its non-toxic nature, excellent dielectric properties and ease of processing [1, 12]. Although it exhibits comparatively lower piezoelectric properties than those of lead-based material like PZT, its low environmental impact and tuneable ferroelectric behaviour makes it a strong candidate for eco-friendly applications [13].

- Bismuth-based systems

Bismuth based perovskite systems are another important class of lead-free piezoelectric materials that have attracted noteworthy attention of researchers due to their strong ferroelectricity and high Curie temperature [14]. The most prominent systems are bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$, or BNT), bismuth potassium titanate ($\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$, or BKT) and their solid solutions with other perovskites. These

materials have emerged as potential alternatives to lead zirconium titanate (PZT) in applications such as actuators, sensors and energy harvesters [11].

Material System	Structure	Key Properties	Applications
KNN-based	Perovskite	High d_{33} , MPB tunability	Sensors, actuators, harvesters
BNT-based	Perovskite	High Curie temp, solid solution friendly	Actuators, MEMS
BT-based	Perovskite	Easy processing, low coercive field	Capacitors, sensors
BiFeO₃	Multiferroic	High Curie temp, magnetic- electric coupling	Spintronics, multifunctional devices
Aurivillius Phases	Layered	Fatigue resistant, high temp stability	Non-volatile memories
LiNbO₃ / LiTaO	Single crystal	Excellent acoustic/electric properties	SAW devices, optical modulators

Table 2.1: Comparison of key lead-free piezoelectric ceramic systems, their structures, major properties and typical applications [10, 11, 15]

- $(\text{K}_{0.5}, \text{Na}_{0.5}) \text{NbO}_3$ (KNN)-based Ceramics

Among the various lead-free piezoelectric materials under research, KNN has emerged as a strong and most promising alternatives to traditional PZT. The material is known for exhibiting relatively and comparatively high piezoelectric coefficients and Curie temperature [16]. First reported in the 1950's, KNN gained renewed attention in the last two decades for its suitability in many piezoelectric applications due to its excellent ferroelectric properties and environmental sustainability. [11, 15]

In addition to KNN, BNT and BT, several other lead-free piezoelectric materials have also been developed to address the growing need for environmentally friendly alternatives to PZT. These materials vary in structure, processing complexity and performance characteristics [11, 13]. Table 2.1 gives a comparison of key lead-free piezoelectric ceramic systems, their structures, major properties and typical applications [10, 11, 15].

2.2 Preparation techniques: Ceramics

The preparation of high-performance lead-free piezoelectric ceramic fillers involves stages like, powder synthesis and calcination. The choice of preparation method greatly influences the final microstructure, density, phase purity and piezoelectric properties of the ceramics [10]. The most widely used techniques for the preparation of lead-free piezoelectric ceramics such as KNN, BNT and BT-based systems are discussed below [17]:

2.2.1 Conventional solid state reaction method

The solid-state reaction method (SSR), also known as the ceramic method, is one of the most traditional and widely used techniques for synthesizing bulk piezoelectric ceramics. The method is simple, cost-effective and scalable depending on the requirements [1, 11]. This method involves weighing of solid precursors in stoichiometric proportions which are then thoroughly mixed using ball milling or mortar and pestle to ensure homogeneity. The mixed powders are then subjected to a calcination process at elevated temperatures (typically 800-1000 °C) for several hours, resulting in solid phase diffusion and eventually, formation of desired crystalline ceramic compound [10]. However, this technique is marred with limitations which include poor control over particle size and morphology. It is also reported that, there is a risk of compositional inhomogeneity due to incomplete mixing and possible loss of volatile elements such as alkali metals during high temperature treatments [15]. Despite the limitations, the method's simplicity and ability allows to produce highly crystalline and dense piezoelectric ceramics, making it a preferred method, especially for bulk applications.

2.2.2 Sol-Gel method

The sol gel method is a low temperature, wet-chemical synthesis route widely employed for preparation of high-purity, homogeneous and nano-structured ceramic materials, including lead-free piezoelectric ceramics [10]. In this technique, metal oxides or metal salts are dissolved in a suitable solvent and hydrolysed in presence of water under acidic or basic conditions, resulting in formation of a colloidal suspension or “sol”. The resultant “sol” consists of reactive precursor species. Polycondensation reactions result in formation of a three-dimensional inorganic network and the “sol” transforms into a gelatinous mass known as a “gel” as the reaction proceeds [15]. The obtained gel is then aged dried to remove the solvent and subsequently calcined at elevated temperatures (typically 600-900 °C), to remove organic residues and induce crystallization of the desired ceramic phase. This sol-gel process offers several distinct advantages, which includes excellent chemical homogeneity, precise stoichiometric control, low processing temperatures and the ability to produce nanoscale particles with tailored morphologies [11]. Besides, this sol-gel method allows the coating of substrates and fabrication of thin films, which is highly beneficial and desired in microelectronics and MEMS applications. However, the process is sensitive to parameters such as pH, moisture content and precursor reactivity and hence requires careful control to avoid phase segregation or unwanted agglomeration [18].

2.2.3 Molten salt synthesis method

The molten salt synthesis method (MSS) is known as high temperature ceramic processing technique used for producing well-crystallized, homogeneous and morphologically controlled piezoelectric ceramic powders [11, 19]. This method employs use of inorganic salts such as sodium chloride (NaCl), potassium chloride (KCl) or their mixtures as a molten flux medium to facilitate the reaction between precursor materials. The selected precursors are then intimately mixed with the salt flux in specific weight ratios and thoroughly grounded to ensure uniformity. The mixture is then subjected to calcination in an alumina crucible at elevated temperatures ranging from 700 °C to 1000 °C [20] during while, the salt melts and serves as a liquid medium. This medium significantly enhances ion mobility, accelerates solid state diffusion and promotes the growth of ceramic grains [15]. Once

the reaction is complete, the product is allowed to cool and the excess salt is removed through repeated washing with deionized water or ethanol. This will be followed by drying at moderated temperatures. The MSS method offers several advantages, including improved phase purity, enhanced crystallinity and the ability to tailor particle morphology which is particularly beneficial for optimizing piezoelectric properties. However, the method also presents certain limitations, such as generation of waste salts, thorough post-synthesis washing and scalability challenges. Despite these drawbacks, molten salt synthesis remains an efficient method for preparing advanced piezoelectric materials with desirable microstructural features [20, 21].

2.2.4 Hydrothermal synthesis method

The hydrothermal synthesis method is a versatile, low temperature chemical process widely used for fabrication of nanostructured ceramic materials, including lead-free piezoelectric ceramics [22]. This synthesis technique involves the crystallization of materials from aqueous solutions under high temperature and pressure within a sealed autoclave. Typically, soluble metal salts or hydroxides are dissolved or suspended in distilled water. Strong alkaline conditions, usually adjusted with sodium hydroxide (NaOH) or potassium hydroxide (KOH) promote the hydrolysis and formation of hydroxide complexes [22, 23]. The resulting solution is then transferred into a Teflon-lined stainless-steel autoclave which is then heated to temperatures between 120 °C and 250 °C for several hours to days, generating autogenous pressures up to 10 MPa. Under these conditions, the precursors undergo nucleation and controlled crystal growth, forming well-crystallized oxide particles. After the reaction, the autoclave is cooled and the precipitate is collected by filtration, washed thoroughly with deionized water and ethanol to remove residual ions and then dried at moderate temperatures (80-100 °C). This method especially suitable for synthesizing nanorods, nanoplates or other anisotropic structures as it offers several advantages such as low synthesis temperature, high purity, phase selectivity and ability to control particle size and morphology. However, challenges such as long reaction time, limited scalability, high alkalinity and restricted applicability to certain oxide systems must be carefully considered while using this method for fabrication. [24, 25].

Method	Precursors	Process Temperature	Advantages	Limitations
Solid-State Reaction	Metal oxides, carbonates	800–1200 °C	Simple, low cost, scalable, good crystallinity	Poor morphology control, possible alkali loss, long processing
Sol–Gel Method	Metal alkoxides or nitrates in solution	600–900 °C	High purity, stoichiometric control, nano-size particles	Requires careful control of chemistry, may be costly
Molten Salt Synthesis	Metal oxides, alkali chlorides/carbonates (flux)	700–1000 °C	Enhances diffusion, better morphology, higher purity	Salt waste generation, requires washing, scalability issues
Hydrothermal Method	Metal salts/oxides in aqueous alkaline medium	120–250 °C (1–10 MPa)	Low temperature, controlled morphology, nanoscale synthesis	Long reaction times, limited to certain systems

Table 2.2: Comparison of common synthesis methods for lead-free piezoelectric ceramics [13, 21, 22, 26]

2.3 Electroding

The Electroding process is a key step in the preparation of piezoelectric ceramic discs. It enables the application of electric field for poling and facilitates electrical measurements for piezoelectric and dielectric properties. Typically, silver paste, gold sputtering or platinum electrodes are used depending on the application requirements

and measurement conditions. The most used method for lead-free ceramic disc such as KNN, BaTiO₃ or BNT-based materials, is application of silver conductive paste on both flat surfaces of the sintered disc. The paste is uniformly applied using a brush and then dried at a moderate temperature (100-150 °C) to remove the solvent. Due care and caution must be taken to ensure uniform coating thickness and coverage in order to avoid field concentration or non-uniform polarization during poling process. Proper electrode formation is critical and essential for ensuring accurate electrical characterization, long-term device performance and reliable energy harvesting or sensing functionality in piezoelectric applications [1, 27].

2.4 Poling

The poling process is a crucial post-fabrication step that imparts piezoelectric activity to ceramic and composite materials as it aligns randomly oriented electric dipoles within the material's domain [1]. In their natural state, the dipoles in a piezoelectric material are randomly oriented. This results in cancelling of net polarization of the material thereby rendering it non-piezoelectric macroscopically. During poling process, the piezoelectric ceramic or composite is exposed to a strong external electric field, typically at an elevated temperature. This external field re-orientates the electric dipoles within the material. However, when subjected to a poling field, the dipoles within the material are provided with sufficient energy that they overcome the potential barriers between domain states, thus rotate and align in the direction of the applied field as shown in the figure 2.1 [28, 29].

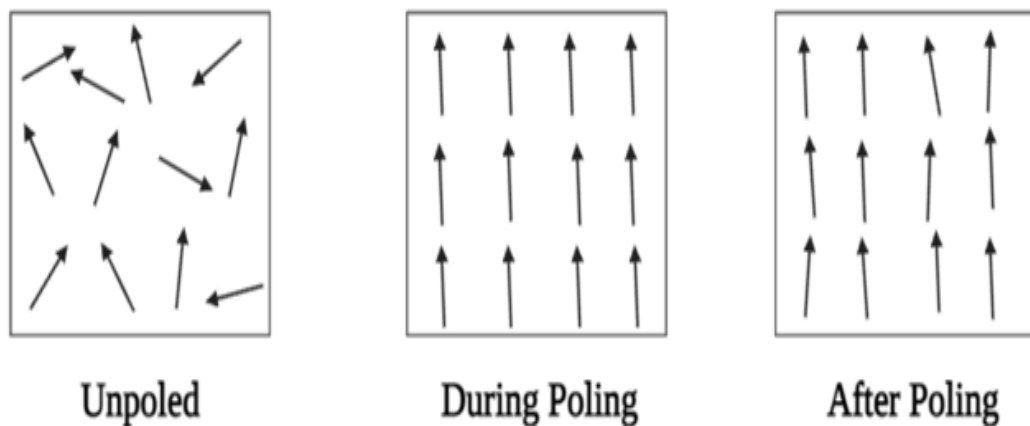


Figure 2.1: Dipole orientation in the direction of applied field

The choice of poling technique depends on the nature of the composite system, particularly the conductivity of the polymer matrix, filler content, dielectric breakdown strength and required field. The most commonly employed method is direct contact poling, which involves application of a DC electric field across the composite sample which is usually sandwiched between electrode plates in the heated silicone oil bath [27, 28]. An in-house direct contact poling setup is shown in figure 2.2. For thin film composites, corona poling is often preferred, wherein a high voltage needle electrode is placed above the composite surface which generates a corona discharge that induces surface charge resulting in dipole alignment without the need for direct electrical contact. This technique is particularly useful for flexible films or composites with soft polymer matrices like PDMS or PVDF [30]. Thermal poling is another technique which involves heating of the composite till softening or glass transition temperature, then subjecting it to an electric field. When cooled under the applied voltage, dipoles align. This method is often employed for thermoplastic polymer composites like nylon-11 [27, 29]. Parameters such as poling field strength, temperature and duration play a significant role in determining the final polarization performance.



Figure 2.2: In-house direct poling setup

2.5 Characterization Technique

To evaluate the structural, electrical and functional properties of piezoelectric ceramic fillers and their composites, a comprehensive characterization is essential. These characterization techniques give valuable insights into the microstructure, phase purity, morphology, dielectric behaviour and piezoelectric performance parameters. These studies are vital for understanding and optimizing the material's suitability for energy harvesting and sensing applications [31, 32]. This section discusses the methodologies used for characterization in this work to investigate the piezoelectric ceramics and ceramic-polymer composites.

2.5.1 Piezoelectric measurements

The piezoelectric properties of the fabricated ceramic filler and composites were evaluated primarily through the piezoelectric charge coefficient (d_{33}) measurement, which reflects the material property, i.e. the ability to generate electric charge in response to mechanical stress. The d_{33} values can be determined using a quasi-static d_{33} meter. A d_{33} meter applies a small dynamic force (typically <1 N) to the sample and measures the resulting electric charge [33]. Prior to measurement, all samples were polished and subjected to electroding with silver paste. Furthermore, the samples were thoroughly poled under optimized conditions to ensure maximum alignment of domains. Post-poling, the samples were aged for 24-48 hours before testing to ensure maximum consistency. The d_{33} response of the composites depends on both the ceramic filler connectivity and the interfacial adhesion between the ceramic and polymer matrix. Multiple measurements of each sample were taken to ensure reproducibility and the average value was reported.

2.5.2 Dielectric property measurements

The dielectric properties were measured to evaluate the ability of the synthesized piezoelectric ceramics and composites to store and dissipate electrical energy. The measurements were carried out using an LCR meter or impedance analyser over a frequency range typically spanning from 10^{-2} Hz to 1 MHz. The dielectric constant, ϵ_c and the dielectric loss tangent ($\tan \delta$), are the key parameters that were assessed. Both parameters were calculated from the measured capacitance and dissipation factor of the electrode disc-shaped samples. Under controlled environmental conditions, the

measurements were taken at room temperature to minimize the influence of humidity and thermal drift. In composites, the dielectric response is influenced by both the ceramic filler content and the dielectric nature of the polymer matrix. The interfacial polarization and space charge accumulation also play a significant role, especially at lower frequencies [34-36]. The dielectric characteristics give valuable insights regarding the electrical insulation behaviour and energy storage potential of the materials, which are crucial for determining the suitability in capacitive sensors and energy harvesting devices [37].

2.5.3 Structural and morphological characterization

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to analyse the structural and morphological characteristics of the synthesized piezoelectric ceramics and their polymer composites. The analysis was carried out to verify phase purity, crystallographic structure, grain size and surface morphology of the synthesized piezoelectric ceramics. XRD analysis was performed using an X-ray with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. The samples were scanned over a 2θ range of 10° to 80° and the phases of the resulting diffraction patterns were identified and compared with standard JCPDS files to confirm crystallinity. Scherrer equation is used for the estimation of the average crystallite size. Any secondary phases or impurity peaks were noted for assessing synthesis quality [38].

To study the surface morphology and microstructure of the sintered ceramics and the dispersion of ceramic particles in the polymer matrix SEM imaging was carried out. To prevent charging under electron beam, prior to imaging, samples were coated with a thin layer of gold or platinum. In pure ceramics, SEM imaging was used to examine grain size and porosity. On the other hand, in composites, the distribution of fillers, interfacial bonding and phase connectivity were evaluated. This morphological analysis is crucial for correlating the microstructure with the observed electrical and piezoelectric properties [39].

2.6 Conclusion

In this chapter, the essential materials, preparation techniques and characterization methods opted in the present study on lead-free piezoelectric composites were

systematically discussed. The material selection of environmental-friendly alternatives to traditional lead-based materials was justified, with a focus on the growing relevance of KNN-based systems [11, 15]. Various synthesis techniques such as solid-state reaction, sol-gel method, hydrothermal and molten salt synthesis methods were reviewed [40]. The fabrication of piezoelectric materials was described in detail, including, electroding and poling process, which are vital for activating piezoelectric response [10]. Multiple poling techniques were outlined with careful consideration of factors influencing domain alignment. Finally, the characterization techniques including piezoelectric, dielectric and structural analysis were discussed in detail to establish the fundamental physical and electrical behaviour of the prepared materials [38, 39]. These methodologies when effectively employed, lays sound foundation for creating, evaluating and optimizing lead-free piezoelectric materials for practical applications.

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OBJECTIVES

To address the hazardous threat associated with lead-based materials to life and environment, also limitations of ceramics imposed by their mechanical rigidity, there is a growing demand for the development of lead-free piezoelectric materials for flexible applications. Therefore, the present study focuses on fabrication, characterization and performance analysis of lead-free KNN-polymer 0-3 composites. Having identified the gaps, the following objectives have been formulated.

1. Synthesis and characterization of lead-free KNN piezoelectric fillers for composite fabrication.
2. 0-3 KNN-polymer composite fabrication.
3. Employing theoretical model for the analysis of 0-3 composites.
4. Performance analysis of 0-3 composites for sensor applications.

Chapter 3

PREPARATION AND CHARACTERIZATION OF KNN FILLERS

3.1 Introduction to KNN fillers

Among lead-free piezoelectric alternatives, potassium sodium niobate (abbreviated as KNN) due to its excellent ferroelectric and piezoelectric properties, has emerged as one of the most promising candidates [1, 2]. KNN-based materials offer a sustainable alternative for lead-based piezoelectric materials, without compromising performance as the environmental and regulatory concerns surrounding lead-based materials intensify [3].

KNN based materials belongs to the family of perovskite oxide with a general formula ABO_3 , where the A-site is occupied by potassium (K^+) and sodium (Na^+) ions in equal molar ratio and the B-site is occupied by niobium (Nb^+) ions [4]. The structure and characteristic properties of KNN is highly sensitive to processing conditions and stoichiometry, exhibiting a range of phase transitions with temperature. At room temperature, KNN typically crystallizes in an orthorhombic phase but undergoes transitions to tetragonal and cubic phases at elevated temperature (orthogonal to tetragonal at $\sim 180^\circ C - 240^\circ C$ and tetragonal to cubic at $\sim 390^\circ C - 440^\circ C$) [3, 5].

KNN with their key advantage of high Curie temperature ($T_C \sim 420^\circ C$), makes them suitable for high-temperature piezoelectric applications. Also, they exhibit large electromechanical coupling factors, good dielectric stability and strong remnant polarization values [1-3]. However, challenges during synthesis like, volatility of alkali elements at high temperatures, difficulty in achieving phase pure materials and controlling grain growth have impeded their widespread commercialization. Therefore, preparation of KNN fillers by optimizing the synthesis and processing routes is crucial for identifying its full potential [3].

The performance of KNN fillers can be further enhanced and modified by doping or compositing with other oxides. Even undoped form of KNN based materials exhibit properties that are comparable to or even surpass certain lead-based counterparts under specific conditions [2]. The present chapter focuses on the preparation and characterization of undoped KNN fillers prepared through conventional solid state reaction method (SSR) and templated grain growth method (TGG). Both SSR and TGG processing routes are chosen due to their ability to yield high-phase purity,

crystalline and texturally controlled fillers that are essential for improving the functional performance [6].

Different characterization techniques were employed like, XRD, SEM to investigate the phase purity, crystal structure and microstructural features of the synthesized KNN fillers. These structural analyses were critical in understanding the relation between processing conditions and resultant properties of KNN fillers. They form the foundation for developing composites using lead-free alternatives with high efficiency and reliability [2, 3].

3.1.1 Properties of KNN

The wide range of properties possessed by KNN fillers makes them suitable for both academic research and industrial applications as illustrated in table 3.1.

Piezoelectric Properties	High piezoelectric coefficients, $d_{33} \sim 80\text{--}160$ pC/N
Dielectric Properties	Dielectric constants typically range between 300 and 600 at room temperature.
Ferroelectric Properties	Strong polarization behaviour and well-defined hysteresis loops.
Thermal Stability	High Curie temperature enables applications in elevated temperature environments
Environmental Safety	Being lead-free, KNN is environmentally benign and complies with RoHS directives.

Table 3.1: Properties of KNN fillers [1-3]

3.2 Preparation methods for KNN fillers

Solid state reaction method is one of the most widely adopted techniques for large scale synthesis of ceramic fillers. Precise control over the synthesis is essential to obtain KNN ceramic fillers with desirable structural and functional properties. In this

study, undoped KNN fillers were prepared using conventional solid state reaction method. Additionally, templated grain growth method was also employed to improve the grain orientation and enhance piezoelectric response [3, 6].

Alkali volatilization is one of the major challenges associated with the fabrication of KNN-based fillers. During high-temperature sintering, partial evaporation of potassium and sodium may occur, leading to A-site non-stoichiometry, which can promote the formation of secondary phases, increase defect-concentration, hinder domain-wall motion and consequently deteriorate the dielectric, ferroelectric and piezoelectric properties. To minimize alkali loss, the KNN fillers in the present study were synthesized under optimized processing parameters, including controlled calcination and sintering temperatures. These parameters were selected to achieve adequate densification while limiting excessive alkali volatilization. Furthermore, the ceramic pellets were sintered in covered alumina crucibles, which helps reduce exposure to the furnace atmosphere and minimizes alkali evaporation during sintering.

3.2.1 Solid state reaction method (SSR)

The solid-state reaction method is a classical ceramic synthesis route, which is based on high temperature reactions between solid oxide or carbonate precursors. It is a simple, cost-effective method known for its ability to produce phase-pure bulk ceramics with controlled stoichiometry [7, 8].

In the present work, stoichiometric proportions (equation 1) of high purity starting materials like potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3) and niobium pentoxide (Nb_2O_5) ($\geq 99.5\%$) were used. Special care was taken in handling and storage of the alkali carbonates due to its hygroscopic and volatile nature, also, all weighing operations were performed in a controlled humid environment.



The weighed powders were thoroughly mixed and hand blended using an agate mortar and pestle using distilled water for 1 hour to ensure homogeneous mixing and particle size reduction. The resulting slurry underwent drying and then mixture was calcined at an optimized temperature of $800^\circ C$ for 6 hours in an alumina crucible to initiate the solid-state reaction and form the $K_{0.5} Na_{0.5} NbO_3$ phase.

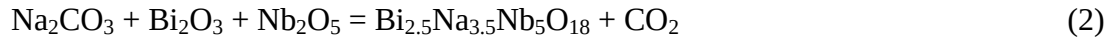
Post-calcination, the powders were again milled using agate mortar and pestle, to break down agglomerates and improve packing density. The resulting fine powder was used for both composite preparation and as the matrix material for templated grain growth processing.

3.2.2 Templated grain growth method (TGG)

Textured ceramics can be developed using templated grain growth method, by introducing anisotropic template particles into a matrix of equiaxed grains. This method promotes grain alignment during sintering, thereby enhancing anisotropic properties such as piezoelectricity along preferred crystallographic orientations. Plate-like NN template particles were synthesized using TGG method, separately under optimized conditions using a high temperature (~ 1000 °C) molten salt method. The prepared templates exhibit well-defined anisotropic morphology. Later NN templates are mixed with KNN matrix powder prepared via solid state reaction method in specific volume fractions. For TGG process to be successful, several factors including aspect ratio of the templates, template-to-matrix ratio, calcination temperature and heating rate should be controlled. In this process, conditions were optimized which helps in yielding KNN fillers with enhanced grain orientation. This enhancement is expected to contribute to improved functional properties such as piezoelectric coefficient and electromechanical coupling [8].

Equations 2 - 4 illustrate the synthesis of KNN fillers via TGG method, consisting of 3 main steps: (i) molten salt synthesis of sodium bismuth niobate, $\text{Bi}_{2.5}\text{Na}_{3.5}\text{Nb}_5\text{O}_{18}$ (BNN) precursor; (ii) topochemical microcrystal conversion synthesis of plate-like sodium niobate, NaNbO_3 (NN) templates. BNN is prepared by using sodium carbonate (Na_2CO_3), bismuth III oxide (Bi_2O_3) and niobium pentoxide (Nb_2O_5) (≥ 99) as starting materials, which were firstly weighed according to the ratio of reaction in step 1 (equation 2). Subsequently, sodium chloride (NaCl) was added, maintaining a weight ratio of 1:1 for salt-to-oxide. All the reactants and salt were mixed in an agate mortar. The dried mixture was calcined at 900 °C for 8 h in the muffle furnace. The residual salts were washed away using hot de-ionized water. The NaNbO_3 template was obtained from BNN precursor, which was subsequently subjected to further reaction with Na_2CO_3 in NaCl flux (equation 3). The reactants were weighed according to the stoichiometric ratios of the reaction in step 2 (equation 3) and then NaCl salt was

added to the mixture. The resulting mixtures were dried and calcined in muffle furnace at 900 °C for 8 h in alumina crucible. Hot de-ionized water was used for removing the residual salts. HNO₃ solution was used to remove the by-product, Bi₂O₃. The NaNbO₃ templates were mixed with KNN matrix powder, synthesized through SSR method. The reactants were mixed in an agate mortar and were kept for drying. The dried mixtures were calcined for 6 h at 1000 °C in an alumina crucible [9].



3.3 Results and Discussions

3.3.1 X-ray diffraction (XRD)

The phase purity and crystal structure of synthesized KNN fillers via SSR and TGG method was confirmed by XRD diffraction pattern shown in figure 3.1. Sharp and well-defined peaks confirming single-phase perovskite structure was obtained at all stages of KNN filler preparation. The phases at different stages of preparation were identified by analysing the diffraction patterns in the two theta (2θ) range of 20° and 60° [10]. In figure 3.1 (a) represents the diffraction pattern of BNN precursor and all peaks were identified as BNN, (b) represents the diffraction pattern of NN templates. NaNbO₃ (NN) perovskite phase was obtained when synthesized at 900 °C for 8 h, where particles are fully crystallized and the peak intensities of (L00) was the strongest as shown in the figure. From the layer structured BNN, pure perovskite NN possessing the same morphology as BNN was obtained. Residual Bi of small amount was observed with no adverse effects on the molten salt synthesis process of NN templates [11]. (c) and (d) in figure 3.1 depicts the XRD of KNN prepared via SSR and TGG method respectively. The phase structure is pure perovskite with orthorhombic symmetry. Figure 3.2 shows the XRD patterns of KNN filler in the 2θ range of 43° to 48°. A clear peak splitting is observed about 45.5° and calculated intensity ration (I_{022}/I_{200}) of 022/200 peak confirmed the orthorhombic structure for KNN filler prepared by both the methods [12].

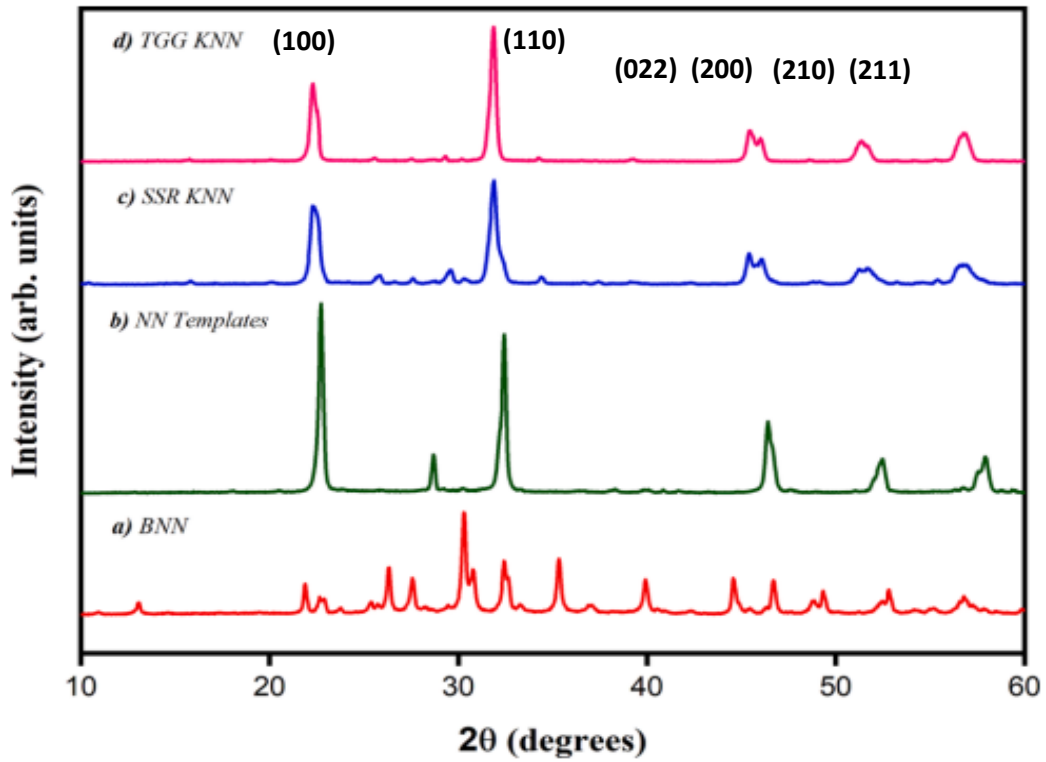


Figure 3.1: Room temperature XRD pattern of (a) BNN precursor (b) NN template (c) KNN prepared by SSR and (d) KNN prepared by TGG

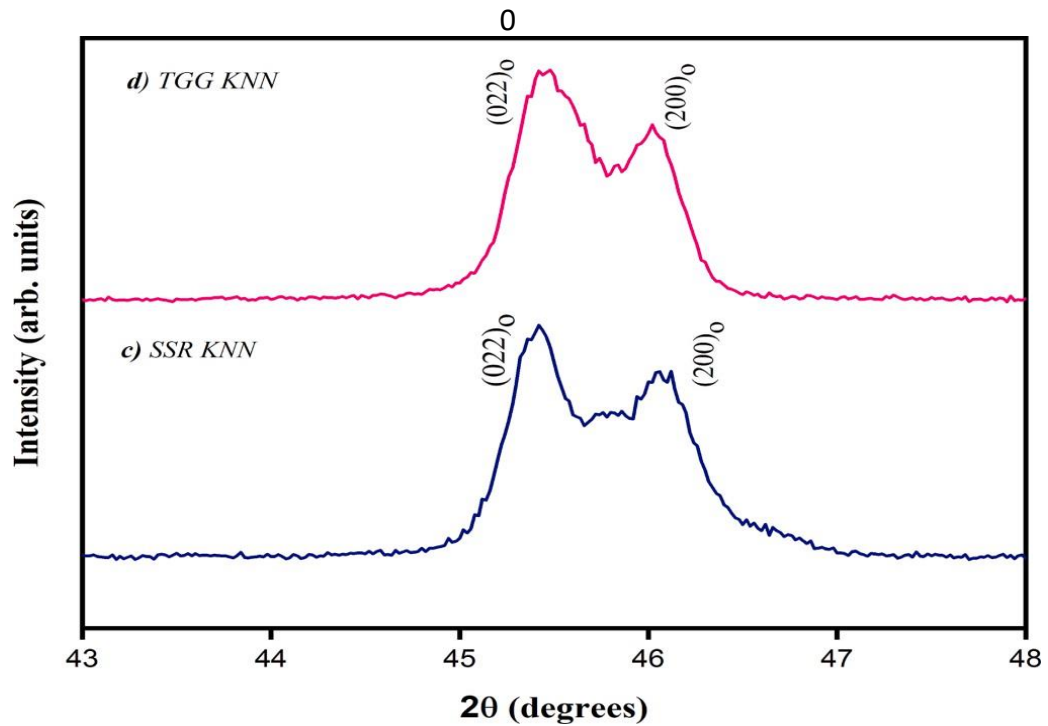


Figure 3.2: Peak splitting observed at about 45.5° for (a) KNN prepared by SSR (b) KNN prepared by TGG.

The effectiveness of the adopted processing conditions is supported by the experimental characterization. The XRD patterns of the sintered KNN fillers showed a well-developed perovskite phase without detectable secondary phases, indicating that significant decomposition or phase instability did not occur during sintering. Nevertheless, it is recognized that a small degree of alkali loss is difficult to eliminate completely during high-temperature processing of KNN fillers. Such minor compositional deviations are inherent to conventional solid-state synthesis and are considered one of the reasons for the slight variations commonly observed in the electrical properties of KNN-based materials. However, based on the phase purity confirmed by XRD and the satisfactory functional properties obtained, it is concluded that alkali volatilization was effectively controlled under the processing conditions employed in this work.

3.3.2 Lotgering Orientation Factor (LOF)

The degree of orientation of the peak <L00> in KNN fillers prepared by TGG was assessed using Lotgering orientation factor (LOF). LOF can be calculated from the XRD pattern using the equation (5) [13].

$$F = \frac{p-p_0}{1-p_0} \quad (5)$$

Where,

F – The measure of the ‘degree of orientation’, which ranges from 0% to 100%

p – The fraction of summation of peak intensities corresponding to the preferred orientation axis to that of the summation of all diffraction peaks.

p_0 – p of the sample with random crystallographic orientation

For KNN prepared via TGG method, LOF of around 21% is obtained which confirms the crystallographic orientation of the particles along the preferred direction. Hisaaki Takao et.al [14] developed crystalline-oriented KNN based piezo-ceramics by reactive templated grain growth method and obtained a Lotgering orientation factor of 95%. Y. Chang et.al [15] reported a Lotgering orientation factor of 99% for CuO-doped KNN by templated grain growth method.

3.3.3 Scanning electron microscope (SEM)

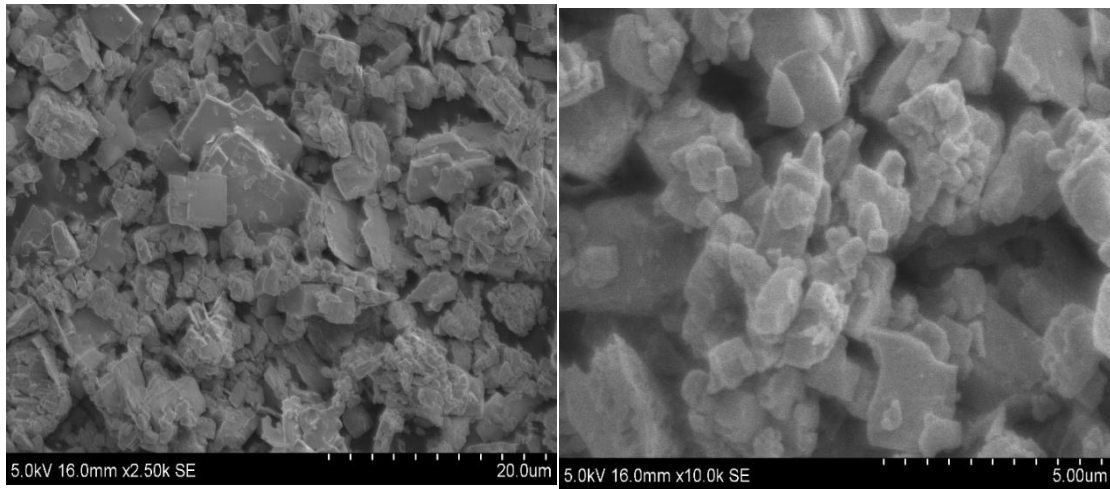


Figure 3.3: SEM micrographs of NN templates

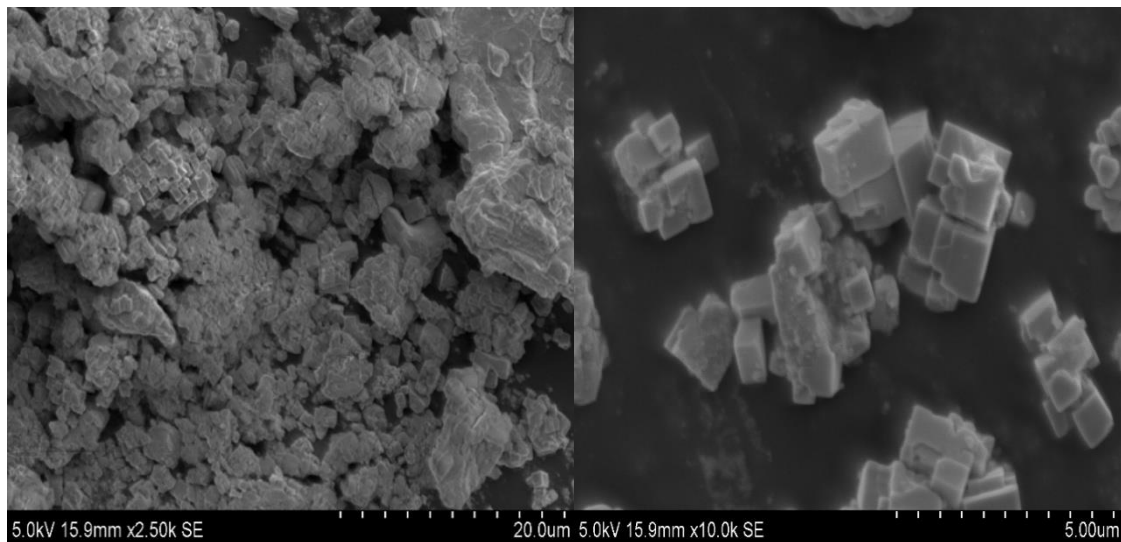


Figure 3.4: SEM micrographs of KNN fillers prepared via solid state reaction method

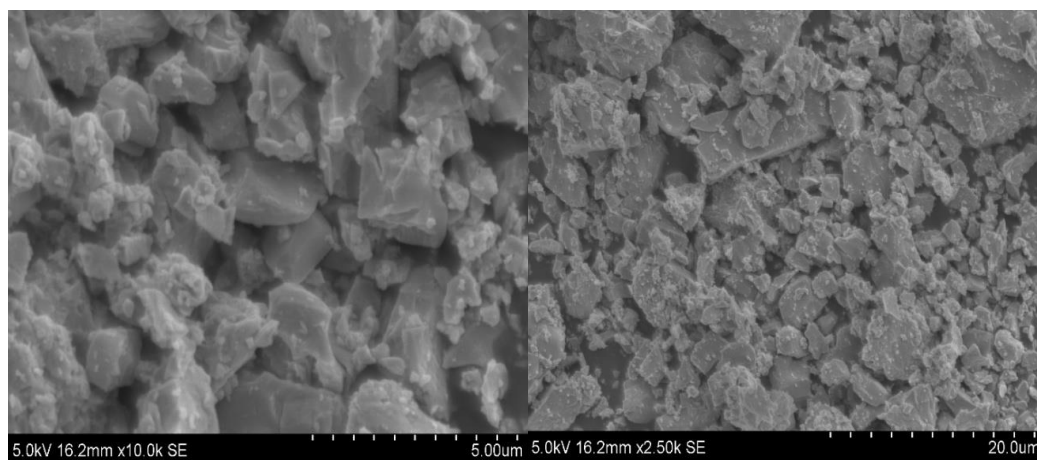


Figure 3.5: SEM micrographs of KNN fillers prepared via templated grain growth method

The SEM images of (a) NN templates (b) KNN filler prepared via SSR and (c) KNN filler prepared via TGG method are presented in figure 3.3 to figure 3.5 respectively. SEM micrographs show densely packed grains with average particle size distribution of 0.4-3 μm , 0.4-0.9 μm and 0.3-3 μm respectively for NN templates, KNN filler prepared via SSR and KNN prepared via TGG.

3.3.3 Electrical characterization

The domains of the prepared KNN fillers are randomly oriented therefore the piezoelectric properties of thus prepared fillers strongly depend on the poling conditions. To obtain highly oriented domains, strong electric field is desired [16]. In this work, the optimized conditions were found to be 2 kV/mm electric field, poling temperature to be 80 $^{\circ}\text{C}$ and poling time of 20 minutes to get enhanced piezoelectric properties [9].

The piezoelectric charge coefficient of KNN fillers prepared through two different processing routes is found to be an average of 295 pC/N for KNN filler prepared via SSR method and 315 pC/N for KNN filler prepared via TGG method. The d_{33} measurements were performed on 4 samples of KNN prepared via both the methods. The measured d_{33} values exhibited only minor variations among the tested samples, demonstrating good repeatability and reproducibility of the fabrication process. The piezoelectric response is consistent across the fabricated samples and that the observed difference between the reported values is reproducible within the experimental uncertainty. KNN prepared via SSR method exhibits moderate piezoelectric coefficient, which is the characteristics of KNN fillers with randomly oriented grains with broader particle distributions. In such materials, the crystallographic structure limits the domain orientation during the poling process, which results in a comparatively less piezoelectric response. In contrast, KNN fillers prepared via TGG exhibited comparatively high electromechanical response. This enhancement is due to the oriented crystallographic microstructure during TGG process. A comparative bar chart of piezoelectric voltage response of KNN ceramics prepared via TGG and SSR is illustrated in figure 3.6.

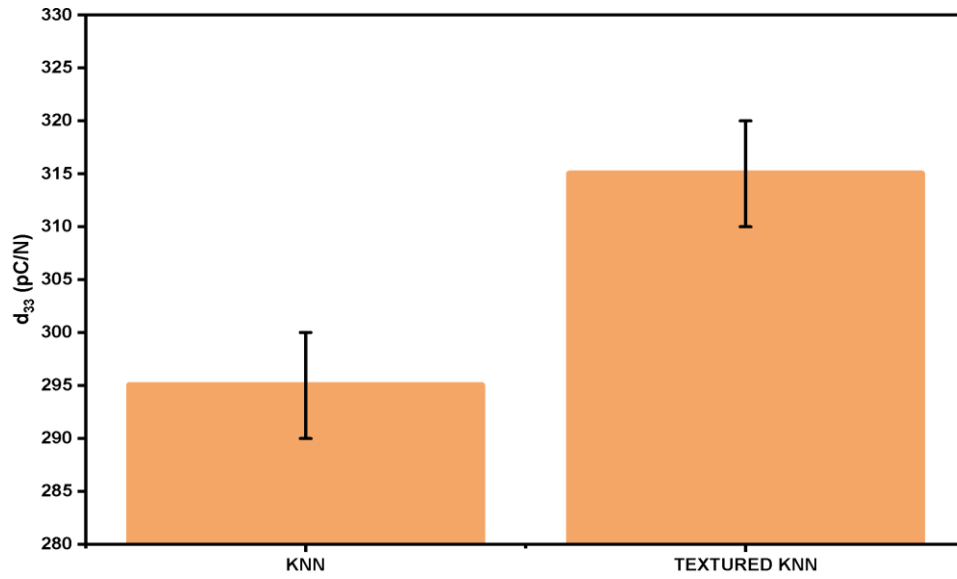


Figure 3.6: Bar chart on piezoelectric response of KNN ceramics prepared through SSR and TGG

3.4 Conclusion

KNN ceramics were successfully prepared using conventional solid-state reaction method and templated grain growth method. This chapter on the preparation and characterization of KNN fillers emphasizes the importance of control over calcination conditions and different processing routes of KNN for achieving the desired phase-purity and microstructure. The formation of KNN perovskite structure was confirmed from the XRD analysis. Well-defined peaks were obtained, indicating successful elimination of secondary phases under optimized processing conditions. Further the SEM micrographs at various processing stages revealed a dense microstructure for KNN fillers with uniformly developed grains, which support the chosen synthesis routes, effective. Structural and microstructural studies are compared for both SSR and TGG processing route and demonstrated that TGG approach significantly improved crystallinity and grain morphology compared to SSR method. These improvements are crucial for achieving enhanced piezoelectric properties. A d_{33} value of 295 pC/N is obtained for KNN prepared via SSR and a value of 315 pC/N for KNN prepared via TGG method. High performance KNN-based composites are prepared and analysed from the strong foundation led by these insights which are explored in the following chapters.

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Chapter 4

KNN-EPOXY COMPOSITES

4.1 Introduction

Epoxy resins are widely used thermosetting polymers. They are renowned for their excellent properties like superior mechanical strength, dimensional stability, chemical resistance and good adhesion to various substrates making epoxy a material of choice [1, 2]. Epoxy can be used in applications ranging from structural adhesives and coating to electronic encapsulation and composite materials. Suitable selection of curing agents and fillers, the mechanical and thermal properties of epoxy can be tailored, which will further broaden its applicability in both industrial and advanced functional domains [3].

Piezoelectric composites based on piezoelectrically active fillers and polymer matrix has gained significant attention in recent years for their role in multifunctional applications which includes sensing, actuation and energy harvesting [4, 5]. Piezoelectric fillers such as ceramics, carbon-based materials and metal oxides, incorporated into polymer matrix can lead to the development of hybrid composite systems that exhibits enhanced dielectric and piezoelectric properties. Material systems fabricated with ceramic fillers and polymer does not compromise with the flexibility and processability of the polymer matrix. Among various piezoelectric ceramic-polymer composite systems, epoxy, a thermosetting polymer-based composites stands out as they exhibited excellent filler-matrix interaction and the rigid three-dimensional crosslinked network formed upon curing. These unique properties of epoxy, helps in maintaining the structural integrity of the composite [6, 7]. Also, in the field of piezoelectric energy harvesting, epoxy composites embedded with ceramic fillers offer a robust platform that combines mechanical durability with functional energy conversion capabilities. The piezoelectric fillers act as the active phase that generates electrical charge under mechanical stress, while the epoxy matrix serves as the passive phase (matrix), that provides mechanical support and improving the composite's reliability under cyclic loading [8, 9]. The choice of ceramic filler and the composite fabrication technique critically determine the overall piezoelectric response of the composite [10].

Piezoelectric ceramic fillers based on potassium sodium niobate (KNN) materials, due to their attractive properties such as, high Curie temperature, good piezoelectric and dielectric properties and relatively high electromechanical coupling properties are

considered as the leading material among the lead-free piezoelectric candidates [11]. The piezoelectric properties of lead-free piezoelectric materials like KNN are far inferior to that of lead-based piezoelectric materials. Therefore, it is important to use the anisotropy in elastic, dielectric and piezoelectric properties in order to achieve the desired performance [12]. Controlling grain orientation without decreasing the Curie temperature is an important approach for enhancing the properties of piezoelectric ceramics to achieve higher piezoelectric response and more establishes properties [13, 14]. Saito et.al. reported piezoelectric stain coefficient, d_{33} 750 pm/V in $\langle 001 \rangle$ oriented KNN using plate like NN templates [15]. Also, many researchers reported their work on TGG KNN, though excellent KNN ceramics were obtained, the improvement in properties was limited [16]. To modulate and enhance mechanical properties and voltage coefficient g_{33} of different piezoelectric ceramic materials, relevant composites have been developed [17].

This chapter focuses on the fabrication, structural analysis and piezoelectric characterization of KNN-epoxy 0-3 composites. KNN fillers prepared via TGG method is chosen for composite fabrication. The influence of KNN filler concentration on the dielectric and piezoelectric behaviour of the composite system is systematically studied and is compared with the existing theoretical models.

4.2 Materials and Methods

4.2.1 Preparation of KNN-epoxy composite

The fabrication of KNN-epoxy composites for different volume percent of KNN in epoxy matrix was carried out by dispersing KNN in the epoxy medium. Firstly, the epoxy medium is prepared by mixing resin (AW 160) and the hardener (HV 953) at equal ratios until gel like paste is obtained. Further, the KNN filler prepared via TGG method is added to the matrix by varying the volume percentage as 10, 20, 30, 40, 50. Pellets with 2 mm thickness for various filler concentration were prepared. Following, the pellets are polished and electrode by applying conductive silver paste on the both surfaces. Thus, prepared composites were poled under a uniform DC field of 2 kV/mm for 20 minutes at 80°C.

4.3 Results and Discussions

By accounting the polymer-ceramic interphase, particle to particle connectivity, constituent's volume fraction, aspect ratio of the particles and morphology, several numerical and analytical models were proposed for piezoelectric and dielectric properties of 0–3 composites [18-20]. Yamada et al. [20] proposed analytical model which treated composite as a spatially uniform distribution of equal sized ellipsoidal particles in an isotropic polymer matrix. The experimental results of piezoelectric and dielectric coefficients of 0–3 composites were fitted with the help of this model. The dielectric constant of the composite proposed by Yamada is given by

$$\epsilon_c = \epsilon_1 \left[1 + \frac{n\phi(\epsilon_2 - \epsilon_1)}{n\epsilon_1 + (\epsilon_2 - \epsilon_1)(1 - \phi)} \right] \quad (2)$$

Where ϵ_c is the dielectric constant of the composite, ϵ_1 and ϵ_2 is that of matrix and ceramic particles respectively, ϕ is the volume fraction of the ceramic and n is the inverse of the depolarization factor for an ellipsoidal particle in the direction of applied electric field [20].

Figure 4.1 shows the variation of dielectric constant of KNN prepared by TGG method along with the theoretical dependences. The dielectric constant was taken as 4.3 and 500 for neat epoxy resin and KNN ceramic phase respectively. The experimental dielectric constants of 0–3 composites fit to the Yamada Model when assuming a depolarization factor $n = 5$ (i.e., slightly elongated particles) [19]. The dielectric constant at elevated volume percentages of TGG-KNN closely corresponds to the dielectric constant predicted by Yamada's model. At the lower filling fraction, the active ceramic phase is completely shielded by the polymer phase whereas, at higher filler loading, the particle-to-particle connectivity increases and there by polarizability.

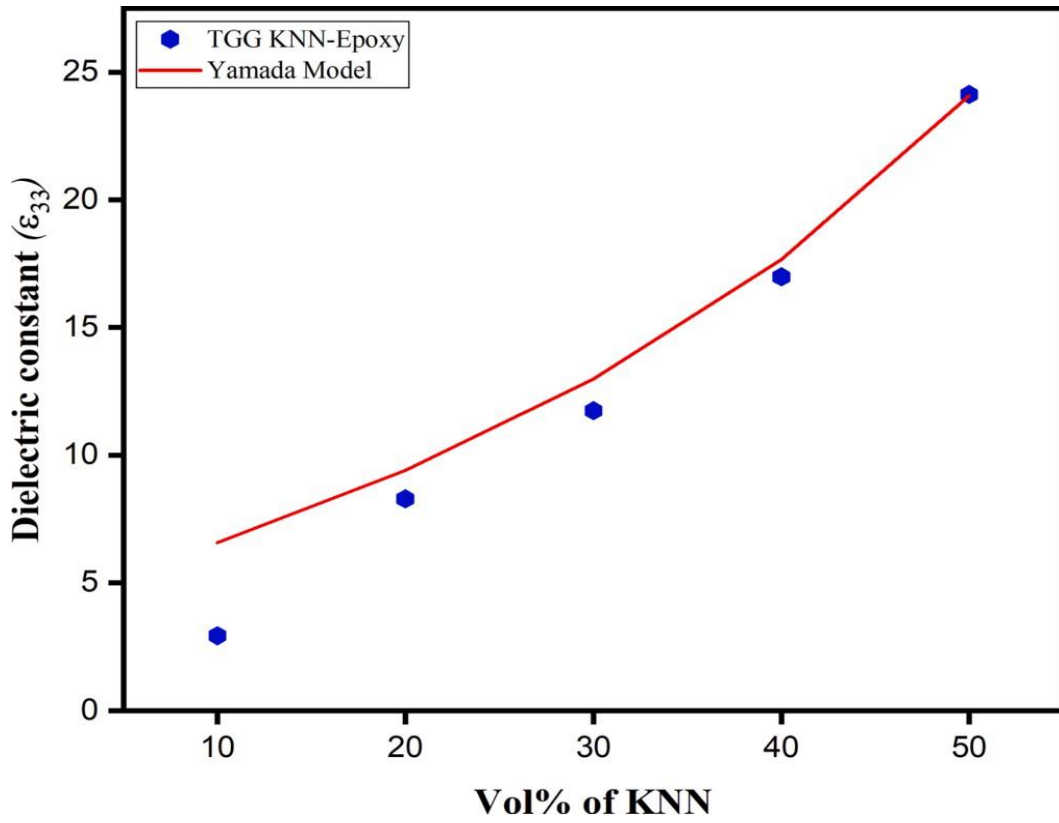


Figure 4.1: Variations of dielectric constant of the composite as a function of TGG KNN volume percent in Epoxy matrix fitted using Yamada model

Yamada's model for the piezoelectric charge constant d_{33} in the poling direction is given by,

$$d_{33} = \frac{\phi n \alpha \epsilon_c d_{33}}{n \epsilon_c + (\epsilon_2 - \epsilon_1)} \quad (3)$$

Where α is the poling ratio of KNN particles and ϵ_c is the dielectric constant of the composite given in equation 2 [19]. For the same depolarization factor i.e., $n = 5$, the d_{33} values of 0–3 KNN-Epoxy composites correlate well with the values predicted by Yamada's model [20]. The experimental values of d_{33} for the 0–3 composites are compared with the theoretical model proposed by Yamada as well as KNN prepared by N. K. James et.al via solid state reaction route [21] and is given in figure 4.2.

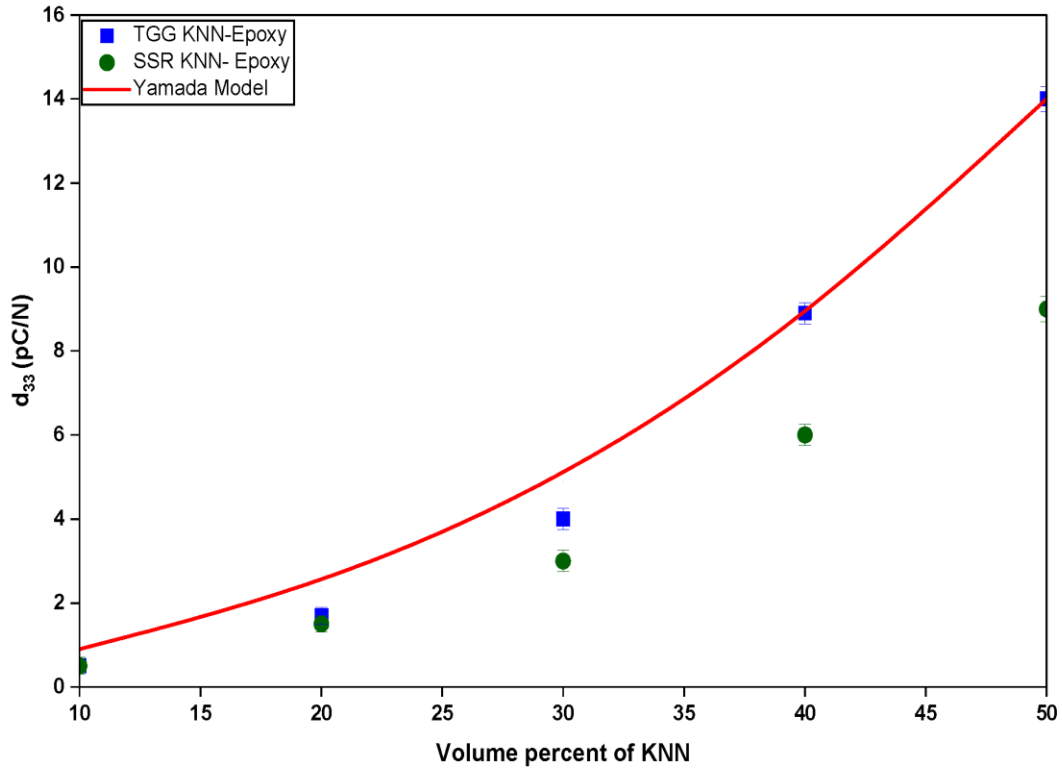


Figure 4.2: Variations of piezoelectric charge constant (d_{33}) of the composite fitted using Yamada model

The significant impact of grain orientation and alignment on piezoelectric properties is evident in TGG KNN composite. The notably higher d_{33} value observed in TGG KNN compared to KNN prepared by SSR is attributed to texturing, which specifically enhances the piezoelectric charge coefficient along a defined direction. In contrast, KNN-SSR exhibits a more isotropic piezoelectric charge coefficient. The piezoelectric voltage coefficient, g_{33} is defined as the ratio of piezoelectric charge coefficient (d_{33}) and dielectric constant (ϵ_c) of the composite system [19], and it is given as,

$$g_{33} = \frac{d_{33}}{\epsilon_0 \epsilon_c} \quad (4)$$

Where, ϵ_0 is the permittivity of the free space. The change of g_{33} as a function of KNN volume percent of both composite systems prepared by TGG method

and SSR is depicted in figure 4.3

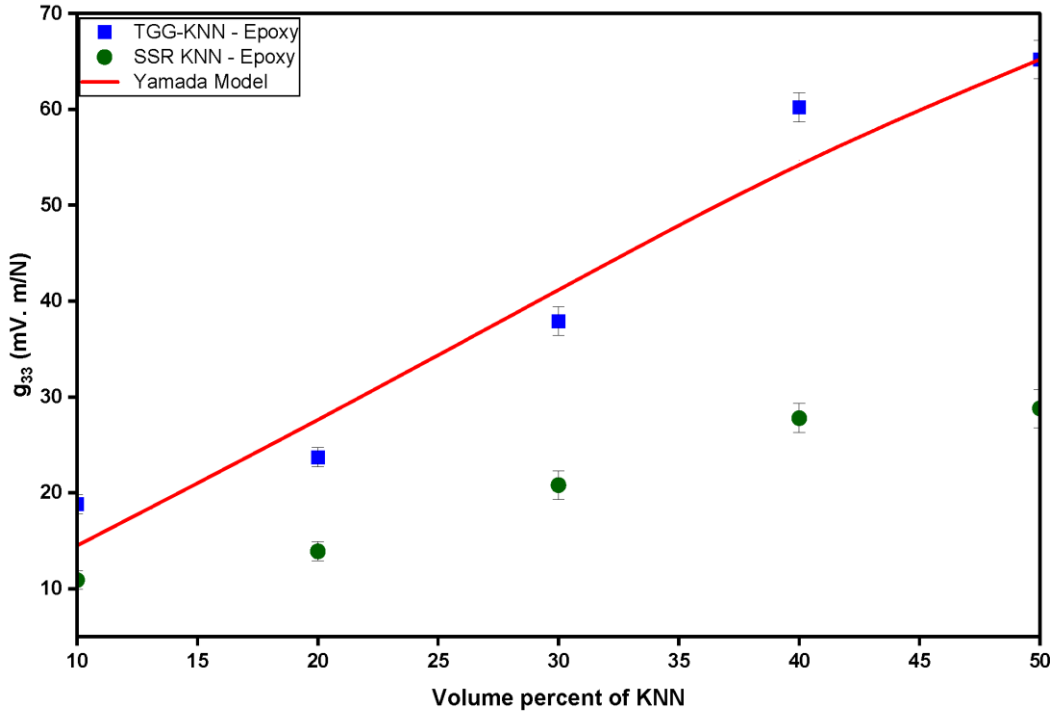


Figure 4.3: Variations of piezoelectric voltage coefficient (g_{33}) of the composite as a function of KNN volume percent in epoxy matrix.

The lowering of dielectric constant and an increase in d_{33} value of the composite system results an increase in the effective piezoelectric voltage coefficient, g_{33} of the composite system. In order to obtain a high g_{33} value the dielectric constant should be low as possible and at the same time the piezoelectric charge coefficient should be as high as possible [19]. The figure 4.3 indicates that the g_{33} values for KNN-epoxy composites for higher volume percent is high and a maximum value of 65.2 mV.m/N is obtained for composite with 50 volume percent of KNN filler in epoxy matrix.

The long-term performance of the composites depends on several factors, including the environmental stability of the polymer matrix, the chemical stability of the KNN ceramic filler, the integrity of the ceramic-polymer interface and the ability of the composite to retain its polarization under prolonged service conditions. In the present study, KNN was selected as the

piezoelectric ceramic because of its well-established chemical stability and lead-free composition. The polymer matrix provides mechanical protection to the ceramic particles while improving flexibility and resistance to mechanical damage. After electrical poling, All composites were allowed to stabilize under ambient laboratory conditions for approximately 48 hours before d_{33} measurements were performed. This stabilization period allows the transient polarization relaxation to subside and endures that the measured d_{33} corresponds to the stable remanent polarization of the composites. This indicates that no significant depolarization occurred during the storage period, demonstrating good short-term polarization stability of the fabricated composites under ambient laboratory conditions.

4.2. Conclusion

Lead-free piezoelectric composites based on textured ($K_{0.476}$, $Na_{0.524}$) NbO_3 particles in an epoxy matrix have been prepared. KNN ceramics with an orthorhombic symmetry is obtained from TGG along with a Lotgering orientation factor of 21 %. The composites were successfully poled with an optimum poling field of 2 kV/mm, poling temperature 80 °C and poling time 20 min. The piezoelectric and dielectric properties were measured and there is an increase in the properties with the increase of ceramic filler volume percent compared to that of reference KNN via solid state reaction route and it shows a similar pattern to that of theoretical model proposed by Yamada. High piezoelectric charge coefficient and low dielectric constant leads to a relatively high piezoelectric voltage coefficient in textured KNN-Epoxy composites which can replace lead based piezo- electric composites for sensor and energy harvesting applications.

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Chapter 5

KNN-NATURAL RUBBER COMPOSITES

5.1 Introduction

Natural rubber (NR) is a naturally occurring polymeric material from the tree latex of *Hevea brasiliensis* [1]. It is a highly versatile elastomer, due to its exceptional elasticity, tensile strength and fatigue resistance is been extensively used across industries. The molecular structural configuration of NR is cis-1, 4-polyisoprene. With this configuration, NR exhibits extensive chain mobility and elastic recovery, making it suitable for applications which involve repeated deformation. NR is an environmentally sustainable alternative to petroleum-based synthetic polymers with additional properties of outstanding mechanical performance [1, 2].

NR is a soft and highly stretchable polymer which makes it particularly attractive for use in flexible electronics, stretchable sensors, wearable devices and biomedical implants. NR has the ability to accommodate large strains over extended periods without permanent deformation. This allows NR to conform to complex surfaces and sustain mechanical loading over extended periods. The other properties of NR like good damping, high resilience and thermal stability over a wide range of operating conditions, further enhances its applicability in dynamic environments [3, 4]. Moreover, through vulcanization process, the mechanical durability and thermal resistance of NR can be enhanced. NR can be easily compounded, molded or cast into desired shapes and forms a crosslinked structure during vulcanization process. Formation of cross-linked molecular chain structure of NR during vulcanization process is as is represented schematically in the figure 5.1. NR offers advantage like ease of processing which can be combined with its inherent elasticity and environment friendliness, making it a promising base material for the development of next generation flexible devices and soft energy harvesting systems [5, 6].

In the perspective of materials design, NR serves as an excellent matrix for developing multifunctional composites. NR is compatible with various fillers, which includes carbon-based materials, metal oxides and ceramic particles, enables the tailoring of electric, thermal and mechanical properties to suit specific functional requirements. The performance of the resulting composites can be significantly improved with proper dispersion of active fillers within the NR matrix, along with effective interfacial interactions. Resulting composites can be applicable in the areas such as sensing, actuation and energy harvesting [8-10].

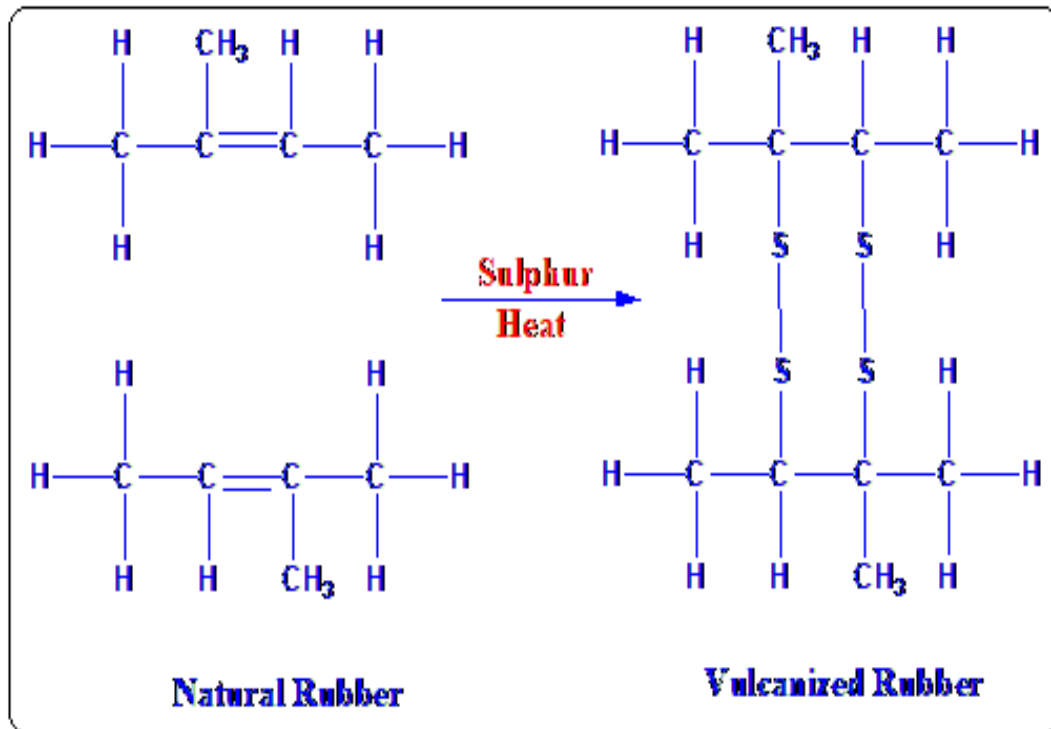


Figure 5.1: Schematic of molecular chain structure of NR and effect of vulcanization to form cross linking [7]

Piezoelectric composite based on potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$ (KNN)) and NR, combine the advantage of both piezoelectric KNN filler and NR polymer matrix, leading to improved piezoelectric and dielectric properties compared to single-phase materials like ceramics and polymers [11, 12]. The processing challenges of KNN with NR composites led to less exploration of the system. Yaonan Yu et.al.[13] presented an innovative approach to develop energy harvesting for sensors by developing a piezoelectric energy harvester with carbon-reinforced polymer electrodes. The composite they developed combines KNN nanoparticles with an epoxy resin yielding a piezoelectric response of 15.21 pC/N. Verma et.al. [14] in their study developed a flexible piezoelectric generator using KNN nanoparticles embedded in PVDF matrix. The authors also observed that piezoelectric coefficient can be improved by increasing the concentration of KNN. Their research demonstrated the potential of KNN-PVDF composites in flexible energy harvesting applications. Mirzazadeh et.al. [15] presented an investigative study on the physical and mechanical properties of PVDF and KNN composites. The KNN-PVDF composites were fabricated using hot compression molding technique. The authors aimed to enhance the piezoelectric properties and mechanical performance of PVDF

by incorporating KNN nanoparticles for different concentrations. The addition of KNN nanoparticles significantly enhanced the piezoelectric characteristics of the composites with a maximum value of 23.06 pC/N obtained as d_{33} value.

The fabrication, functional and mechanical characterization of KNN-NR piezocomposites in 0-3 configuration for flexible applications is presented in this chapter. The combination of KNN filler and NR polymer gives a novel approach offering efficient mechanical to electrical energy conversion which is well suited for applications like self-powered sensors. The work presented in this chapter also aims to bridge gap and study the synergy between piezoelectric properties of KNN and mechanical properties of NR for building potential composites. These composites may lead to innovations in smart textiles and health monitoring systems, offering sustainable and high-performance material solution for modern energy and sensor technologies [16, 17].

5.2 Materials and Methods

5.2.1 Materials

In this work KNN fillers prepared via conventional solid state reaction method is used for composite preparation. The NR used in this study was Indian Standard Natural Rubber (ISNR) grade 20 (Kilkotagiri and Thirumbadi Plantations Limited, Kerala, India), which is commonly found in brown, compact blocks. The accelerators and activators used for rubber compounding are ZnO, stearic acid, MBTS, TMTD, and sulfur (Common Facility Service Center (CFSC) Manjeri, Kerala, India). Figure 5.2 shows the ISNR-20 NR prior to processing. After the compounding of NR and vulcanization, the material was formed into flexible sheets, as shown in figure 5.3. The transition from raw rubber phase to cured sheet is visually highlighted.



Figure 5.2: Photograph of ISNR Grade 20 natural rubber before processing



Figure 5.3: Vulcanized KNN-NR sheet (composite)

5.2.2 Compounding: KNN-NR Composite Preparation

KNN-NR composites were compounded using an industrial two roll mill (CFSC Manjeri, Kerala, India). After the mastication of NR, the activator, ZnO and stearic acid were added to make the vulcanization process more efficient. Thereafter, the weighed quantity of KNN filler was incorporated into the mixture. Subsequently, accelerators such as MBTS and TMTD were added to increase the speed of vulcanization, enabling it to proceed at lower temperatures and with greater efficiency. Following that, the vulcanizing agent, sulphur, was added, and the mixture was thoroughly mixed to ensure homogeneity. The mixes were passed through a 2 mm tight nip gap 5–6 times to produce identical sheets with dimension of 150 × 150 mm (h × w). These KNN-NR composite sheets were allowed to mature at room temperature before molding. The curing time for each composite mix was determined using rheographs to analyse the processing conditions of rubber composites. The cure characteristics for KNN-NR composites are presented in table 5.1. Subsequently, the composite mixes were vulcanized in standard molds at 150 °C using a hot press [18–20].

Sample^a	T₉₀ [min]
NR neat	3.15
10% KNN-NR	2.41
30% KNN-NR	1.80
50% KNN-NR	1.38
60% KNN-NR	1.35

^aFor each composite mix: ZnO-5, stearic acid-3, MBTS-1.3, TMTD-0.2, and sulphur-2.

Table 5.1: Cure Characteristics of KNN-NR composites

KNN is a chemically stable inorganic perovskite oxide. The vulcanization of natural rubber is typically carried out at moderate temperatures, where crosslinking reaction occurs primarily between the rubber chains and sulphur in the presence of activators

and accelerators. These chemicals are specifically designed to promote sulphur crosslinking within the elastomeric matrix and are not sufficiently reactive to alter the crystal structure of the KNN filler under the processing conditions employed in this study. Furthermore, the KNN fillers act as inert particulate fillers dispersed within the rubber matrix rather than as reactive chemical species. Since KNN do not participate in the vulcanization reaction, the crosslinking process occurs predominantly in the continuous natural rubber phase surrounding the KNN particles. Consequently, the role of KNN is primarily to provide piezoelectric functionality while the vulcanized rubber matrix imparts flexibility and mechanical integrity.

5.2.2 Characterization of KNN-NR Composites

The structural characteristics of KNN filler were investigated using an X-ray diffractometer (XRD), Cu K α radiation, and Rigaku Miniflex 600 XRD (Nirmalagiri College, Kerala, India). The morphology and particle size of the synthesized KNN fillers were observed using a field emission scanning electron microscopy (FESEM), ZEISS Sigma 300 (National Institute of Technology, Calicut, India). The piezoelectric coefficient of the composites for different filler percentages is measured using PM300 (CMET, Thrissur, Kerala, India) and the percentage of error is calculated which indicates the variability, across measurements taken from different samples of the same filler percent composite. The dielectric constant of the composite system was measured using Novocontrol dielectric analyzer (University of Calicut, Kerala, India). The tensile strength and tear resistance of the KNN-NR composites were evaluated using an Instron universal testing machine (UTM) with a 5 kN load capacity (CFSC, Manjeri, Malappuram, India). The tests, conducted at a cross-head speed of 500 mm min⁻¹, as per ASTM D412 and ASTM D624 standards. These tests assessed stress, elongation at break, Young's modulus, and the modulus at 300% elongation at room temperature.

5.3 Results and Discussions

The FESEM micrograph of KNN-NR composites with 30% KNN in NR matrix is as shown in figure 5.4. It is clear from the figure that KNN fillers well dispersed in NR matrix leading to filler-matrix interaction.

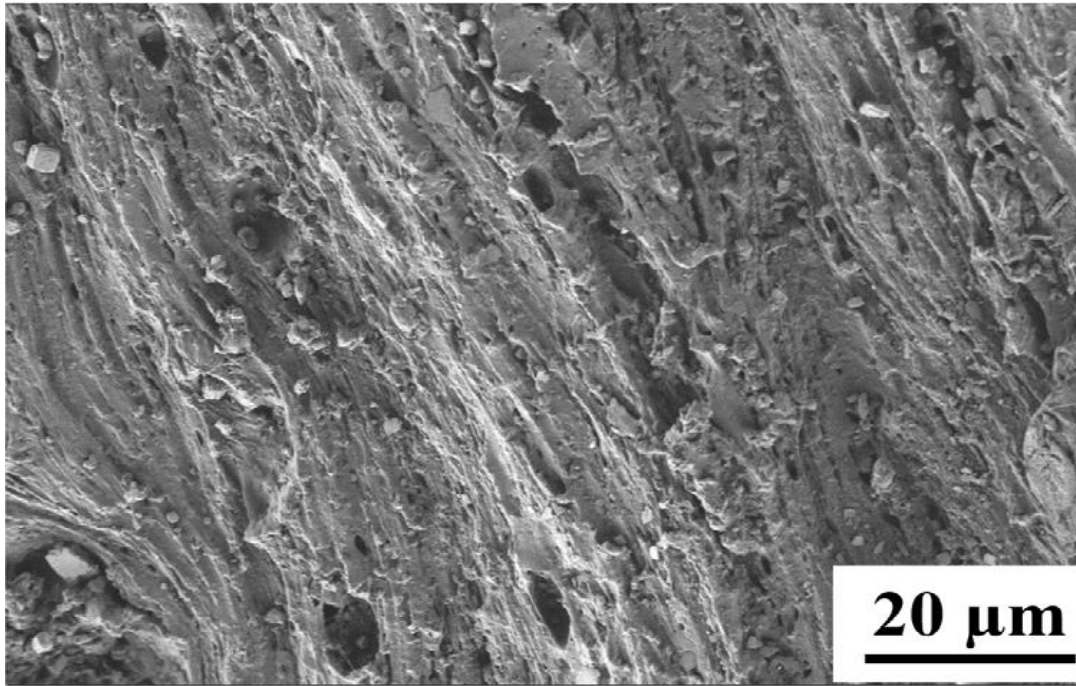


Figure 5.4: FESEM micrograph of 30% KNN-NR composite

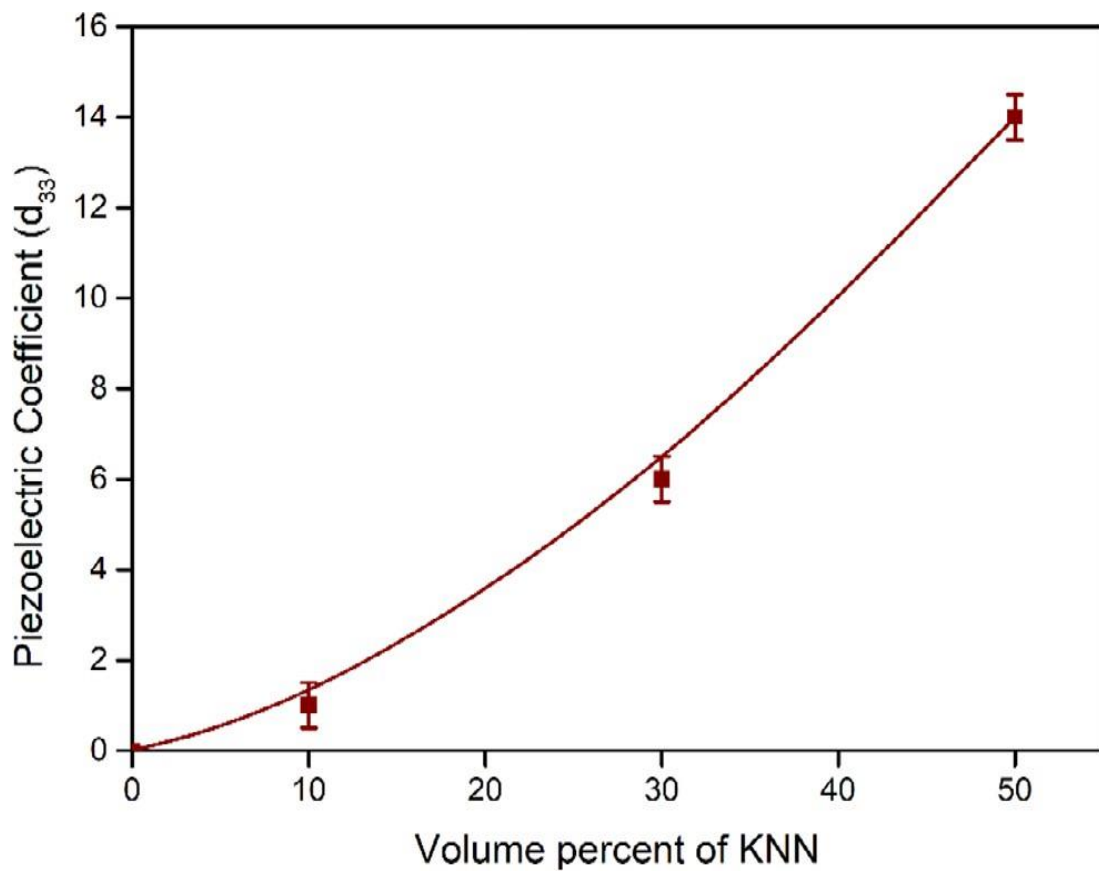


Figure 5.5: Variation of d_{33} of KNN-NR composites

KNN-NR composites were poled to align the randomly oriented domains and to make them piezoelectrically active. The optimized poling conditions were determined as the electric field- 3.5 kV/mm, temperature- 80 °C for 20 minutes. The d_{33} measurements were performed on 6 samples of each composition. Three composite samples were prepared independently, while the remaining three were cut from different regions of the same composite sheet. For each sample multiple d_{33} measurements were recorded and the reported values represent the average of these measurements. The measured d_{33} values exhibited only minor variations among the tested samples, demonstrating good repeatability of the measurements and satisfactory reproducibility of the fabrication process. The variation of piezoelectric charge coefficient (d_{33}) of the composite as a function of KNN filler volume percent in NR matrix is shown in figure 5.5. It is clear that the d_{33} value increases with higher KNN filler loading, attaining its highest value at 50% of filler loading. However, KNN-NR composite with 60% KNN filler loading could not be poled. This is because exceeding the optimal filler loading results in increased filler-filler interactions rather than favourable filler-matrix interactions. At higher loadings, there is a greater likelihood of agglomeration of KNN particles, which can lead to non-uniform dispersion within the matrix. This agglomeration reduces the composite's overall piezoelectric and dielectric performance by disrupting the poling process [21].

The dielectric constant of KNN-NR composite as a function of KNN filler concentration at different frequencies is illustrated in figure 5.6. As KNN filler percent increases, the dielectric constant also increases, reaching a maximum peak value at 50% filler loading, before decreasing sharply at 60%. Murali et.al. [21, 22] discusses about dielectric properties of the composite and explain that the interface region, along with the matrix and filler significantly impacts the dielectric properties. Filler agglomeration becomes more pronounced at higher filler loadings within the composite structure, which results the formation of voids and increased porosity. These agglomerates create localized regions of heterogeneity which disrupts the continuity of the dielectric medium. This disruption leads to increased scattering of the electric field and reduces the effective permittivity of the composite. Therefore, while initial filler additions may improve dielectric properties, excessive filler concentrations can degrade the dielectric performance due to structural in-homogeneities and increased porosity.

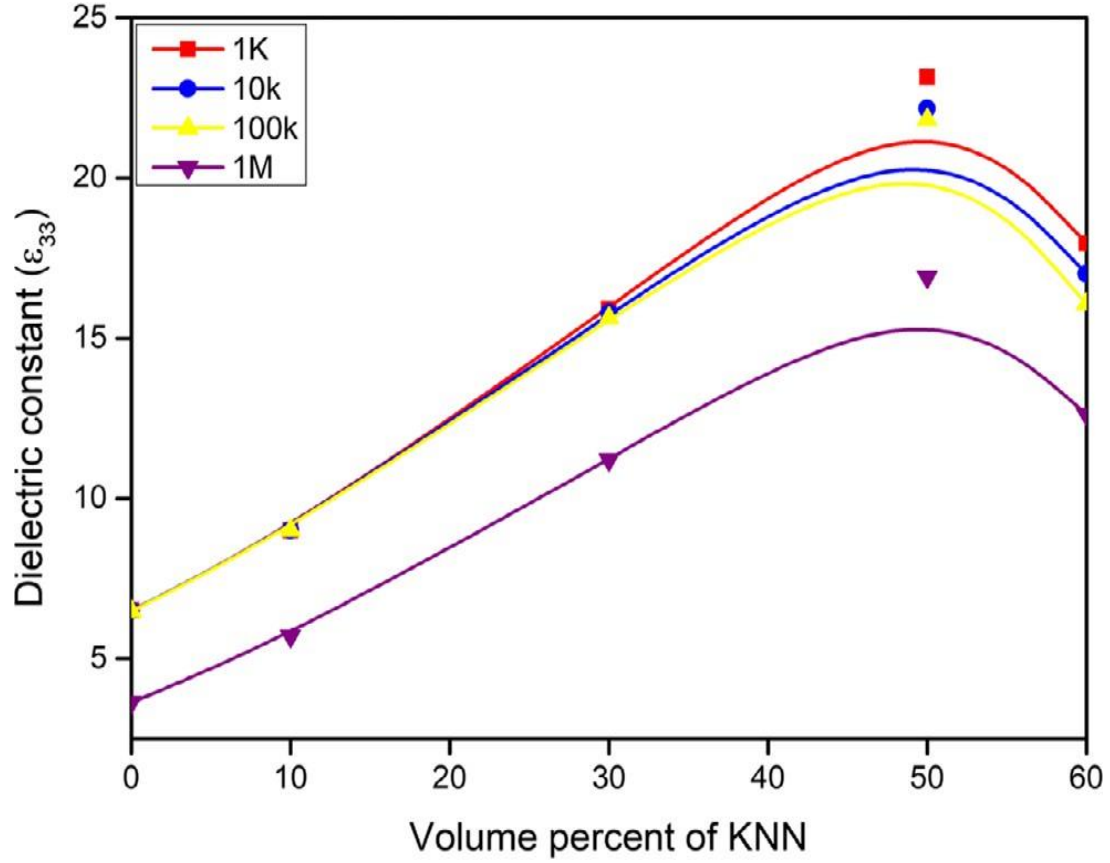


Figure 5.6: Variation of dielectric constant of KNN-NR composite

The piezoelectric voltage coefficient, g_{33} , is defined as the ratio of the piezoelectric charge coefficient (d_{33}) to the dielectric constant (ϵ_c) of the composite (23). It is given by the following equation, Equation (1)

$$g_{33} = \frac{d_{33}}{\epsilon_0 \epsilon_c} \quad (1)$$

Where,

ϵ_0 is the permittivity of free space.

Figure 5.7 shows the variation of piezoelectric voltage coefficient, g_{33} , as a function of KNN volume percent in the KNN- NR composite. The increase in the effective g_{33} is attributed to low dielectric constant and high d_{33} value of the composite. To achieve a high g_{33} value, the dielectric constant should be minimized while maximizing the piezoelectric charge coefficient d_{33} [23]. Figure 5.7 indicates that the g_{33} value increases with increasing KNN volume percent, with a maximum value of $72.519 \text{ mV m N}^{-1}$ achieved for the composite with 50% KNN filler loading,

which enhances its potential for sensor systems.

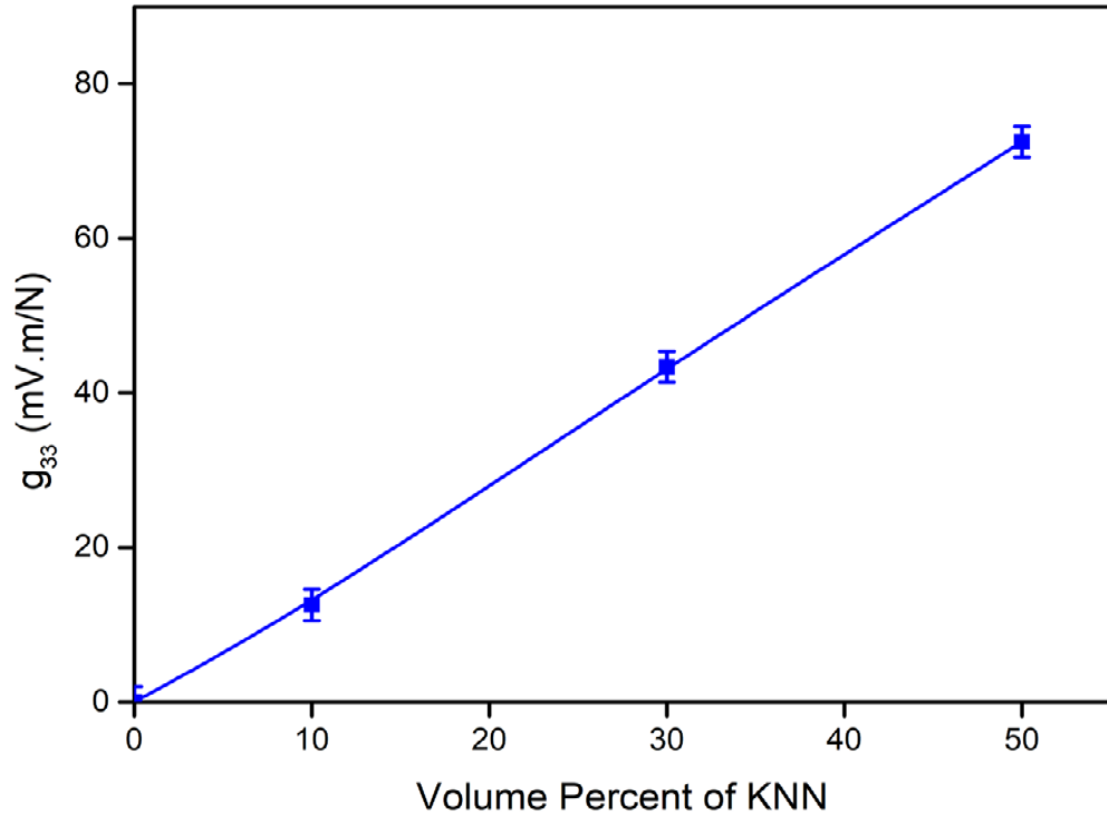


Figure 5.7: Variation of g_{33} of KNN-NR composites

When comparing the piezoelectric properties of KNN-NR composites with those of conventional piezoelectric materials such as PZT, it is found that the d_{33} value of the composites was significantly lower than those of PZT. However, the obtained g_{33} value of the composites was notably higher than those of ceramic-based piezoelectrics like PZT, which typically has a g_{33} value of around 11, as reported in previous studies [24]. The voltage coefficient plays a critical role in energy generation efficiency and a higher g_{33} value of the composites highlight their potential for energy harvesting applications [15].

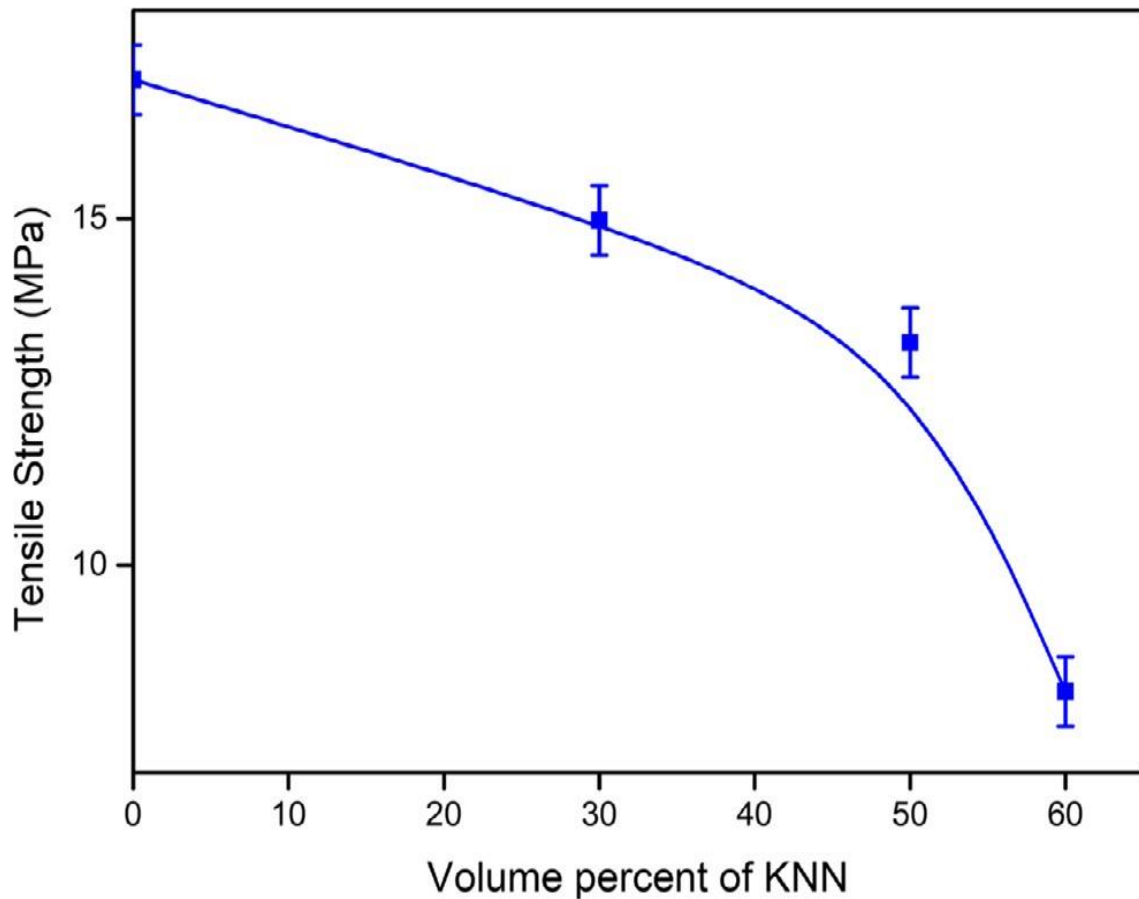


Figure 5.8: Tensile strength of KNN-NR composites

The tensile strength and Young's modulus of KNN-NR composites for different volume percentages of KNN filler is illustrated in figure 5.8 and figure 5.9 respectively. The maximum stress that a material can endure is represented by its tensile strength and Young's modulus measures how readily a material can deform. From figure 5.8 and 5.9, as the volume percent of KNN filler increases, the tensile strength and Young's modulus as well decreases. Although piezoelectric properties of the composites can be enhanced by the addition of filler, mechanical properties are adversely affected. The increased concentration of filler, beyond permissible limit, can lead to particle agglomeration or disruption of the NR matrix. Further, particle agglomeration diminishes the effectiveness of the filler-matrix interaction and weakening the overall mechanical integrity of the composite. Thus, the importance of balancing the piezoelectric properties with the need to maintain sufficient mechanical strength is highlighted [25].

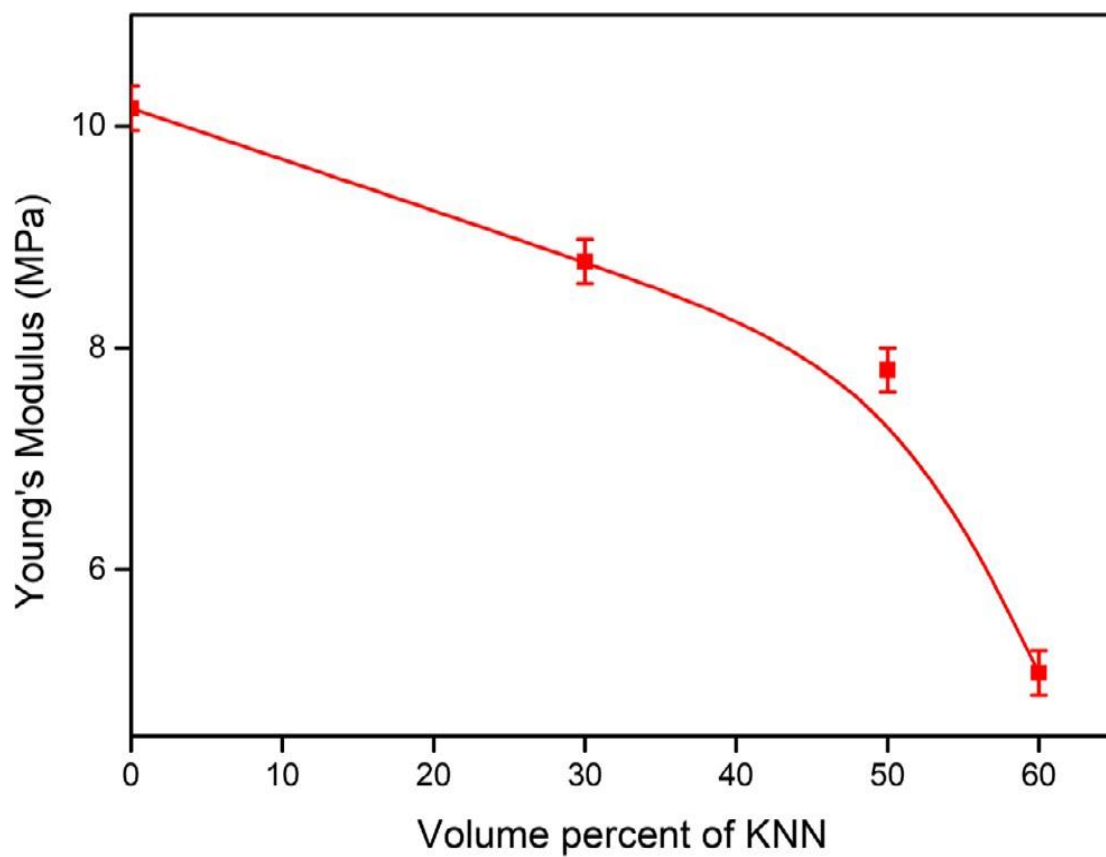


Figure 5.9: Young's modulus of KNN-NR composites

5.4 Conclusion

In this chapter, KNN-NR piezoelectric composites are successfully developed and characterized for potential energy harvesting applications. The composites were fabricated using conventional method of NR sheet preparation, i.e. conventional mixing and vulcanization method, with KNN as the active filler phase and NR as matrix, resulted in 0-3 KNN-NR composites. The piezoelectric properties of the developed composites exhibited a composition-dependent behaviour. Dielectric studies confirm the interfacial polarization and micro capacitive effects at the ceramic-polymer interface, attributed by the increased permittivity with filler percentage. By the incorporation of ceramic fillers in NR matrix, the tensile strength and elongation at break of NR is decreased. Overall, a promising balance is observed between flexibility, piezoelectric properties and mechanical durability of KNN-NR

composites, making them viable candidates flexible and wearable energy harvesting devices.

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Chapter 6

KNN-NYLON 11 COMPOSITES

6.1 Introduction

Polyamide-11 is a semi-crystalline thermoplastic synthesized from 11-aminoudecanoic acid, a monomer derived from castor oil [1]. Polyamide 11, commonly known as nylon 11, belongs to the family of long chain aliphatic polyamides. They are known for its excellent chemical resistance, thermal stability, mechanical flexibility and low moisture absorption compared to other polyamides like nylon 6 and nylon 6, 6. The bio-based origin of nylon 11 makes it significantly relevant for increasing demand for sustainable and green materials development [2, 3, 4]. The molecular structure of nylon 11 comprises of repeating amide linkages which exhibits strong hydrogen bonding, resulting in a well-organized crystalline phase. This contributes to the robust mechanical behaviour and semi-rigid nature of nylon 11 under varying environmental conditions [5, 6].

Beyond the conventional use of nylon 11, it has also attracted attention in textiles like automotive parts and engineering plastics in the field of functional materials. In addition to this, promising results have been given by nylon 11 in the field of ferroelectric and piezoelectric properties [7]. These characteristics of nylon 11 are exhibited in its γ -phase, which can be attributed to the alignment of dipoles within the crystalline domains under external electric field [8]. Nylon 11, when comparing with traditional piezoelectric ceramics have modest piezoelectric coefficient. Moreover, nylon 11 is a promising candidate for polymer based piezoelectric systems, with the combination of flexibility, processability and environmental benignity. Nylon 11 can also be used in applications where mechanical compliance and lightweight features are essential [9-11].

When effectively used as a matrix in ceramic-polymer composite systems, nylon 11 can act as a flexible binder that enables mechanical durability and improved flexibility. This makes nylon 11 based piezoelectric composites suitable for dynamic and wearable applications [12, 13]. The compatibility with ceramic fillers combined with its moderate melting point ($\sim 180^\circ\text{C}$) makes nylon 11 favourable for developing 0-3 piezoelectric composites with lead-free ceramic fillers [14, 15]. This combination of nylon 11 with KNN fillers enhances the overall functionality of the composite for example; improved electromechanical coupling, acoustic impedance matching and the

properties of composites can be tuned through filler content and orientation control [16, 17].

The δ' -crystalline phase of nylon 11 exhibits intrinsic piezoelectric behaviour due to the alignment of its molecular dipoles. In the present work, the incorporation of KNN into the nylon 11 matrix is expected to produce a synergistic enhancement in the overall piezoelectric response through the combined contributions of the piezoelectric ceramic filler and the polar polymer matrix. The KNN particles act as the primary source of high piezoelectric activity, while the nylon 11 contributes additional polarization and provides a flexible medium for efficient transfer of externally applied mechanical stress to the ceramic particles. Moreover, the presence of KNN filler can promote local electric field concentration during poling, facilitating improved dipole alignment within the nylon 11 matrix and more effective polarization of the ceramic phase. The intimate interfacial interaction between the filler and polymer matrix also enhances stress transfer, enabling more efficient electromechanical coupling under mechanical deformation.

Among different polymer matrices, nylon 11 has emerged as a promising polymer matrix in recent years [1, 18]. The ability to crystallize into polar phases enables nylon 11 to exhibit ferroelectric and piezoelectric properties [19]. Several studies explored the compatibility of nylon 11 with ceramic fillers like BaTiO₃, PZT, which showed improved dielectric and piezoelectric responses, while retaining flexibility, under proper poling conditions [15, 20].

The objective of this chapter is to develop KNN-nylon 11 0-3 composites by integrating the piezoelectric response of lead-free KNN with the flexibility and processability of nylon 11. This work will yield materials that are suitable for flexible sensors, energy harvesting devices and wearable electronics [16, 20]. Nylon11's biocompatibility and environmental stability also open avenues for its potential use in implantable and biomedical piezoelectric devices [21]. In spite of KNN's position as a leading lead-free piezoelectric ceramic, the literature on KNN-nylon11 composites remains relatively sparse. Challenges in the form of particle agglomeration, poor dispersion and weak interfacial bonding with polymers like PVDF and nylon have been highlighted in some of recent studies [22, 23]. While limited work has specifically focussed on the thermal melt processing routes and their effect on

piezoelectric behaviour, especially using brabender mixing or industrial scale melt blending techniques. This gap, however, provides an opportunity to explore the systematic processing and characterization of KNN-nylon11 composites [9, 24].

The present work builds upon these foundational principles with an aim to produce well dispersed flexible KNN-nylon 11 composites by adopting a controlled melt blending and hot-pressing approach. The goal is to study the conditions that influence structural, dielectric, piezoelectric properties and how these materials can potentially contribute to the development of next generation flexible piezoelectric systems.

6.2 Chemical structure of nylon11

Nylon 11, a semi-crystalline aliphatic polyamide, synthesized from the monomer 11 aminoundecanoic acid ($\text{NH}_2-(\text{CH}_2)_{10}-\text{COOH}$). With an amino group ($-\text{NH}_2$) at one end and a carboxylic acid group ($-\text{COOH}$) at the other end, the monomer is a bifunctional compound which can undergo self-condensation polymerization to form long chain polyamides [1, 4]. The repeating unit in nylon11 is as follows [25]:



$(-\text{CO}-\text{NH}-)$	$(\text{CH}_2)_{10}$
The amide linkage ($-\text{CO}-\text{NH}-$) is formed through a condensation reaction between carboxylic acid group of the monomer and the amine group of another.	The $(\text{CH}_2)_{10}$ methylene chain between the amide bonds gives nylon11 its aliphatic flexibility, hydrophobicity and semi-crystalline nature.

Table 6.1: Nylon 11 structure

Structure and properties:

- When compared to shorter-chain nylons like nylon 6 or nylon 66, the long hydrocarbon chain (ten methylene units) between the amide bonds in Nylon 11 results in low moisture absorption and high hydrophobicity. This gives nylon 11 superior dimensional stability and resistance to hydrolysis [4].
- The amide group ($-\text{CONH}-$) being polar, is capable of forming intermolecular hydrogen bonds contributing to the polymer's crystallinity and mechanical strength. These hydrogen bonds occur between the $-\text{NH}$ group of one chain and the $-\text{C}=\text{O}$ group of an adjacent chain which leads to formation of ordered regions (crystallites) in the polymer matrix [19].
- Nylon 11 can exist in different crystalline phases depending on the processing conditions, such as α , γ and δ' phases. The γ -phase of nylon 11 is important as it allows partial alignment of the dipoles in the amide group when subjected to an external field and is particularly important for ferroelectric and piezoelectric behaviour [26, 27].
- The regularity and symmetry in the chemical structure of nylon 11 help in forming highly oriented films or fibres through processing techniques like stretching or hot pressing. This characteristic is especially crucial for enhancing piezoelectric performance in polymer-ceramic composites [20, 23].

6.3 Processing and fabrication of KNN-nylon11 composites

Fabrication of KNN-nylon 11 composites require careful control over processing conditions to ensure uniform dispersion of ceramic particles within the polymer matrix in order to maintain desirable crystallinity and interfacial interaction. These composites are typically prepared in a 0-3 connectivity configuration, where KNN ceramic fillers are uniformly dispersed throughout a continuous nylon11 matrix. The fabrication method significantly influences the final microstructure and functional properties of the composite [20, 28, 29].

In the present work, melt blending was employed for composite preparation, followed by hot pressing to obtain dense, flexible composite sheets. A brabender mixer, shown in figure 6.1 below, was used to carry out the melt blending. Pre-weighed nylon 11 was mixed with synthesized KNN ceramic fillers via solid state

reaction method and then melt blended in the brabender mixer at 200 °C for 30 minutes. This temperature was specifically chosen to exceed the melting point of nylon 11. This continuous mixing process promotes uniform distribution of the KNN fillers throughout the molten polymer matrix and minimizes agglomeration. The mixing was carried out for 10, 20, 30, 40, 50 volume percent of KNN in nylon 11 matrix.



Figure 6.1: Brabender

After the melt blending, the composite mixture was transferred to a hydraulic press, shown in figure 6.2, for sheet formation.



Figure 6.2: Hydraulic press (hot press)

The blended material was hot pressed at 200 °C for 40 minutes under constant pressure to produce flat composite sheets of 2 mm thickness as shown in figure 6.3. The pressing temperature was carefully maintained to retain the molten state of nylon 11 while allowing the ceramic particles to become well embedded within the matrix.



Figure 6.3: KNN-nylon 11 composite sheets and pellets

This fabrication approach resulted in the formation of flexible composite sheets with improved structural integrity and dielectric performance. The processed composites are subsequently subjected to poling under a high DC electric field to align the molecular dipoles and activate piezoelectric response.

6.4 Results and Discussions

6.4.1 Microstructure

FESEM micrograph of the cross-sectional view of 30 volume percent of KNN in nylon 11 matrix is shown in figure 6.4 and figure 6.5. A higher magnification FESEM micrograph of the matrix clearly shows the primary particles inside the composite.

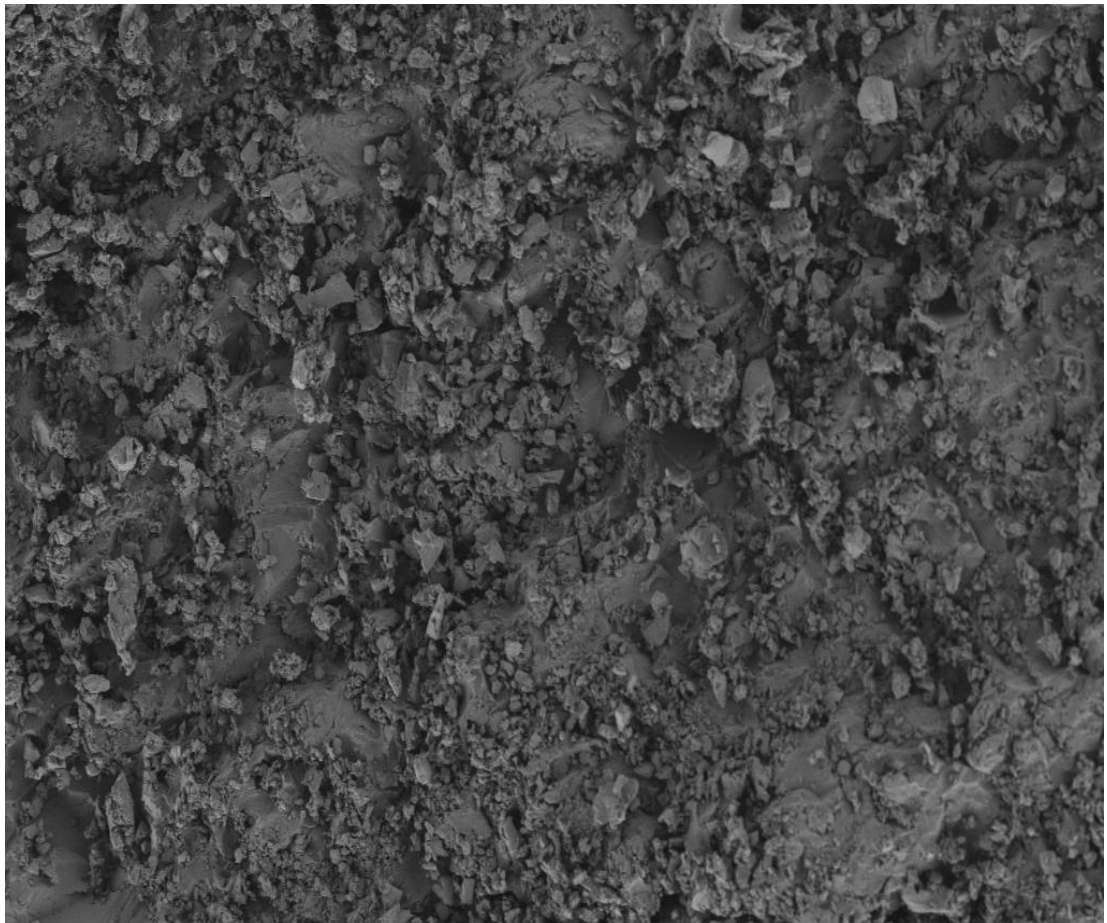


Figure 6.4: FESEM micrograph of 30 volume percent of KNN in nylon11 matrix

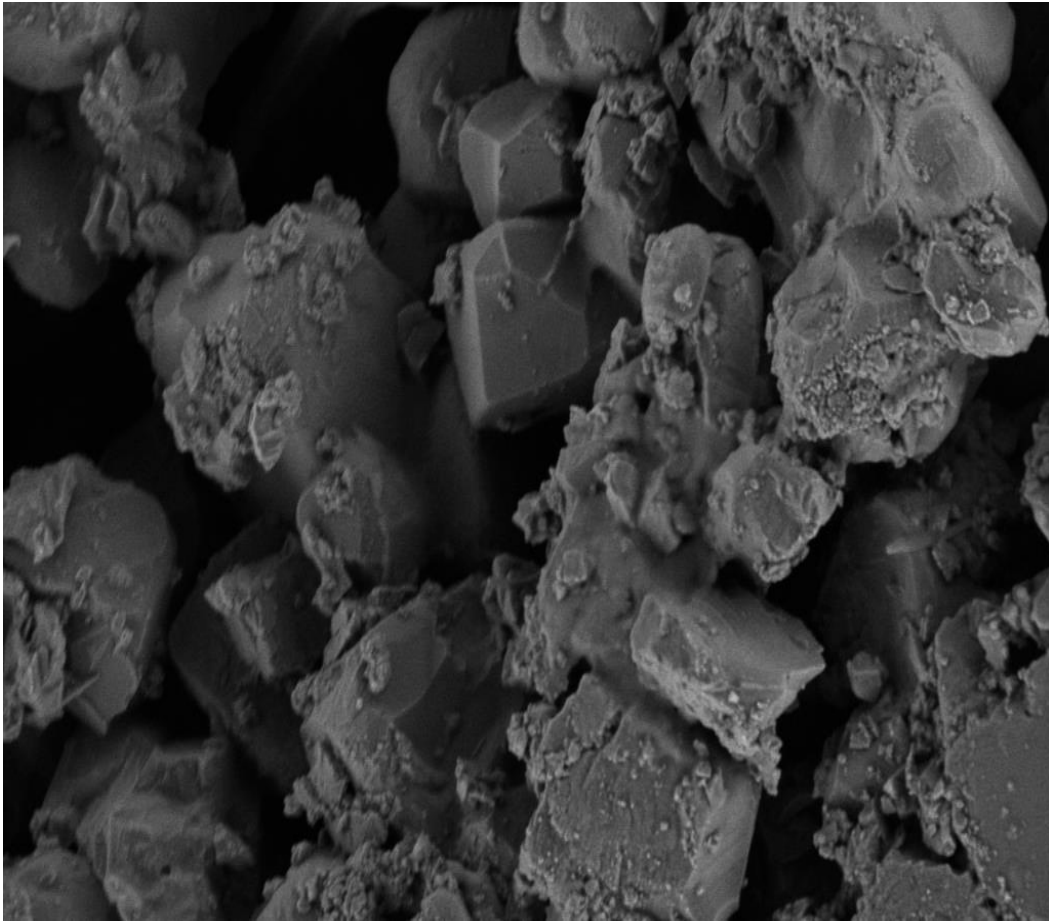


Figure 6.5: FESEM micrograph showing the primary particles

The micrographs confirm the formation of fully dense KNN-nylon 11 composites with a spatially uniform distribution of the KNN fillers. The KNN fillers are well distributed and show limited agglomeration, hence 0-3 configuration.

6.4.2 Electrical properties

In figure 6.6, the dielectric constant of the composite for varying volume percent of KNN in nylon 11 matrix at various frequency ranges are shown. The figure clearly shows a trend wherein the dielectric constant increases significantly with increasing KNN volume percent and after 30 volume percent KNN loading, a subsequent decrease in the dielectric values is seen. The decrease in the dielectric constant after 30 volume percent is possibly due to particle agglomeration, percolation threshold thereby affecting dielectric uniformity and increased interface defect [20, 29]. This trend was consistent across all tested frequencies. The peak observed at 30 volume percent, suggests that this represents the optimal ceramic loading at which interfacial polarization reaches its maximum without

excessive agglomeration or percolation. These findings clearly highlight the importance of KNN loading optimization in order to achieve superior dielectric performance in the composites.

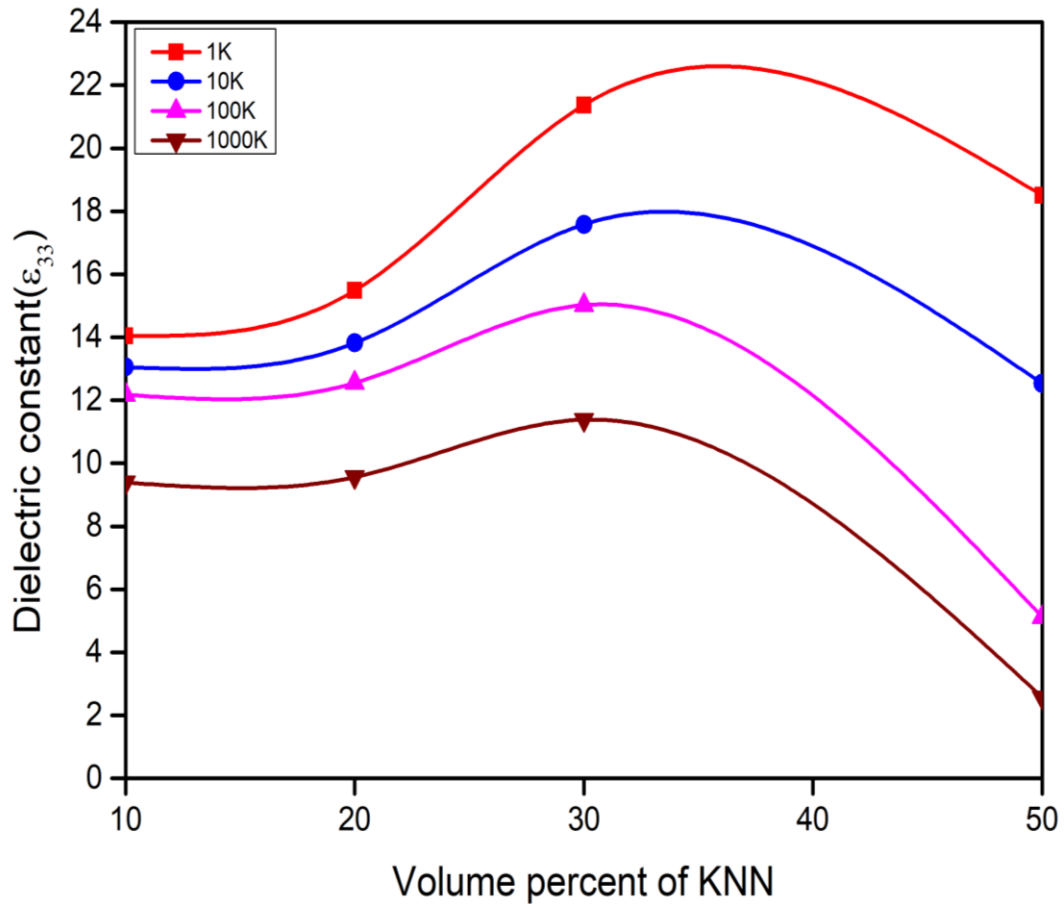


Figure 6.6: the dielectric properties of the composites as a function of KNN volume percent.

The variation of dielectric loss ($\tan \delta$) of KNN-nylon 11 composites with respect to the volume percent of KNN, measured at different frequencies is shown in Figure 6.7. The dielectric loss of KNN-nylon 11 composites exhibits a composition-dependent behaviour at low frequencies. At lower frequencies (particularly 1 kHz), an increase in the $\tan \delta$ with KNN volume percent is observed. A gradual rise beyond 30 volume percent indicates enhanced energy dissipation due to interfacial polarization and possible space charge accumulation. However, the dielectric loss remains low and nearly constant at higher frequencies (100 kHz and above), reflecting suppressed polarization relaxation and minimal conductive losses [29, 30]. These results suggest that the composites with up to 30

volume percent of KNN maintain favourable balance between dielectric constant and loss, thereby making them suitable for piezoelectric and energy harvesting applications, particularly at mid-to-high frequencies.

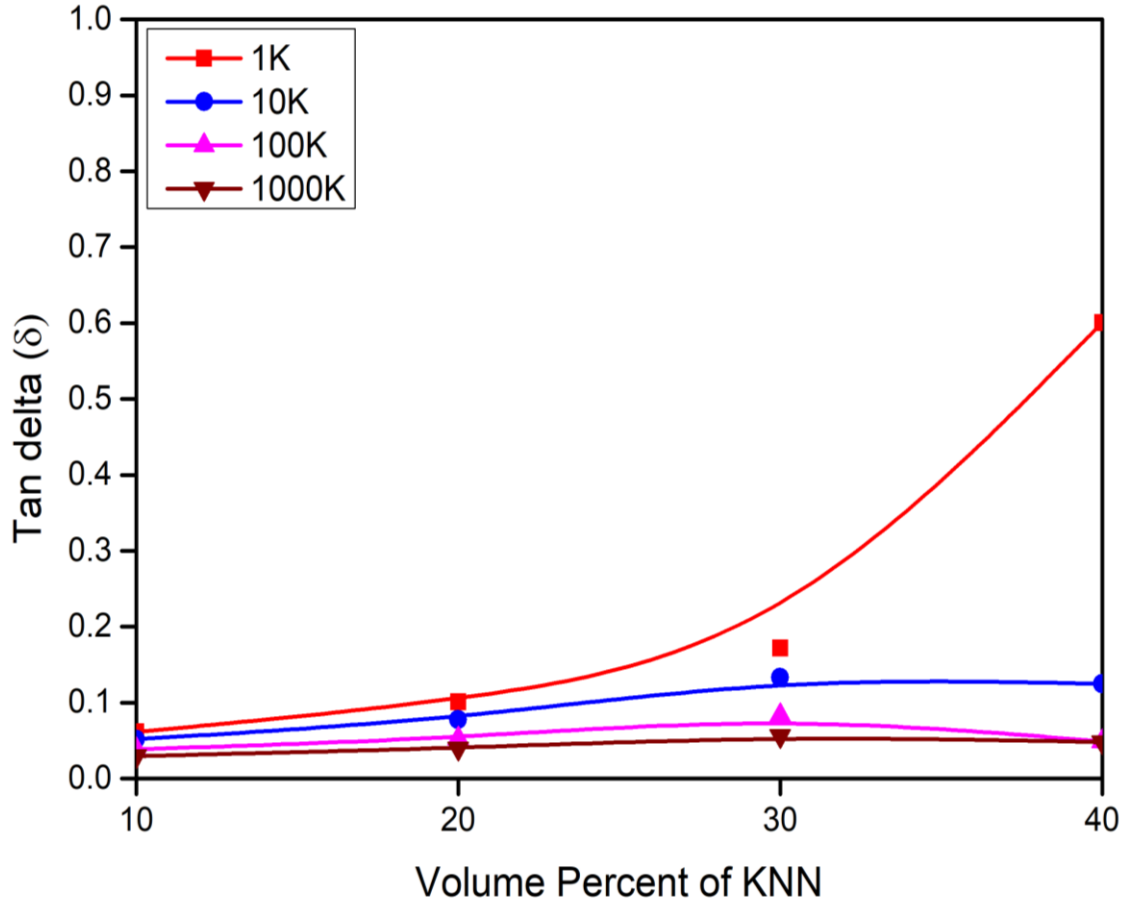


Figure 6.7: Variation of dielectric loss with volume percent of KNN-nylon 11 composites at different frequencies.

The electrical resistivity of KNN-nylon 11 composites shown in figure 6.8 explains a strong dependence on both filler volume percent and frequency. It is observed that at lower frequency (1 kHz), the composites demonstrate high resistivity at low KNN content, which progressively decreases as the ceramic loading increases which is likely due to enhanced charge transport pathways and interfacial conduction [31, 32]. The resistivity remains consistently low at higher frequencies (100 kHz and 1 MHz), indicating suppressed interfacial polarization and dielectric losses [33]. At lower frequency, it is observed that the resistivity initially decreases with increasing KNN

filler content, reaching a minimum at near 30 volume percent of KNN filler in nylon 11 matrix. A slight increase in resistivity is observed around 40 volume percent of KNN filler in nylon 11 matrix, which may be attributed to the onset of filler agglomeration. The filler agglomeration leads to non-homogeneous dispersion and disruption of the percolative conduction network. Additionally, microstructural changes such as void formation and weak interfacial bonding may also contribute to this behaviour [29, 32, 33]. These characteristics of KNN-nylon 11 composite highlight the complex interplay between filler percentage, structural and piezoelectric properties in composite system. These trends suggest that, higher KNN content on one hand enhances dielectric properties, on the other hand, it also introduces leakage pathways. In order to obtain a balanced performance for applications, these properties of the KNN-nylon 11 composites must be balanced.

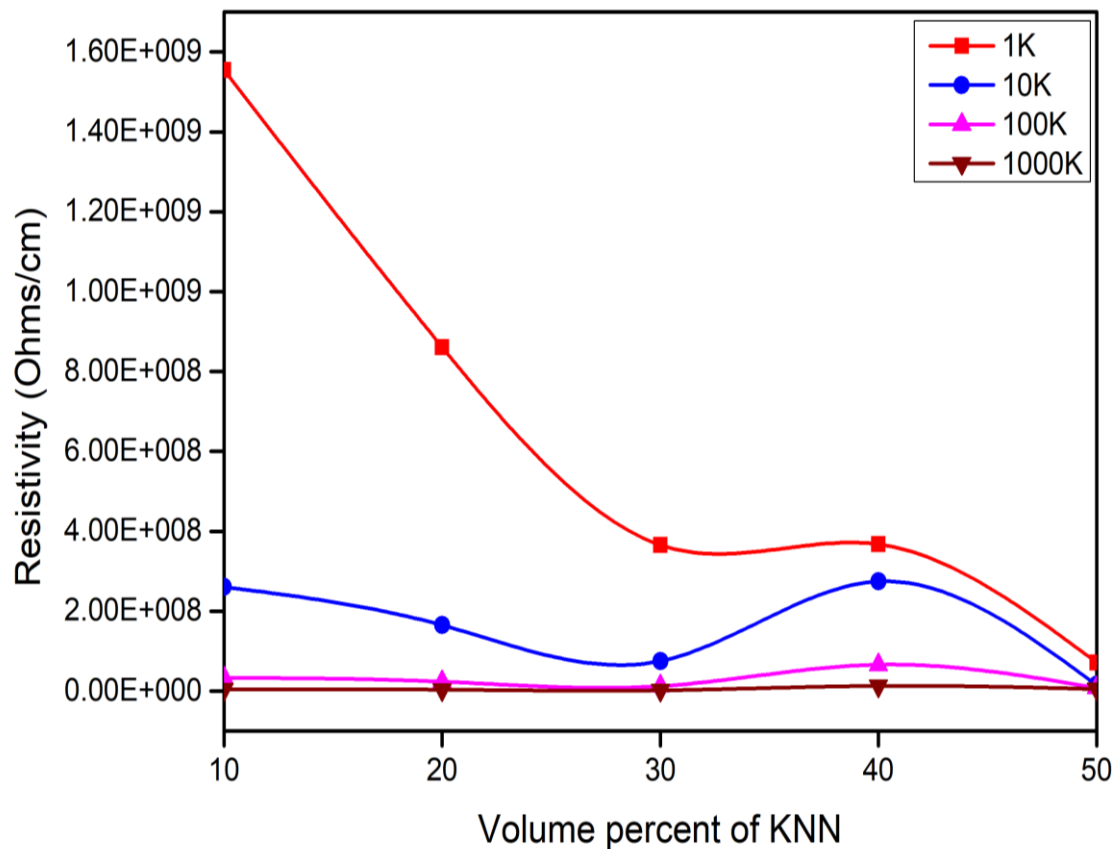


Figure 6.8: Variation of electrical resistivity of KNN-nylon 11 composites with volume percent of KNN at different frequencies.

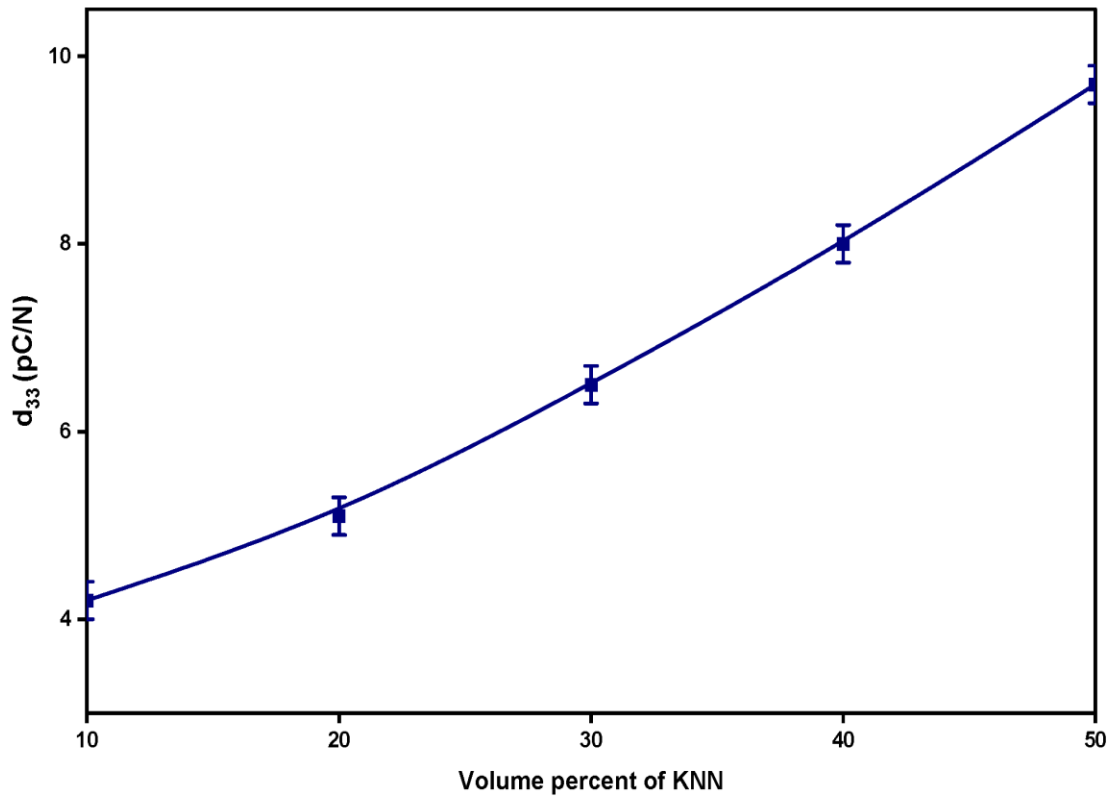


Figure 6.9: Variation of d_{33} with KNN volume percent

Figure 6.9 illustrates the variation of d_{33} value of KNN-nylon 11 composites with varying volume percent of KNN filler in nylon 11 matrix. The d_{33} measurements were performed on 6 samples of each composition. Three composite samples were prepared independently, while the remaining three were cut from different regions of the same composite sheet. For each sample multiple d_{33} measurements were recorded and the reported values represent the average of these measurements. The measured d_{33} values exhibited only minor variations among the tested samples, demonstrating good repeatability of the measurements and satisfactory reproducibility of the fabrication process. A gradual trend of increasing d_{33} is observed from the graph. From the graph a maximum value of 9.8 pC/N is achieved at 50% of KNN filler in nylon 11 matrix. The contribution of active piezoelectric KNN phase provides efficient stress-to-charge conversion lead to the enhancement of d_{33} value. . The observed non-linear d_{33} value demonstrates a synergistic effect, potentially due to improved poling efficiency and KNN fillers being well dispersed within the insulating nylon11 matrix [34].

Piezoelectric voltage coefficient g_{33} , with increasing volume percent of KNN filler in nylon 11 matrix is shown in figure 6.10. It is observed that g_{33} value increases steadily with increase in KNN filler volume percent and a maximum of 37.1 mV.m/N is obtained at 50% KNN filler content. This can be attributed to the enhanced piezoelectric response of the composite as the active piezoelectric ceramic phase content increases. The observed gain in g_{33} with increasing filler content clearly highlights the potential of KNN-nylon 11 composites as flexible piezoelectric sensors.

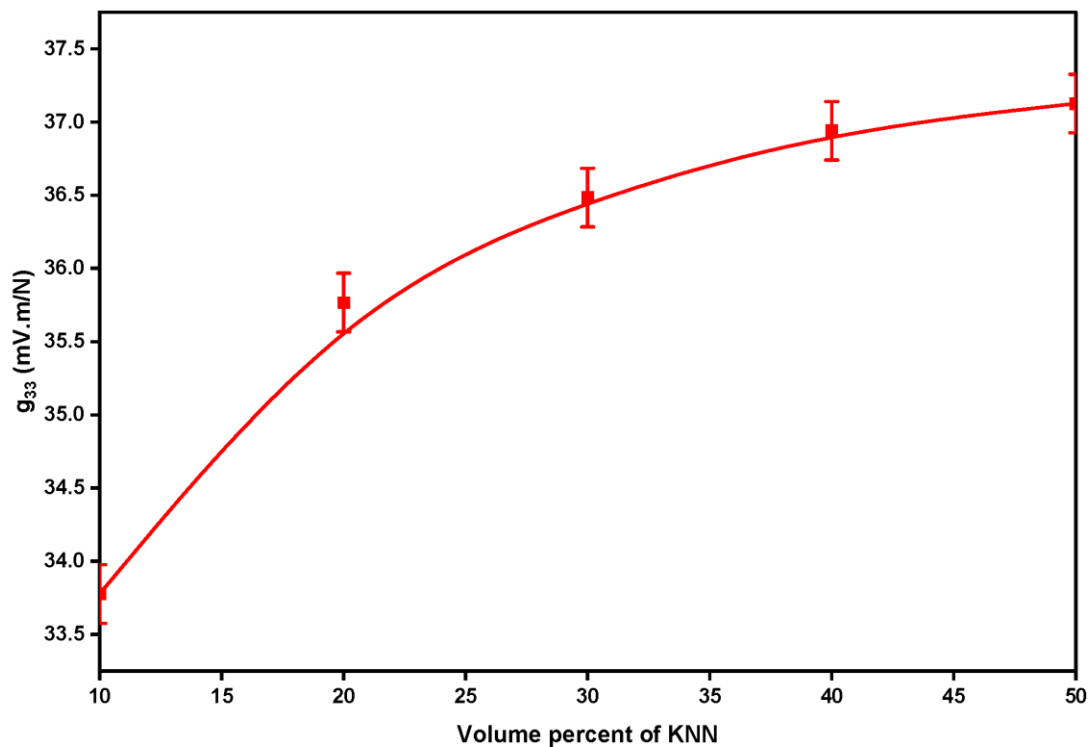


Figure 6.10: Variation of g_{33} with KNN volume percent

P-E hysteresis loop measurements give valuable insight into the ferroelectric and dielectric behaviour of polymer-ceramic composites. In this study, the polarization behaviour of KNN-nylon 11 composites at room temperature is investigated using TF analyser 3000 for CMA. The measurements were carried out at a fixed frequency (1 Hz), under a triangular waveform voltage and the field was varied up to a maximum of ± 500 V. The composites with varying KNN volume percent (10–50) were tested to evaluate the effect of ceramic content on the ferroelectric response and are shown below in figure 6.11-6.15 respectively.

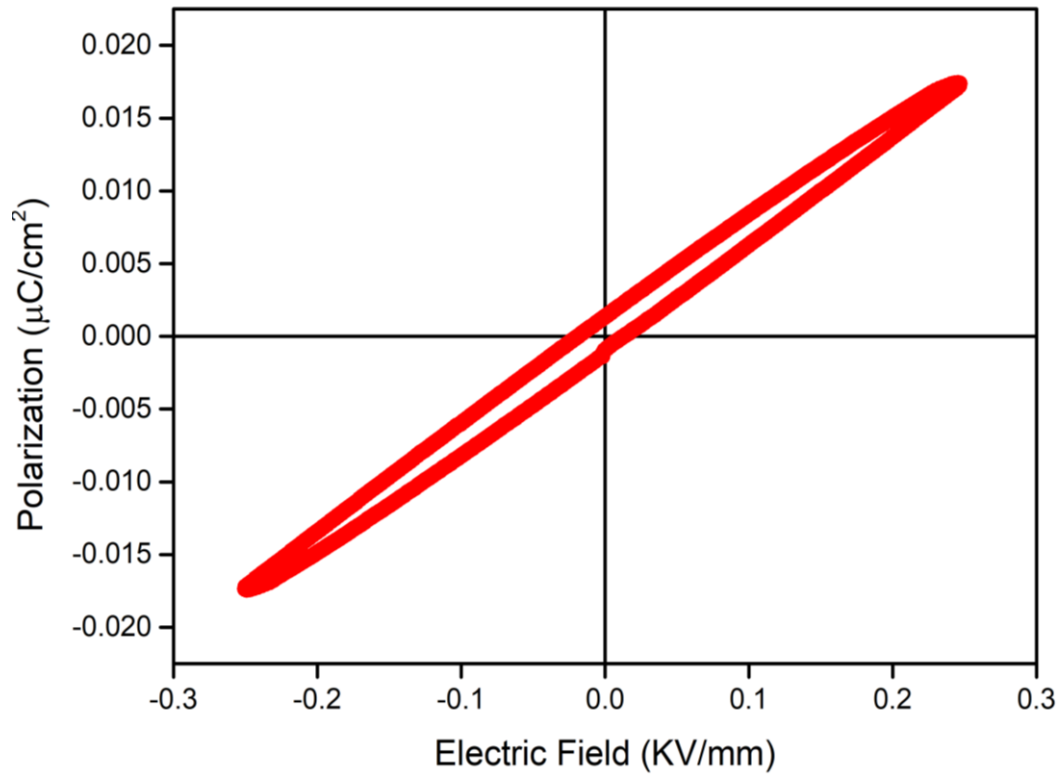


Figure 6.11: Polarization hysteresis loop for 10% KNN-nylon 11 composites

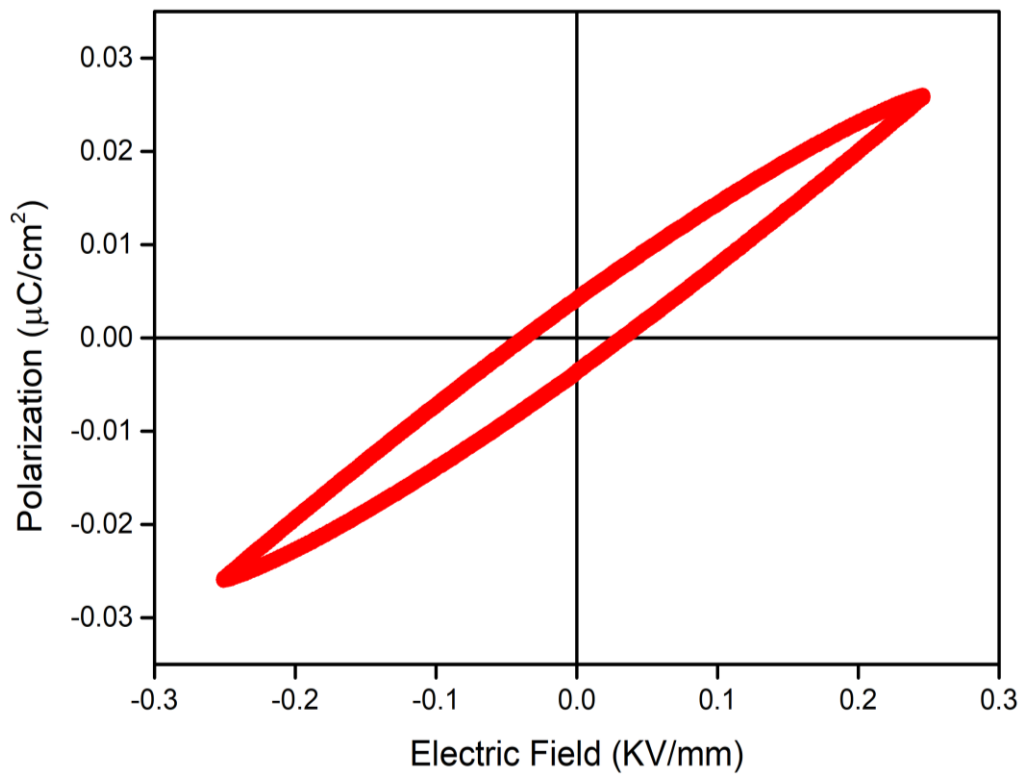


Figure 6.12: Polarization hysteresis loop for 20% KNN-nylon 11 composites

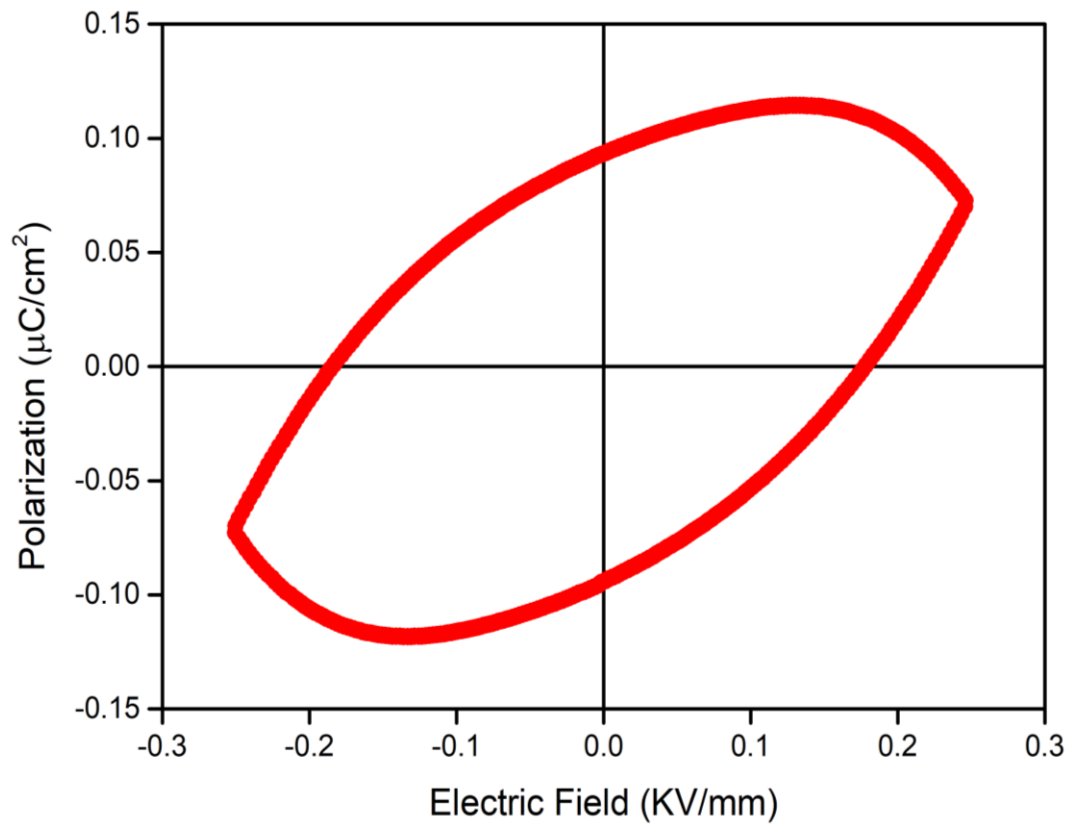


Figure 6.13: Polarization hysteresis loop for 30% KNN-nylon 11 composites

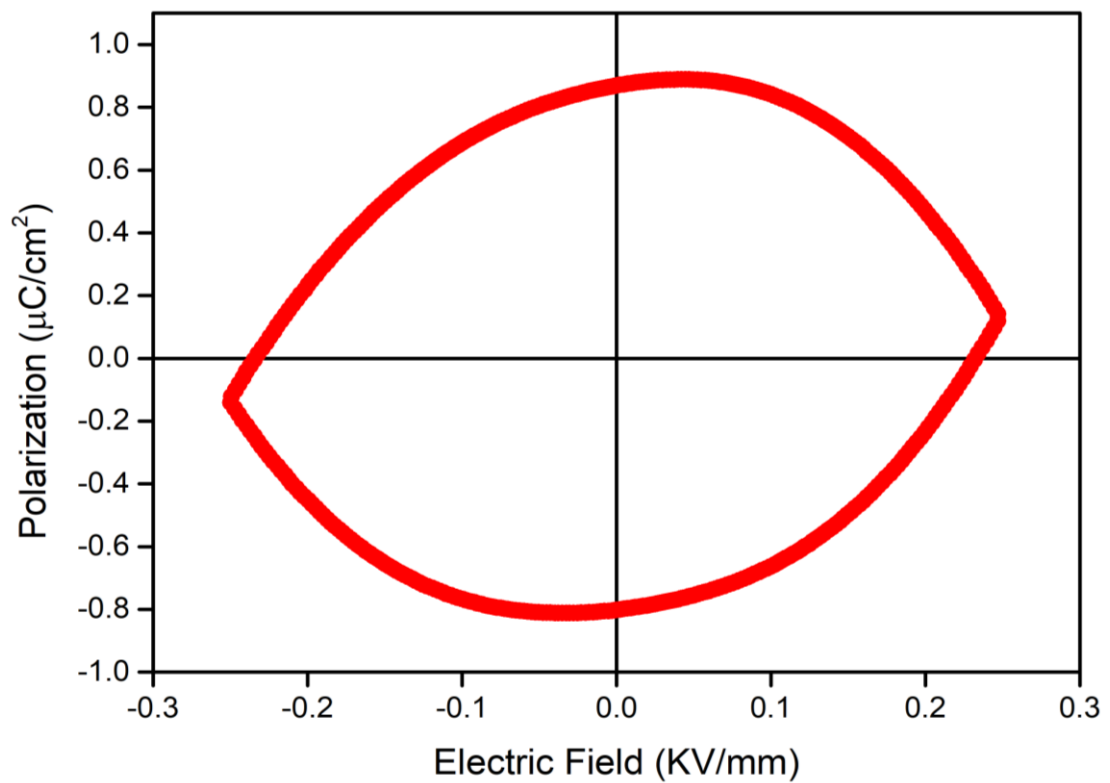


Figure 6.14: Polarization hysteresis loop for 40% KNN-nylon 11 composites

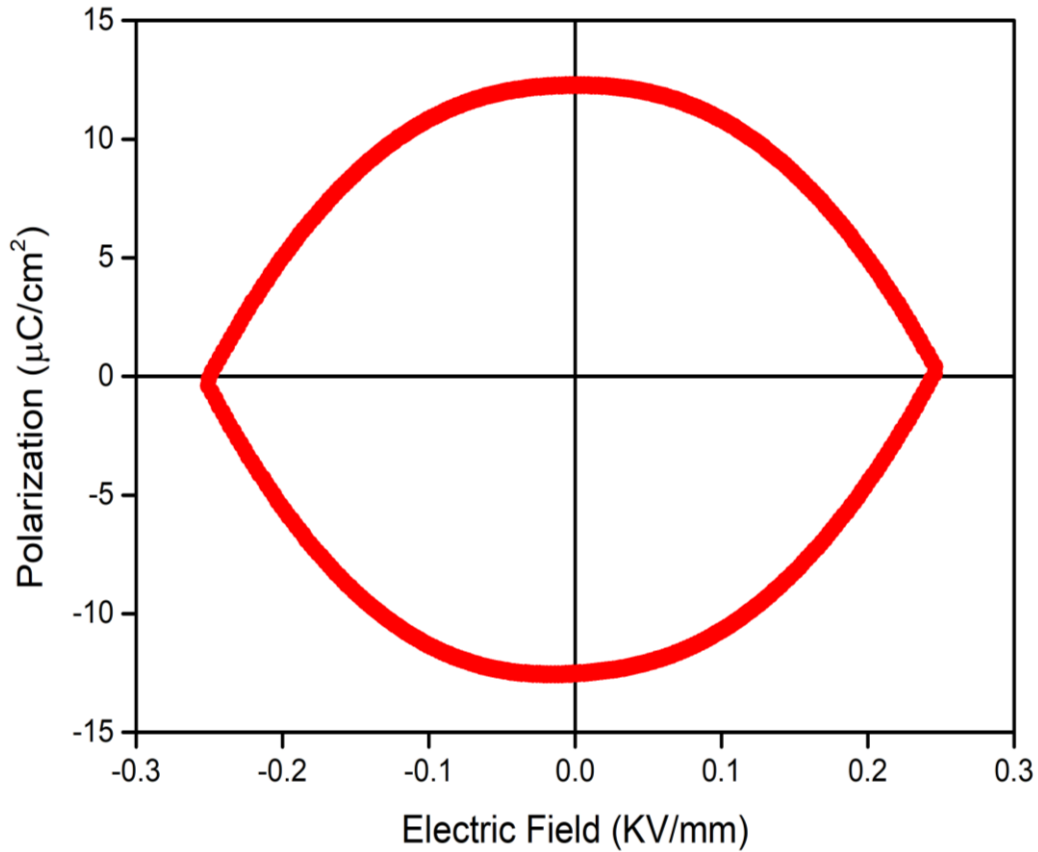


Figure 6.15: Polarization hysteresis loop for 50% KNN-nylon 11 composites

The P-E loop of KNN-nylon 11 composites reveals a composition dependent behaviour at lower filler content (10-20%) and the loops were comparatively narrow which indicates dielectric behaviour with negligible polarization switching. On the other hand, a significant loop opening was observed from 30% onwards, which can be characterized by increased remnant polarization and coercive field, signifying effective ferroelectric contribution from KNN ferroelectric phase. Saturation effects are observed at 50%, possibly due to filler agglomeration and increased leakage [35, 37]. The observed P-E hysteresis loop for 50% KNN is closed and nearly symmetric with identifiable remanent polarization and coercive field, indicating that the measured response is predominantly ferroelectric in nature. Although complete saturation may not have been achieved within the applied electric field range, the observed loop characteristics indicate that the measured polarization primarily arises from the intrinsic ferroelectric behaviour of KNN filler phase embedded in the nylon 11 matrix rather than from leakage-induced distortion.

A comparative result is given in table 6.2. These results clearly highlight that 30-40% ceramic filler is the optimum range for achieving enhanced ferroelectric behaviour in KNN-nylon 11 composites.

Volume percent of KNN	Loop shape	Ferroelectric behaviour
10	Linear/Elliptical	Dielectric dominant
20	Slightly open	Beginning ferroelectric
30	Clear hysteresis	Intermediate behaviour
40	Rectangular loop	Strong ferroelectric
50	Distorted/flat	Possible saturation/leakage

Table 6.2: P-E loop characteristics of KNN-nylon 11 composites (34-37)

6.4.3 Moisture absorption

Nylon 11 is a polar polyamide containing amide functional group. The interaction of nylon 11 with moisture is an important characteristic that directly influences its dielectric, mechanical and long-term performance. Therefore, rather than evaluating only the surface wettability, the present study focused on moisture absorption behaviour. It will provide more application-oriented assessment of the interaction between the composite and moisture. Moisture uptake reflects not only the surface characteristics but also the diffusion of water into the bulk material, making it particularly relevant for polymer composites intended for flexible piezoelectric applications. When compared to other polyamides, nylon 11 exhibits significantly low moisture absorption [11]. The polar amide group present in nylon 11, forms hydrogen bonds with water molecules which leads to notable moisture absorption [13]. The moisture absorption of KNN-nylon 11 piezocomposites for different percentage of

KNN filler in nylon 11 matrix is illustrated in the figure 6.16. From the graph it is evident that the incorporation of KNN filler significantly reduced the overall moisture absorption of the composite. This reduction in the moisture absorption is attributed to the ceramic filler replacing the hydrophilic polymer regions, thus hindering water diffusion [10].

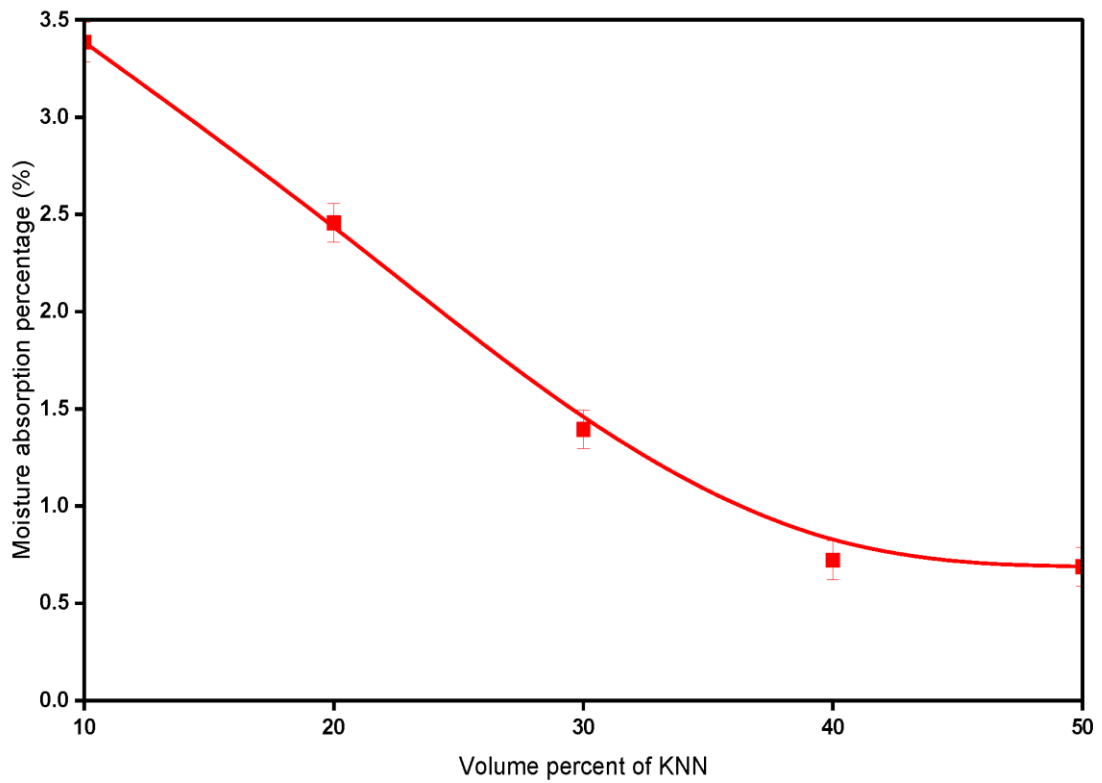


Figure 6.16: Moisture absorption behaviour of KNN-Nylon 11 composites

6.5 Conclusion

The fabrication and characterization of KNN-nylon 11 0-3 composites are presented in this chapter. Nylon 11, a semi-crystalline bio-based polymer was chosen as the polymer matrix due to its inherent flexibility and moderate dielectric response. The compatibility of nylon 11 with KNN fillers and its processability makes KNN-nylon 11 an excellent candidate for wearable electronics applications. Melt blending technique using brabender mixer was employed for composite fabrication, followed

by hot pressing to form sheets. Piezoelectric and dielectric properties of KNN-nylon 11 composite exhibited a composition dependent behaviour, indicating effective stress transfer across ceramic-polymer interface. Compositional dependent behaviour was also observed for ferroelectric properties, with well-defined loops obtained at higher volume percentage. The environmental stability of KNN-nylon 11 was confirmed from the moisture absorption behaviour analyses. It has been observed that, nylon 11 being hydrophilic in nature is moderated by KNN ceramic content. This work highlights the foundation for further research into robust and sustainable KNN-nylon11 composites for sensor and energy harvesting applications.

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Chapter 7

PERFORMANCE ANALYSIS OF COMPOSITES

7.1 Introduction

In the modern era, a surge in technological advancement is observed in the field of self-powered smart sensors and portable electronics. This has channelized global research towards finding efficient, environmentally sustainable materials that are capable of converting mechanical energy into usable electrical signals and vice versa. Piezoelectric materials have been emerged as a promising area for research and development, predominantly due to their ability to harvest low-frequency mechanical vibrations and their effective response to external stimuli [1]. Within the field of piezoelectric composites, 0-3 ceramic polymer composites, have gained widespread attention. The widely acceptance of 0-3 composites is due to the fact that they consist of isolated piezoelectric filler embedded within a continuous polymer matrix, which offer a unique balance of mechanical flexibility, tunable electrical properties and ease of fabrication [2]. This is true especially in the microstructural arrangement of 0-3 composites, which facilitates enhanced processability while retaining the functional characteristics of the active ceramic phase. These improved characteristics and features of composites in 0-3 configuration facilitate enhanced processability while retaining the functional characteristics of the active ceramic phase. In addition, these functionalities make 0-3 configuration suitable for use in varied real world and emerging applications like structural health monitoring, wearable electronics, human-machine interface and low-power energy harvesting systems [3, 4].

The preceding chapters comprehensively analysed the structural, dielectric and piezoelectric characteristics of the fabricated lead-free KNN based composites. The synthesized ceramic powders were embedded within three different polymer matrices-epoxy, natural rubber and nylon11 and based on their electrical performance and microstructural uniformity, optimized compositions were identified. However, the real usefulness of such materials can be assessed only through their practical performance when subjected to actual mechanical inputs. Essential insights into the intrinsic material properties of these composite systems can only be figured out by carrying out detailed analysis of their Fundamental material parameters such as dielectric constant, piezoelectric charge coefficient and polarization-electric field behaviour. However, such analyses fail to fully capture device level functionality of these composite systems. Hence, it becomes necessary to evaluate the dynamic

response of the composite systems under real time mechanical excitation which is crucial for determining their suitability for practical sensing and energy harvesting applications.

In this chapter the performance evaluation of 0-3 composites with 30% KNN filler loading in various polymer systems like- epoxy, natural rubber and nylon 11 (composites prepared in chapter 4, 5, 6) is being analysed. The optimal filler loading was selected in order to balance the piezoelectric activity and polymer-ceramic interfacial compatibility. Composites with 30% KNN filler loading exhibited favourable electrical properties as discussed in detail in the preceding chapters, thus making 30% KNN-polymer composites an ideal candidate for device level testing. The piezoelectric response of the composites under practical conditions is evaluated using Arduino Uno based measurement platform. Arduino system allows real-time signal acquisition which serves as a versatile and cost-effective tool for voltage monitoring and digital data processing [5]. This is one of the common methods for evaluating the dynamic behaviour of piezoelectric materials by allowing precise recording for voltage output generated during mechanical tapping [6]. Mechanical tapping can be attributed to common low frequency vibrations such as, foot pressure, finger tapping, machine vibrations or human motions, which can be encountered in practical environment, which provides an accurate representation of how the composite sensors would perform in real-world scenarios [7, 8].

The Arduino based test setup consists of composites connected to the analog input of the microcontroller through resistance network with proper grounding and calibration. The direct piezoelectric effect exhibited by piezoelectric materials enables each mechanical tap to produce transient voltage spikes. This generated voltage spikes can be captured and analysed in real-time to understand the behaviour of the composites under repeated mechanical stimuli. LED is connected to the circuit, which act as digital indicator, providing visual confirmation of tap detection. The designed setup also allows an in-depth evaluation of performance parameters such as, generated voltage, response sensitivity, signal stability and tap-count accuracy which are important for assessing the functionality of piezoelectric materials intended for sensing and energy harvesting applications [1, 4].

The electromechanical performance of KNN filler embedded in different polymer matrices like, epoxy, natural rubber and nylon 11 are studied and compared in this chapter. In the stress transfer, mechanical flexibility, dielectric insulation and overall quality of the piezoelectric response of the composites depends mainly on the choice of polymer matrix [9]. Epoxy is a thermoset polymer with its inherent rigid nature; therefore, efficient stress transfer is expected, thereby producing sharp spikes [10]. On the other hand, due to high flexibility and damping properties of NR, might affect the magnitude and sharpness of the generated signals [11]. The semi-crystalline structure of nylon 11 and strong interfacial bonding tendencies is likely to exhibit a balanced and stable voltage response [12]. The comparative behaviour of these polymer systems not only highlights their performance but also, provide how material selection and composite fabrication influence real-world sensor performance.

During the tapping experiments, the voltage outputs obtained were recorded using the developed Arduino code. Continuous monitoring of analog voltage values and counting the number of stimuli was carried out after setting a definite threshold. The recorded data was then plotted as tap count vs output voltage. The graph allows a clear visualization of the sensitivity and response characteristics of each composite system. This is one of the approaches which gives meaningful correlation between mechanical input and electrical output which also reflects the inherent piezoelectric nature of the material and the role of polymer matrix in modifying its response. A detailed performance evaluation by considering all these factors is crucial for understanding the operational behaviour, identifying strengths and limitations and determining the most suitable applications for each composite [5].

This chapter presents a comprehensive performance analysis of 30% KNN in different polymer matrices based on real-time measurement system. By bridging material level characterization with device level testing, the chapter highlights the practical feasibility of the developing lead-free composites for applications in self-powered sensors, low-frequency energy harvesting, human-motion detection and smart materials technology. The insights gained here contribute substantially to the overall objective of the thesis, which is to develop sustainable, high-performance piezoelectric composite materials with strong potential for real-world implementation.

7.2 Arduino UNO

The Arduino is an open-source microcontroller based on ATmega328P which is widely used for prototyping, sensor interfacing and real-time data acquisition. Its simplicity, cost-effectiveness and flexibility make it an excellent platform for evaluating piezoelectric sensors and energy harvesting materials [13]. In the present work, the Arduino UNO served as the core data-acquisition unit for recording voltage signals generated by the 0-3 KNN-polymer composites under mechanical excitation.

The board contains 14 digital input/output pins, 6 analog input channels (A0-A5), a 16 MHz quartz crystal, USB interface, power jack and reset button. The analog inputs allow measurement of voltages in the range 0-5 V with a resolution of 10 bits (0 – 1023 steps). This enables the microcontroller to convert the transient voltage spikes produced by the piezoelectric composites into digital values which are suitable for processing, display and storage. The built-in ADC (Analog-to-digital converter) ensures reliable sampling of fast electrical signals generated during tapping tests [5, 13]

An experimental setup was specifically developed for this study in which each composite was connected to the A0 analog pin through a suitable resistor network to ensure safe voltage levels. Input voltages corresponding to the mechanical taps were measured using the controller. A user defined threshold is set which enabled the precise detection of voltage variations and counting of individual events. In the Arduino system, the digital pin 13 was also used to flash an LED whenever a tap was detected. LED provided visual feedback immediately during testing and made the setup robust, interactive and easy to calibrate

Arduino Uno was programmed using Arduino IDE. The Arduino code was specifically written to capture voltage readings, detect tapping events and transmit the data to a computer via serial communication. This allowed the freedom of subsequent analysis of real-time monitoring and logging of the voltage output. Arduino works at a sampling speed sufficient to capture low frequency mechanical responses. It is also highly suited for the evaluation of piezoelectric composite-based sensors designed for human-motion, pressure sensing and low-energy harvesting applications [13, 14].

The application of Arduino Uno in this study provided multiple benefits, including cost efficiency, excellent compatibility with sensors, resistors, and interface circuits, as well as ease of programming. It also enabled quick adjustments of threshold limits, sampling intervals, and data formats, along with real-time data acquisition. Overall, the Arduino Uno proved to be a reliable, robust and versatile platform for carrying out performance analysis of the prepared 0-3 KNN-based composites. Its ability to capture low-amplitude voltage outputs with good temporal resolution made it instrumental in validating the sensing capability and electromechanical performance of the developed materials. The Arduino Uno was used to carry out the performance analysis of 30% KNN in different polymers like epoxy, natural rubber and nylon 11 and is discussed in the preceding sessions.

7.3 Circuit configuration

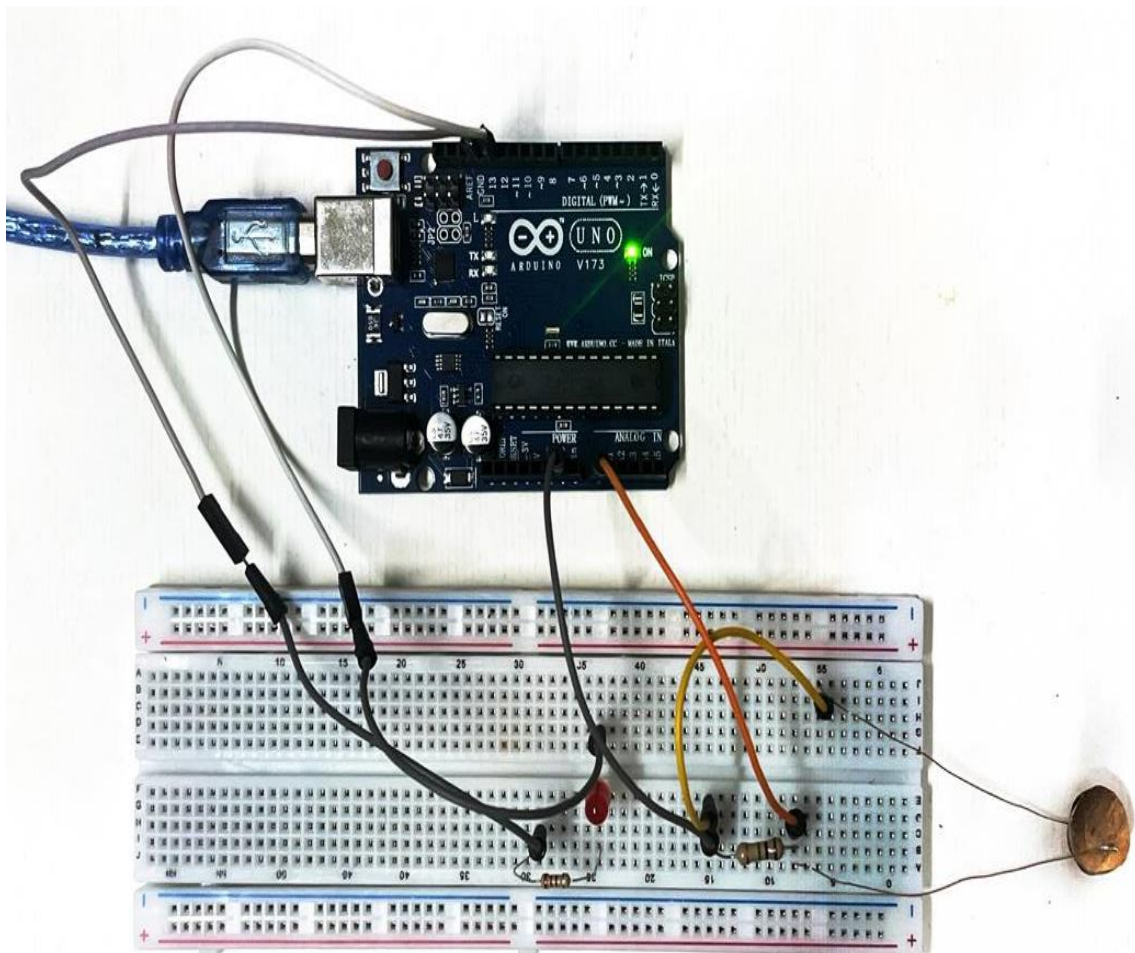


Figure 7.1: Pictorial representation of circuit

Sensor pins	LED pins
+ve to A0	+ve to A13
-ve to GND	-ve to GND
Bypassed by 1 M ohm resistor	Bypassed by 220 ohm resistor

Table 7.1: Connection pins

7.4 Microcontroller code for piezoelectric response analysis

```
const int sensorPin = A0;
const int ledpin = 13;
const float THRESHOLD = 0.2;
float voltage = 0.0;
int tapCount = 0;

void setup() {
    Serial.begin(9600);
    pinMode(ledpin, OUTPUT);
    Serial.println("CLEARDATA");
    Serial.println("Label, Tap Count, Peak Voltage (V)");
}

void loop() {
    int sensorValue = analogRead(sensorPin);
    voltage = sensorValue * (100.0/1023.0);
    static bool tapping = false;
    static float peakVoltage = 0.0;

    if(voltage>THRESHOLD){
```

```
tapping = true;
digitalWrite(ledpin, HIGH);

if(voltage>peakVoltage){
    peakVoltage = voltage;
}
}
else {

If(tapping){
    tapCount++;
    Serial.print("DATA,");
    Serial.print(tapCount);
    Serial.print(",");
    Serial.println(peakVoltage, 3);
    peakVoltage = 0.0;
    tapping = false;
    digitalWrite(ledPin, LOW);
    delay(200);
}

}
delay(5);
}
```

7.5 Voltage output under mechanical excitation

7.5.1 Performance analysis: KNN ceramics

Both SSR-derived and TGG-derived KNN ceramics exhibited measurable piezoelectric response when subjected to controlled tapping. However, the TGG ceramics consistently generated higher peak voltages. This enhancement can be attributed to the improved crystallographic alignment and anisotropy induced by the

templated grain growth process. The textured microstructure facilitates more efficient polarization switching and charge accumulation along the preferred crystallographic directions, thereby increasing electromechanical coupling.

The piezoelectric response of the conventionally processed KNN ceramic was evaluated by subjecting the sample to repeated mechanical taps and recording the corresponding peak voltage output using the Arduino based measurement setup. The variation of peak voltage as a function of tap count for 100 consecutive taps is illustrated in figure 7.2.

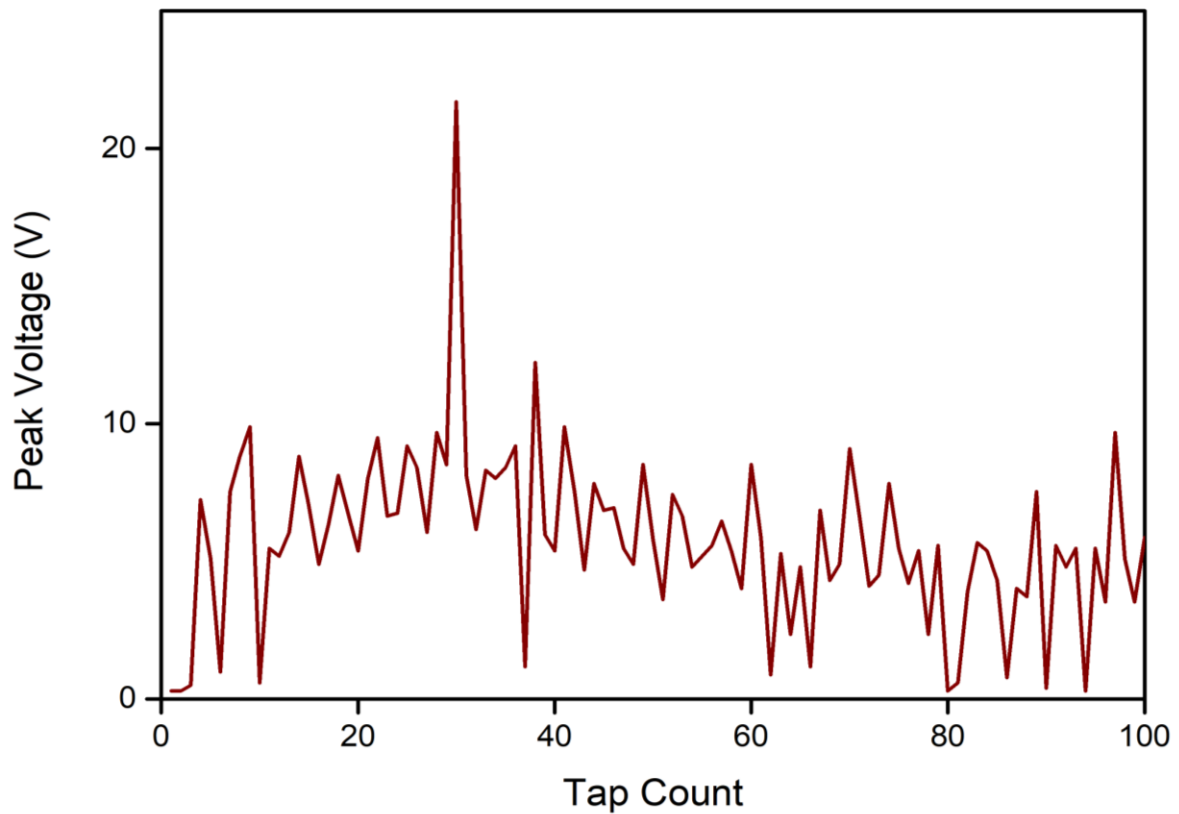


Figure 7.2: Performance analysis of SSR KNN

As shown in the graph, the KNN fillers prepared via SSR method exhibited a highly fluctuating voltage. The peak output values range approximately between 2 – 10 V for most tapping events. A high amplitude peak as the one exceeding 20 V was also observed. This sudden spike observed may be associated with short duration

mechanical impulse of higher intensity or localized stress concentration on the ceramic surface. SSR-KNN possesses moderate electromechanical sensitivity but show inconsistencies likely due to its microstructural heterogeneity which lead to the absence of a uniform and repeatable voltage pattern. SSR-KNN ceramics, despite all these variations consistently produced 5 V for significant number of taps. This demonstrated the materials ability for energy harvesting experiments by retaining functional piezoelectric response.

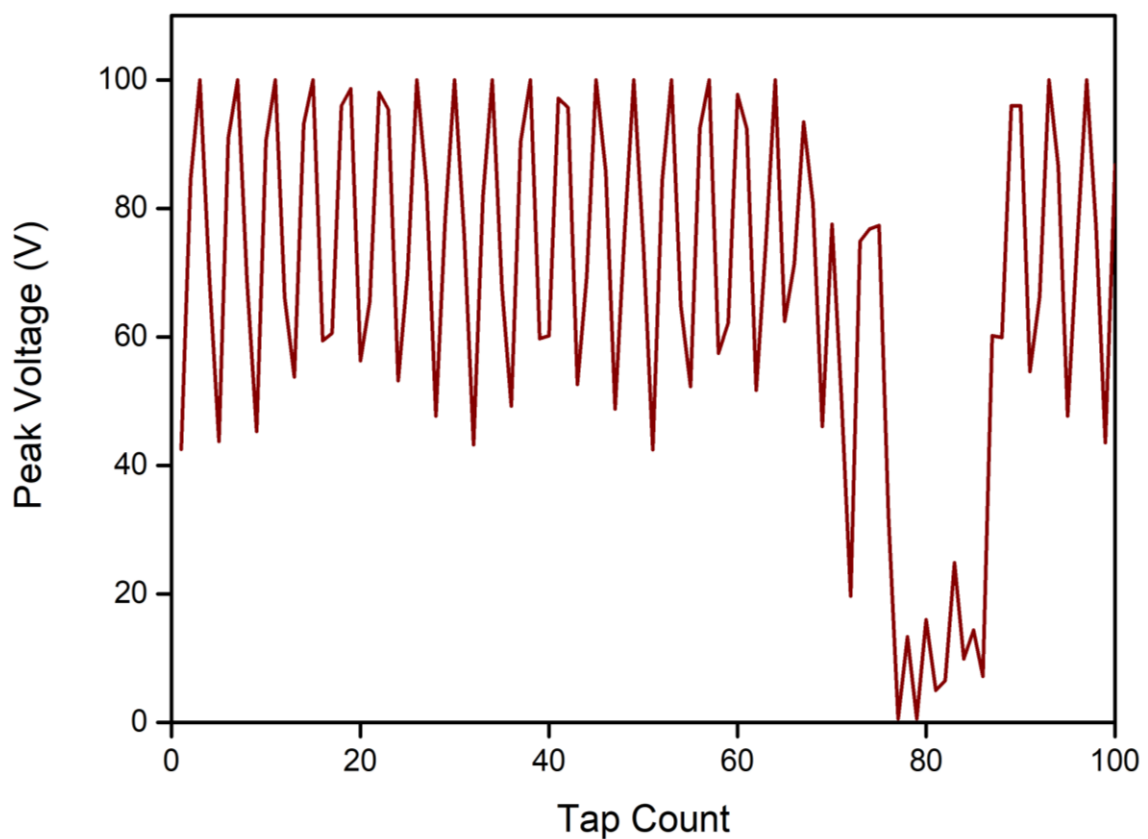


Figure 7.3: Performance analysis of TGG-KNN

In contrast to the performance analysis of SSR-KNN, the KNN ceramics prepared via TGG method exhibited substantially higher or more consistent voltage output as shown in figure 7.3. Almost every peaks fall under the voltage range 60 V – 100 V. this enhancement is nearly tenfold when compared to the results shown by SSR-KNN.

This improvement in the electromechanical response of TGG-KNN can be directly attributed to the advantages brought by the ceramic synthesis route.

The generated output voltage is influenced by several factors, including- dielectric constant, domain orientation, internal resistance, sample geometry, charge collection efficiency etc. In contrast the impact-based experiment involves transient mechanical excitation, where the measured voltage depends on the overall electromechanical response of the sample rather than solely on its piezoelectric charge coefficient. The TGG-KNN ceramics possess highly oriented grains and improved domain alignment, leading to superior electromechanical coupling and voltage generation efficiency compared to SSR-KNN.

Reliable and repeatable energy conversion behaviour is observed which is attributed to the periodic oscillation of voltage output. Around 70-80 tap regions, a sudden drop in the voltage is observed, which can be due to the temporary misalignment of the tapping force, mechanical relaxation of the test setup or local domain instability. However, after this region the system quickly recovers and returns to the high-output regime, reaffirming the structural stability and superior piezoelectric response of TGG-KNN.

7.5.2 Performance analysis: KNN-polymer composites

Figure 7.4 demonstrates the piezoelectric response of the KNN-epoxy 0-3 composites. An Arduino-based tapping setup was used to measure the generated peak voltage and was recorded as a function of tap count. The electromechanical efficiency, stress-charge conversion capability and signal stability of the KNN-epoxy composite is analysed using the obtained result.

A distinct piezoelectric response under repeated mechanical taps was observed for KNN-epoxy composites. From the graph (figure 7.4), it is observed that peak voltages fall mostly in the range of 1 V – 3 V, with occasional higher spikes reaching close to 3.3 V. A combined behaviour of dielectric polymer matrix and the dispersed KNN fillers can be attributed to this behaviour of KNN-epoxy composites. However, the flexibility of epoxy binder allows the composite to withstand repeated mechanical stress without cracking, thereby, enhancing its durability and life cycle [15].

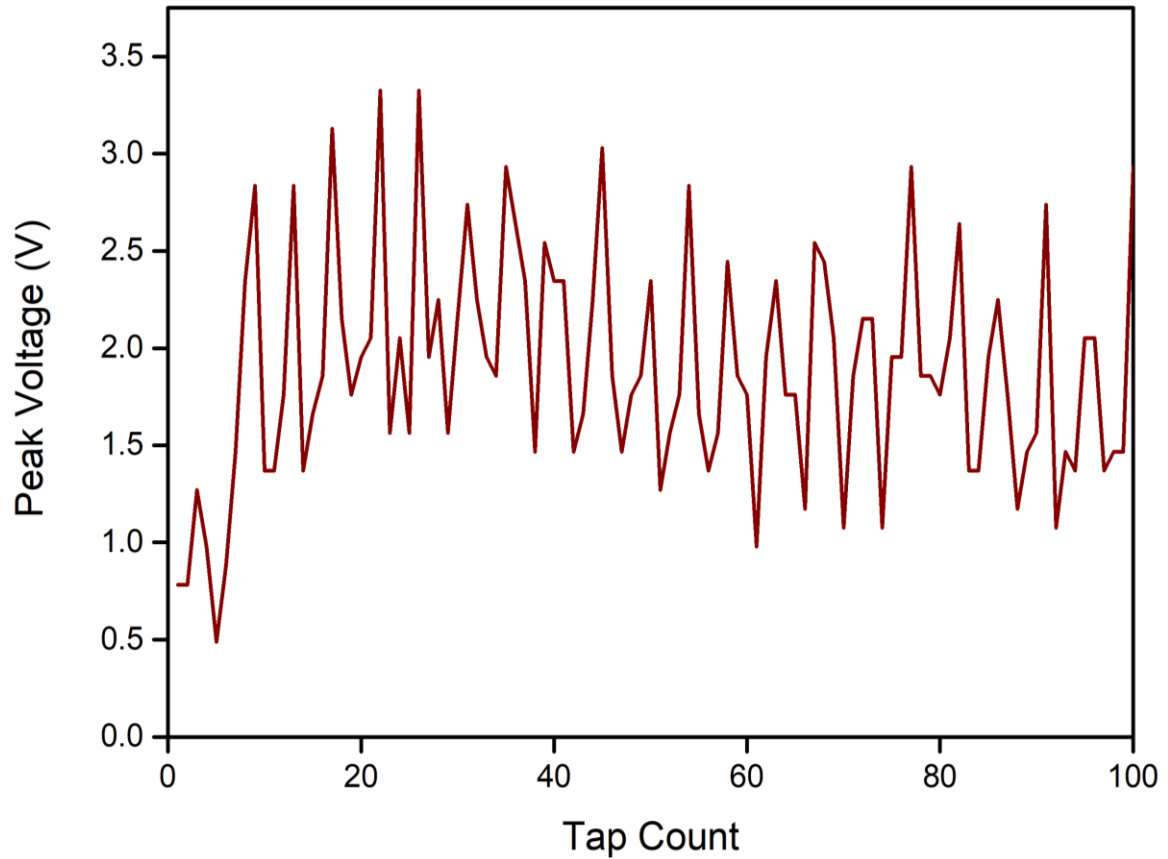


Figure 7.4: Performance analysis of KNN-Epoxy composite

The performance of KNN-NR composites was also evaluated using Arduino setup and is illustrated in figure 7.5 with variation of peak voltage as a function of tap count over 100 consecutive taps.

From the output waveform of KNN-NR composite it can be observed that consistent peak voltages in the range of 9-16 V are obtained, with most values clustering around 12-15 V. The narrow voltage spread indicates good reproducibility of the electromechanical conversion process of KNN-NR composite, even under repeated loading cycles which highlights the effective mechanical coupling between KNN particles and the flexible NR matrix. NR, being a highly elastic polymer, facilitates efficient stress transfer to the dispersed KNN ceramic particles during tapping. The inherent elasticity stores mechanical energy momentarily before releasing it, thus producing sharp voltage spikes. This behaviour is reflected in the periodic up-down

waveform seen throughout the tap sequence, which is typical for elastomer-based piezocomposites under dynamic loading [16].

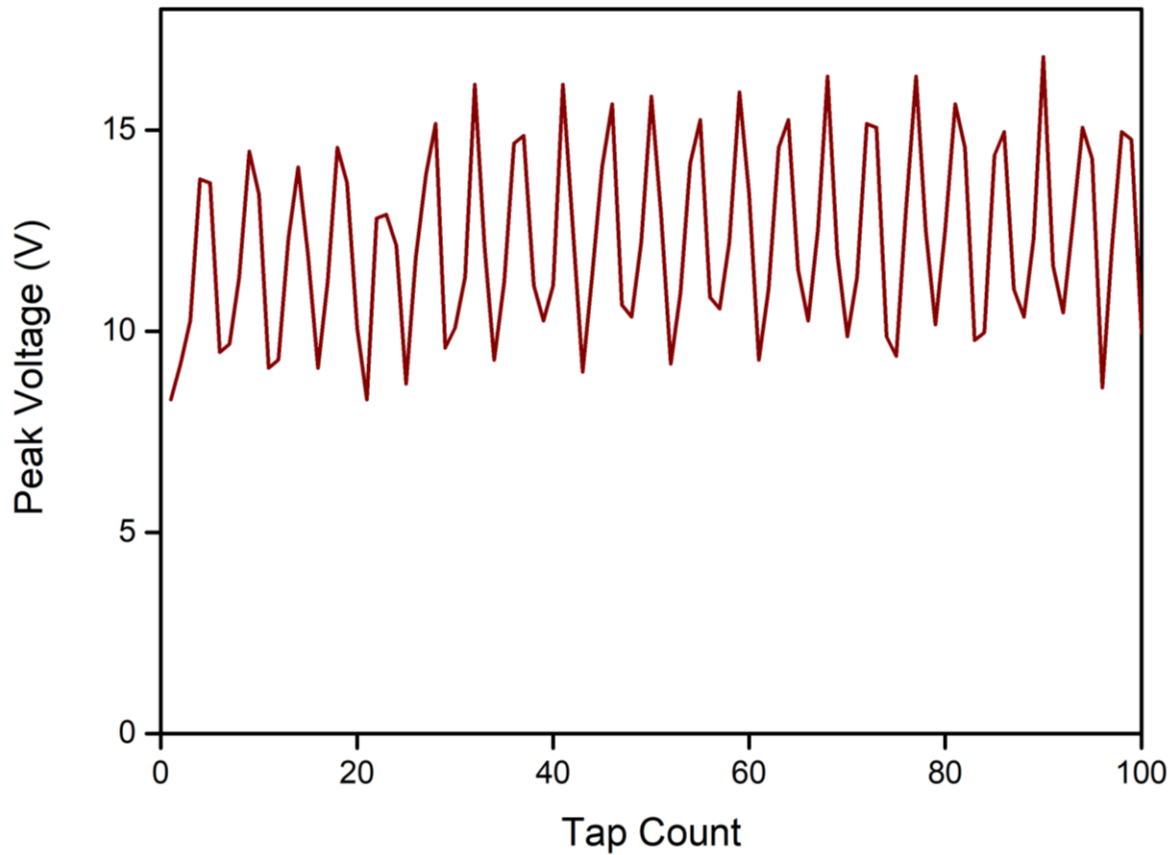


Figure 7.5: Performance analysis of KNN-NR 0-3 composite

The output voltage profile of the KNN-nylon11 composite under repeated mechanical tapping is shown in figure 7.6. The composite produced peak voltages ranging approximately from 0 to 50 V over 100 tap cycle, with frequent sharp rises and falls throughout the measurement window. As tapping progresses, the voltage peaks become more prominent, frequently reaching values between 30-50 V, demonstrating that the composite maintains a strong and active electromechanical response throughout the tapping experiment. The observed irregularity in peak heights is characteristic of flexible polymer-ceramic composites, where the local strain distribution, loading conditions and filler-polymer interactions influence the instantaneous voltage generation. Nylon11, being a semi-crystalline and flexible

polymer, allows effective stress transfer to the embedded KNN particles, enabling substantial voltage generation despite the composite's mechanical softness [15].

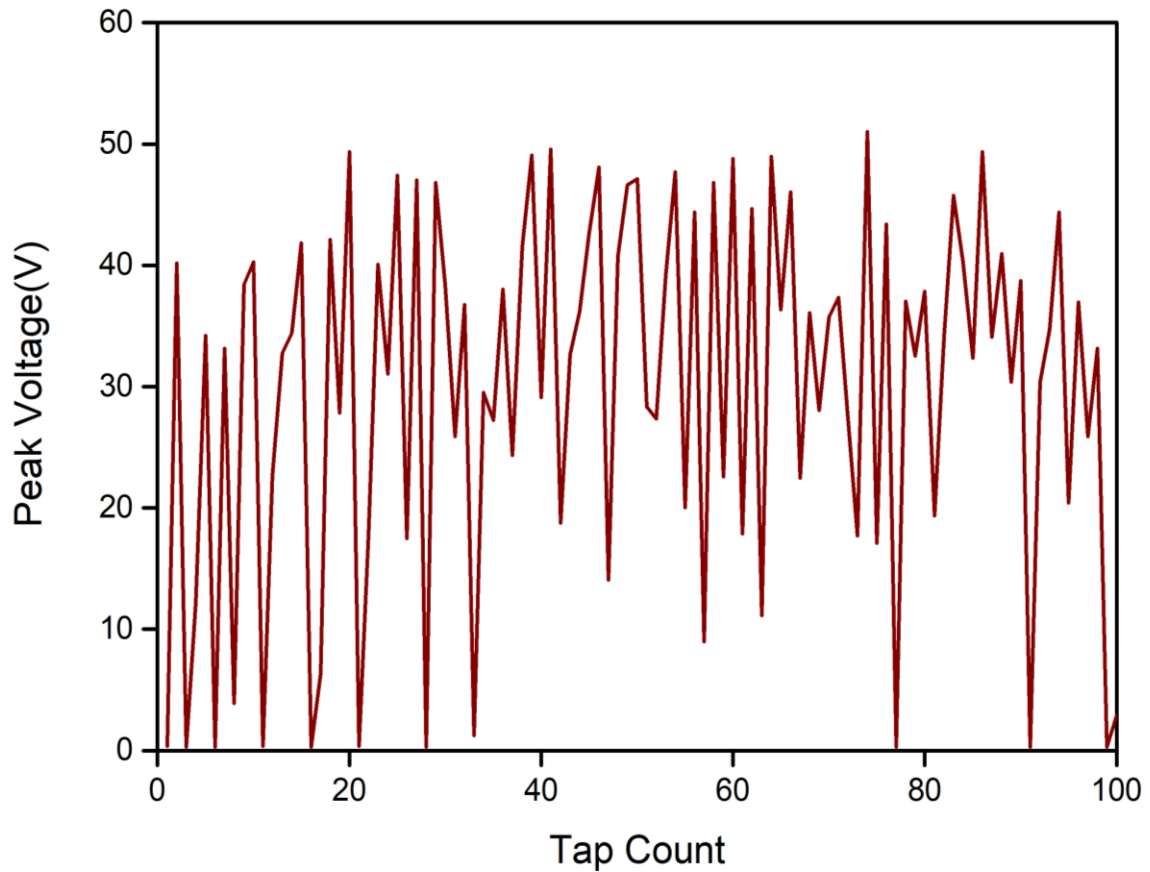


Figure 7.6: Performance analysis of KNN-nylon11 composites

Table 7.2 gives the comparison and summarizes the performance of various 0-3 KNN-polymer composites with 30% KNN filler under mechanical excitation. It is evident that the polymer matrix plays a critical role in determining the piezoelectric output. KNN-nylon 11 composites exhibited the highest maximum and average voltage output, indicating superior flexibility and efficient stress transfer to the KNN fillers among all the tested composite systems. In contrast, KNN-epoxy composite is relatively rigid and it generated lower voltage values. It is also notable that KNN-epoxy composites generated uniform peak responses, reflecting a consistent load transfer and minimal local deformation. From the electromechanical response of

KNN-NR composite it is observed that, KNN-NR demonstrated intermediate behaviour, balancing flexibility and peak stability.

Composite System	Peak Voltage Range	Mechanical Nature	Electromechanical Response	Suitability
KNN-Epoxy	~0.7–3.3 V	Rigid, brittle	Low	Low-voltage sensing, rigid sensors
KNN-NR	~9–17 V	Highly elastic	Moderate–High	Flexible harvesters, wearable applications
KNN-Nylon 11	~1–50 V	Semi-crystalline, polar	Very High	High-power energy harvesting, dynamic strain sensors

Table 7.2: Comparative piezoelectric response of KNN-polymer composites

7.6. Conclusion

The performance analysis of KNN ceramics synthesized through SRR and TGG routes and KNN-polymer composites, gives a comprehensive understanding of electromechanical response of the systems under mechanical tapping. Voltage output was recorded for 100 consecutive tap using Arduino based data acquisition setup. The results obtained from Arduino offered real-time insights into the energy harvesting potential, stability and durability of each material system. Three different polymer systems were tested among which, nylon 11 has given the highest electromechanical response. The polar nature and strong strain induced dipole alignment of nylon 11, enables efficient stress transfer to KNN particles. NR also provided moderate to high

output which can be directly attributed to its elasticity and excellent mechanical coupling, which makes them ideal for flexible applications. Among the polymers, epoxy restricts strain transfer and hence exhibited the lowest voltage generation. The results of performance analysis obtained from Arduino Uno confirmed that the choice of polymer also plays in determining the electromechanical performance of 0-3 KNN-polymer based composites.

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Chapter 8

SUMMARY AND FUTURE SCOPE

Summary

PhD thesis entitled “Fabrication and Electromechanical Studies of KNN-Polymer 0-3 Composites”, provides new routes and concepts for manufacturing lead-free piezoelectric ceramic-polymer composites with adequate piezoelectric properties while retaining ease of mechanical flexibility. The studies carried out during the course of this PhD thesis explored new possibilities to maximize the voltage sensitivity while taking into account environment relevant issues.

In the beginning of this thesis a scientific context explaining the theory, history of piezoelectricity and the necessity for lead-free piezoelectric materials was established. Lead-based ceramics like PZT are dominant in the industry due to their exceptional piezoelectric properties, pose significant health and environmental concerns. KNN-based piezoelectric materials because of their properties like high Curie temperature, comparable piezoelectric coefficient with PZT and compatibility with lost cost processing routes, emerged as a strong alternative for PZT. Due to inherent brittle nature of piezoelectric ceramics, a new set of piezoelectric systems were explored in this study by combining the functional properties of KNN fillers with the mechanical properties of polymers. Three different polymer matrices like- epoxy, natural rubber and nylon 11 were used. All three polymer matrices offered advantages like distinct mechanical flexibility, dielectric behaviour, chemical interaction and processing pathways. From this study, a comparative understanding of how polymer influences the behaviour of the composites when paired with KNN fillers was understood.

KNN fillers for composite preparation were synthesized using conventional solid state reaction method and templated grain growth method, which was a critical part of this work. Well crystallized ceramics with good morphology, improved density and enhanced texturing was obtained from both the mentioned ceramic synthesis routes, all of which contributed to more effective stress charge interactions in the composite. Phase purity, grain connectivity, and uniform distribution of KNN fillers were confirmed using XRD and SEM analysis.

Focussing on optimizing the filler loading, improving ceramic-polymer interfacial contact and achieving uniform particle distribution within each polymer matrix, KNN-polymer 0-3 composites were fabricated. Distinct processing challenges and

advantages exhibited by each composite system- KNN-epoxy, KK-NR and KNN-nylon 11, ultimately contributed to their electromechanical response. KNN-epoxy composite offered good dielectric stability, but limited flexibility. KNN-NR composite on the other hand provided exceptional flexibility but lower breakdown strength. Nylon 11 composites delivered a balanced combination of toughness, semi-crystalline ordering and improved dielectric compatibility, making it especially promising for sensor and energy harvesting applications.

The fabrication procedures for each composite were specifically selected to promote homogeneous filler dispersion. For epoxy composites, KNN powder was thoroughly dispersed in the medium-viscosity epoxy resin before curing using continuous mechanical mixing, which minimizes particle sedimentation and facilitates uniform filler distribution. For KNN-NR composites, the KNN filler was incorporated into the NR matrix using a two-roll mill prior to vulcanization. The repeated shearing and folding action during milling facilitate the breakdown of filler clusters and promotes uniform distribution of KNN throughout the NR matrix before vulcanization process. For Nylon-11 composites, melt blending was carried out using a Brabender internal mixer at the processing temperature, where the combined effects of elevated temperature and high shear promote effective dispersion of KNN filler within the polymer melt. The processing conditions were optimized to reduce particle agglomeration prior to hot pressing.

The incorporation of high-volume fraction of KNN filler increases the stiffness of the composites and consequently reduces their flexibility compared to the neat polymer. In the present study, although the KNN loading was increased up to 50%, the composites retained sufficient flexibility for handling and mechanical deformation because the polymer matrix remained the continuous phase. However, increasing the KNN filler loading beyond 50 volume percent significantly reduced the processability and flexibility of the composites, making effective electrical poling difficult. This clearly indicate that the flexibility decreases significantly due to restricted polymer chain mobility, increased particle-particle interactions and increased composite stiffness. This trade-off is characteristic of 0-3 composite and has widely reported in the literature.

Dielectric studies on different composite systems were carried out and the results demonstrated that the permittivity of the composites increased with ceramic content, aligning well with theoretical predictions for 0-3 connectivity. Among the different composite systems, KNN-nylon 11 composites exhibited the most desirable combination of modest permittivity, low dielectric loss and stable frequency response, which makes them strong candidates for sensorial applications.

The importance of filler quality and polymer selection was further highlighted with the analysis of piezoelectric and electromechanical properties. Epoxy composites exhibited stable piezoelectric activity but, limited mechanical flexibility restricted strain transfer between the filler and the matrix. Even though NR composites showed improved mechanical to electrical conversion efficiency due to their softness, they suffered from high dielectric loss. On the other hand, nylon 11 composites demonstrated an optimal balance. The mechanical rigidity of KNN-nylon 11 composites was sufficient for effective stress transfer while still offering enough flexibility to support strain-driven responses. This resulted in the enhancement in piezoelectric charge coefficients of KNN-nylon 11 composites making them efficient among the other composites.

In the final chapter, the material level findings were translated into the application-scale performance. Arduino Uno- based microcontroller setup was used to evaluate the practical sensing and energy harvesting capabilities. Successful detection of mechanical stimuli and measurable voltage outputs confirmed that these systems can be integrated into lightweight, flexible and low-cost sensors. The performance of different systems correlated strongly with the electromechanical and dielectric behaviour discussed earlier, reinforcing the ceramic-polymer composite relationships established in this study. The quantitative determination of the applied force and excitation frequency using a calibrated force sensor, impact hammer or electrodynamic shaker would provide a more rigorous assessment of the harvesting performance and facilitate comparison with other reported studies. However, such instrumentation was beyond the scope of the present work.

Overall, this PhD thesis supports that the KNN-polymer 0-3 composites are viable, environmentally friendly alternatives to traditional lead-based piezoelectric systems. Among the developed different ceramic-polymer composites, nylon 11 emerged as

the most promising polymer matrix due to its synergistic mechanical and dielectric compatibility with KNN fillers. The study not only substantiates the feasibility of using KNN-based polymer composites for sensing and energy harvesting applications, but it also provides a clear roadmap for future enhancements of the system through microstructural control, filler orientation, surface functionalization and composite architecture design.

In summary, this study offers a comprehensive insight into how lead-free KNN ceramics can be effectively combined with polymers matrices to produce sustainable, flexible and functional piezoelectric composites. The insights generated from this study add depth to the scientific knowledge of piezoelectric composite systems and pave the way for future research focused on developing next generation electromechanical materials for diverse technological applications.

Future Scope

This thesis focuses on the fabrication and electromechanical analysis of lead-free piezoelectric composites with good sensorial properties, improved mechanical flexibility and fatigue resistance. This study developed different sets of composites using lead-free potassium sodium niobate (KNN) prepared via solid state reaction method and templated grain growth method as fillers in different polymer matrices. Overall, the thesis establishes a systematic understanding of how filler composition, polymer selection and microstructural engineering influence the functional properties of lead-free piezoelectric composites and their potential for sensor and energy harvesting applications.

This research addresses the environmental challenges associated with toxic lead-based piezoelectric systems, the rising energy demand for self-powdered portable electronic devices and the ongoing technological shift toward green, flexible and intelligent material platforms by contributing to the advancement of sustainable materials science. Developing lead-free piezoelectric composites and demonstrating their potential in practical sensing applications, directly contribute to the UN's sustainable development goals (SDG- 7, 9, 11, 12, 13).

Chapter 9

RECOMMENDATIONS

In the present work, KNN–polymer composites of different filler loadings were successfully fabricated and characterized, with performance analysis showing promising electromechanical properties. However, several key challenges remain unexplored to enhance piezoelectric response and broaden application potential.

- More detailed characterization and orientation control of KNN ceramic fillers for 1-3 type composite structures may be incorporated in the future studies. Enhanced piezoelectric properties and stress transfer could be improved by the alignment of ceramic phase in polymer matrix. This will facilitate in determining the effectiveness of filler orientation on piezoelectric, dielectric and electromechanical properties of the composites.
- By exploring nano-structuring, surface functionalization and chemical modification of the ceramic fillers, the interfacial bonding between the KNN particles and polymer matrix may be further improved. Tailoring the surface attributes of KNN fillers can be utilized for better dispersion, stronger adhesion, and more efficient stress transfer across the interface, thereby improving the piezo response of the composites.
- Alternative polymer matrix can be explored for the fabrication, embedding the flexibility, mechanical stability, and long-term functional performance of the manufactured composites. Secondary polymer phases can be incorporated or mixed with bio compactible host system and the electrical and mechanical studies will be a subject for further study. This would offer a systematic knowledge on the influence of the polymer matrix on piezoceramic particles on the distribution of strain and voltage output during dynamic loading.
- Better understanding of reliability of the composites can be achieved by systematic assessment under varying humidity, elevated temperatures, UV exposure, and long-term storage conditions. Further characterizations and testing can be carried out for applications in wearable electronics and energy harvesting systems.
- Dynamic Mechanical Analysis (DMA) would provide valuable insights into morphology, viscoelastic properties, relaxation behaviour and temperature dependent mechanical responses of the composite. Therefore, DMA characterization has been identified as an important future work.

- The results of present study signify that the developed composites are suitable for flexible sensors applications. Therefore, future work will focus on the designing of device architectures and these prototypes may then be evaluated under real-time conditions for applications such as functional devices.
- Finally, the development and transition of these materials from laboratory research to potential industrial adoption by evaluating various parameters like the life-cycle, environmental impact assessment, and performance analysis. This knowledge could serve as the foundation for future technological advancements in sustainable piezoelectric materials for flexible electronics and energy harvesting applications.