Energy conversion through local piezoelectric effect in polymer foams for enhancing sound absorption

Ayman Mahmod Mohamed Khalil Shahin

2019

Ayman Mahmod Mohamed Khalil Shahin. (2019). Energy conversion through local piezoelectric effect in polymer foams for enhancing sound absorption. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/137057>

<https://doi.org/10.32657/10356/137057>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 20:57:47 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**ENERGY CONVERSION THROUGH LOCAL PIEZOELECTRIC
EFFECT IN POLYMER FOAMS FOR ENHANCING SOUND
ABSORPTION**

AYMAN MAHMOD MOHAMED KHALIL SHAHIN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

**ENERGY CONVERSION THROUGH LOCAL PIEZOELECTRIC
EFFECT IN POLYMER FOAMS FOR ENHANCING SOUND
ABSORPTION**

AYMAN MAHMOD MOHAMED KHALIL SHAHIN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

22 August 2019

Date

Ayman Mahmod Mohamed Khalil Shahin

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

22 August 2019

Date

Dr. Yao Kui

Prof. Junling Wang

Authorship Attribution Statement

This thesis contains material from papers published/submitted in the following peer-reviewed journals where I was the first author.

Chapter 4 is partially published as: A. M. Mohamed, K. Yao, Y. M. Yousry, S. Chen, J. Wang, and S. Ramakrishna, Open-cell poly(vinylidene fluoride) foams with polar phase for enhanced airborne sound absorption. *Appl. Phys. Lett.* **113**, 092903 (2018). DOI: 10.1063/1.5048336.

The contributions of the co-authors are as follows:

- Dr. Yao Kui and Prof. Wang Junling provided the initial project direction.
- Dr. Yao Kui and I co-designed the experiments and planned the work. I performed most of the laboratory work at the Institute of Materials Research and Engineering and I also analyzed the data.
- Dr. Chen Shuting assisted in data analysis and technical discussion.
- Ms. Yasmin Mohamed Yousry assisted in the interpretation of the spectroscopy data, carried out the spectral interpretation, and technical discussion.
- Dr. Yao Kui, Prof. Wang Junling, and Prof. Seeram Ramakrishnah assisted in the technical discussion and advice.

Chapter 5 is partially in the submitted manuscript: Ayman Mahmoud Mohamed, Kui Yao, Yasmin Mohamed Yousry, Junling Wang, and Seeram Ramakrishna, Open-cell P(VDF-TrFE)/MWCNTs Nanocomposite Foams with Local Piezoelectric and Conductive Effects for Airborne Sound Absorption.

The contributions of the co-authors are as follows:

- Dr. Yao Kui provided the initial project direction.
- Dr. Yao Kui and I co-designed the experiments and planned the work. I performed most of the laboratory work at the Institute of Materials Research and Engineering. I also analyzed the data.

- Ms. Yasmin Mohamed Yousry assisted in the interpretation of the spectroscopy data, carried out the spectral interpretation of ATR-FTIR and XRD. She also assisted in technical discussion.
- Dr. Yao Kui, Prof. Wang Junling, and Prof. Seeram Ramakrishnah assisted in the technical discussion and advice.

Chapter 6 is partially in the accepted manuscript by Journal of Applied Polymer Science, and it is going to be published soon as: Ayman Mahmoud Mohamed, Kui Yao, Yasmin Mohamed Yousry, Junling Wang, and Seeram Ramakrishna, Enhanced Airborne Sound Absorption Effect in Poly(vinylidene fluoride)/(K_{0.5}Na_{0.5})NbO₃-nanofiber Composite Foams.

The contributions of the co-authors are as follows:

- Dr. Yao Kui and Prof. Wang Junling provided the initial project direction.
- Dr. Yao Kui and I co-designed the materials, experiments, planned the work, and I performed most of the laboratory work at the Institute of Materials Research and Engineering. I also analyzed the data.
- Ms. Yasmin Mohamed Yousry for preparing the KNN nanofibers, and in the interpretation of the ATR-FTIR absorption spectroscopy data, XRD patterns and carried out the spectral interpretation and technical discussion.
- Dr. Yao Kui, Prof. Wang Junling, and Prof. Seeram Ramakrishnah assisted in the technical discussion and advice.

22 August 2019

Date

Ayman Mahmod Mohamed Khalil Shahin

Abstract

Airborne sound absorption in porous materials is a complex process that involves multiple working mechanisms of converting mechanical acoustic energy into heat, including thermal effect due to the dynamic heat conduction forced by the rarefaction and the densification of the air, viscous effect caused by the adherence of the fluid at the interface with the solid, and structure's damping effect with mechanical energy dissipation when the sound wave impacts on the solid. Electromechanically active coupling effect, particularly piezoelectric effect, has so far been studied mainly for structural vibration damping but not for airborne sound absorption. This thesis examines contributions of the electromechanical conversion mechanism to the airborne sound absorption effect, particularly local piezoelectric effect in porous polar materials.

The study on the local piezoelectric effect on airborne sound absorption properties tested in a standard impedance acoustic tube was carried out in three sections. Firstly, open-cell poly(vinylidene fluoride) (PVDF) homopolymer foams were prepared and used in order to obtain porous samples with comparable morphology and structure, but with and without substantial piezoelectric property, for providing an example showing the local piezoelectric property effect on sound absorption. Secondly, composite foams comprising piezoelectric poly(vinylidene fluoride-co trifluoroethylene) (P(VDF-TrFE)) matrix and multi-walled carbon nanotubes (MWCNTs) were fabricated and tested, with the experimental results and theoretical analyses showing how an optimal conductivity of the piezoelectric composite foams improved sound absorption coefficient. Thirdly, composite foams comprising PVDF matrix and inorganic piezoelectric potassium sodium niobate ($\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) nanofibers were produced and tested, with the investigation results showed that introducing the piezoelectric KNN nanofibers in the foams improved sound absorption coefficient.

The experimental results and theoretical analyses indicate that the introduction of piezoelectric property with mechanical-into-electrical energy conversion effect in porous

polymer materials can substantially enhance the airborne sound absorption performance, which is valuable to be explored for noise mitigation applications.

Lay Summary

Noise is one of the vitally important factors determining the quality of life and liveability in urban areas. The harm of noise pollution is well recognized. Exposure to a high level of noise can cause hearing loss and some other health problem. Even at a low noise level, noise disturbance has a significant negative effect on psychological health and quality of life, and reduction in working and learning efficiency.

In contrast to active noise control technology, passive noise control is widely applied, as it does not consume energy or involves any active control. However, a drawback of passive noise control is that it is only effective at relatively high frequencies or over a narrow frequency range.

This thesis aims at finding and understanding a novel airborne noise mitigation solution by incorporating additional sound absorption mechanism into those well-known conventional sound absorption mechanisms. The contribution from local piezoelectric effects has been introduced in the foam materials for improving their airborne sound absorption performance. The thesis investigates the structures and properties of the foam materials with polar phases and the effects of local piezoelectric properties on enhanced airborne sound absorption in a broad frequency range.

Acknowledgments

I would like to sincerely thank almighty Allah for all his grants that he bestowed on me.

I would like to express my deepest gratitude to my supervisor, Dr. Yao Kui, for accepting me as a Ph.D. student working under his supervision at the Institute of Materials Research and Engineering (IMRE). I would like to thank him for all the guidance and supports during my Ph.D. research. I would like to express my most sincere gratitude to my supervisor Professor Wang Junling, for the numerous discussions, inspiring suggestions, and for having shared his broad scientific knowledge with me.

I want to thank all the colleagues at the Sensor and Transducer (S&T) Laboratory at Institute of Materials Research and Engineering (IMRE), and in particular, Ms. Yasmin Yousry, Dr. Meysam Sharifzadeh Mirshekarloo, Dr. Chen Shuting, and Mr. Poh Chong Lim for their great assistances. I would also like to thank Dr. Sreenivasa Reddy Puniredd for his help in the supercritical carbon dioxide (scCO₂) foaming system. My sincere gratitude to my friends Dr. Amr Ali Alhossary, Dr. Eleftherios Christos, Dr. Karim Aly, Eng. Mohamed Afifi, and Mr. Amr Abdelsamie for the long discussions about science, research, and life.

I would also like to take this opportunity to thank all of my past educators that have gradually pushed me in the direction of scientific research, albeit not easily. There are far too many to list here. However, I would like to personally thank Prof. Osama El-Bayoumi and Prof. Moataz Soliman, who, even in my young and troublesome adolescence, recognized abilities and thoughts that were often lost on others.

I would like to present my sincere thankfulness to my dear late father and mother for their great role in my life and their numerous sacrifices for my brothers and me. I would like to thank my brothers, Islam, Ehab, and Amir for supporting me through my years as a graduate student, and their supports are deeply appreciated.

Words fail me to express my most deepest appreciation to lovely son Osama, and Yasmin, my precious wife, and friend, whose dedication, love, and persistent confidence in me have encouraged me throughout this journey.

I wish to express my gratitude to the A*STAR (Agency for Science, Technology, and Research) for their financial support in the form of SINGA (Singapore International Graduate Award) during my Ph.D. studies. I would also like to acknowledge the partial supports by Singapore Maritime Institute under the Maritime Sustainability R&D Programme, Project ID: SMI-2015-MA-07 (IMRE/16-7P1125), and by the Singapore Ministry of National Development and National Research Foundation under L2NIC Award No. L2NICCFP1-2013-9 (IMRE/14-9P1112).

Dedication

My God (ALLAH)

*In Memory of my father,
Mahmoud and my mother, Hala
May ALLAH reward them for all their good deeds and grant them
the highest of ranks in Jannah!*

*To my wife, Yasmin, my son, Osama, and my brothers, Islam,
Ehab, and Amir*

Table of Contents

Abstract.....	I
Lay Summary	III
Acknowledgments	IV
Table of Contents	IX
Table Caption	XIV
Figure Captions	XV
Abbreviations	XX
 CHAPTER 1 Introduction.....	 1
1.1. Problem Statement	2
1.1.1 Active Noise Control	3
1.1.2 Passive Noise Control	4
1.1.3 Hybrid Noise Control.....	8
1.2. Motivation.....	10
1.3. Objectives and Scope	11
1.4. Dissertation Overview.....	12
1.5. Findings and Outcomes.....	13
References	14
 CHAPTER 2 Literature Review	 17
2.1. Acoustic Properties of Porous Absorbing Materials	18
2.1.1 Properties of the Fluid Phase	18

2.1.2	Properties of the Skeleton	19
2.1.3	Properties that Define Coupling between the Fluid and Skeleton	19
2.1.3.1	Porosity ϕ	20
2.1.3.2	Flow Resistivity σ	21
2.1.3.3	Tortuosity α_{∞}	22
2.1.3.4	Viscous Characteristic Length λ	22
2.1.3.5	Thermal Characteristic Length λ'	23
2.2.	Acoustic Modeling of Porous Absorbing Materials	23
2.3.	Piezoelectricity	25
2.3.1	Piezoelectric Effect	25
2.3.2	Piezoelectric Constitutive Relationship	29
2.3.3	Piezoelectric Coupling Factor	29
2.4.	Piezoelectric Polymers	30
2.5.	Ferroelectric Polyvinylidene Fluoride (PVDF)	32
2.5.1	Production of PVDF β Phase	34
2.6.	Ferroelectric PVDF Co-polymer	35
2.7.	Polymer Foams	36
2.7.1	Physical Foaming Agents	37
2.7.2	Chemical Foaming Agents	37
	Summary	38
	References	38
CHAPTER 3 Experimental Methodology		41
3.1.	Rationale for Selection	42
3.2.	Experimental Methods	42
3.2.1	Materials	42
3.2.2	Method for Preparing Open-cell PVDF Foams	43

3.2.3	Method for Preparing Open-cell P(VDF-TrFE)/MWCNTs Nanocomposite Foams	43
3.2.4	Method for Preparing Open-cell PVDF/KNN-nanofiber Composite Foams	44
3.2.4.1	Potassium Sodium Niobate (KNN)-nanofibers Preparation	44
3.2.4.2	PVDF Solution Preparation.....	44
3.2.4.3	Method for Preparing Open-cell PVDF/KNN-nanofiber Composite Foams.....	44
3.2.5	Charging of PVDF Foams	46
3.3.	Characterization	46
3.3.1	Fourier Transform Infrared Analysis (FTIR).....	46
3.3.2	X-ray Diffraction (XRD)	47
3.3.3	Scanning Electron Microscopy (SEM)	48
3.3.4	Differential Scanning Calorimetry (DSC)	49
3.3.5	Acoustic Impedance Tube.....	49
3.3.6	Dynamic Mechanical Analyzer.....	50
3.3.7	Electrical Characterization.....	51
3.3.7.1	Dielectric Characterization.....	51
3.3.7.2	Piezoelectric Characterization.....	51
	References	52
 CHAPTER 4 Open-cell Poly(vinylidene fluoride) Foams with Polar Phase for Enhanced Airborne Sound Absorption		53
4.1.	Introduction	54
4.2.	Results and Discussion.....	54
4.2.1	Crystal Phases	54
4.2.2	Morphology and Mechanical Properties	56

4.2.3	Sound-absorption Properties	58
4.2.4	Electrical and Dielectric Properties	60
4.2.5	Converting the Sound Energy into Electrical Output Energy	62
4.2.6	Mechanism for Energy Dissipation with Local Piezoelectricity	63
	Conclusions	64
	References	65

CHAPTER 5 Open-cell P(VDF-TRFE)/MWCNT Nanocomposite Foams with Local Piezoelectric and Conductive Effects for Airborne Sound Absorption 67

5.1.	Introduction	68
5.2.	Results and Discussion	68
5.2.1	Crystal Phases	68
5.2.2	Morphology	69
5.2.3	Thermal Analysis	72
5.2.4	Sound-absorption Properties	73
5.2.5	Electrical Conductivity	76
5.2.6	Theoretical Model	78
	Conclusions	81
	References	81

CHAPTER 6 Enhanced Airborne Sound Absorption Effect in Poly(vinylidene fluoride)/(K_{0.5}Na_{0.5})NbO₃-nanofiber Composite Foams 83

6.1.	Introduction	84
6.2.	Results and Discussion	84
6.2.1	Crystal Phases	84
6.2.2	Morphology	86
6.2.3	Thermal Analysis	87

6.2.4	Sound-absorption Properties	88
6.2.5	Electrical and Piezoelectric Properties.....	89
6.2.6	Theoretical Model	91
	Conclusions	93
	References	93
CHAPTER 7 Discussion and Future Work		95
7.1.	General discussion	96
7.2.	Recommendations and Future Work.....	99
	References	101
PUBLICATIONS		103

Table Caption

Table 6.1 Noise reduction coefficient (NRC) of the open-cell PVDF/KNN-nanofiber composite foams with different KNN-nanofiber concentration.....	89
--	----

Figure Captions

Figure 1.1 Effectiveness of active and passive noise techniques at different frequency. [7]	3
Figure 1.2 (a) Broadband feedforward ANC system and (b) narrowband feedforward ANC system. [13].....	4
Figure 1.3 Schematic cross-section of a porous solid material. [14]	5
Figure 1.4 Three main types of porous absorption materials. [14]	6
Figure 1.5 Typical variation of a sound-absorbing coefficient for different passive noise absorbers. [21]	8
Figure 1.6 Schematic diagram of active hybrid panels of (a) AHSP and (b) AHDP. [25]	9
Figure 1.7 Schematic diagram of a passive hybrid panel. [25].....	9
Figure 2.1 Schematic diagram of a porosimeter. [1].....	20
Figure 2.2 Schematic diagram of the resistometer. [1]	21
Figure 2.3 Propagation models assuming a motionless skeleton. [13]	24
Figure 2.4 Piezoelectric applications of piezoelectric polymers. [25]	31
Figure 2.5 Unit cell of (A) α -phase, (B) δ -phase, (C) γ -phase, and (D) β -phase. Schematic chain conformation of (E) α -phase and δ -phase, (F) γ -phase, and (G) β -phase. The green arrow indicates the direction of the dipoles. [28]	33
Figure 2.6 Phase transformation between the different crystalline phases of PVDF. [32]	35

Figure 3.1 Processing flow chart for preparing PVDF/KNN-nanofiber composite foams.	45
Figure 3.2 Corona poling apparatus.	46
Figure 3.3 X-ray diffraction of a crystalline structure with interplanar spacing satisfying Bragg's law. [2]	48
Figure 3.4 Diagram of the impedance tube showing components of the acoustic wave. [5]	50
Figure 4.1 The ATR-FTIR spectra of the porous PVDF foams before and after thermal annealing. The unmarked peaks are common for both β and α phases.	55
Figure 4.2 XRD patterns of open-cell PVDF foams before and after thermal annealing.	56
Figure 4.3 SEM image and pore size distribution histogram of (a, b) unannealed, and (c, d) annealed open-cell PVDF foams.	57
Figure 4.4 a) Dynamic stiffness, and b) damping factor ($\tan \delta$) of open-cell PVDF foams before and after thermal annealing.	58
Figure 4.5 The sound absorption coefficient of the PVDF foams before and after thermal annealing.....	59
Figure 4.6 Surface acoustic impedance of the open-cell PVDF foams before and after annealing.....	59
Figure 4.7 Volume resistivity of the PVDF foams before and after thermal annealing. .	61
Figure 4.8 Dielectric constant and dielectric loss of PVDF foams at room temperature before and after thermal annealing.	61

Figure 4.9 The setup for testing voltage response at different sound pressure levels of open-cell PVDF foams.....	62
Figure 4.10 Voltage output at different sound pressure levels for open-cell PVDF foams before and after thermal annealing and electrical poling.....	63
Figure 4.11 Schematic illustration of (a) an open-cell PVDF foam, and (b) mechanisms of acoustic energy absorption with polar β phase.....	64
Figure 5.1 a) ATR-FTIR spectra, and b) XRD patterns of open-cell P(VDF-TrFE) and P(VDF-TrFE)/MWCNT nanocomposite foams. The unmarked peaks are common for both α and β phases.	69
Figure 5.2 SEM images and pore size distribution histograms of the cross-section position of (a) P(VDF-TrFE), (b) P(VDF-TrFE)/3 wt.% MWCNT, (c) P(VDF-TrFE)/5 wt.% MWCNT, (d) P(VDF-TrFE)/7 wt.% MWCNT, and (e) P(VDF-TrFE)/9 wt.% MWCNT foams at different locations: A circumference surface, B top surface, and C cross-section. These images demonstrated that there is no substantial difference in the morphology or pore distribution among these foams.....	71
Figure 5.3 DSC (a) heating and (b) cooling curves of the open-cell P(VDF-TrFE) and P(VDF-TrFE)/MWCNT nanocomposite foams.	73
Figure 5.4 Sound absorption coefficient of open-cell P(VDF-TrFE) and P(VDF-TrFE)/MWCNT nanocomposite foams with different amount of MWCNTs (a) from 500 Hz to 6400 Hz, and (b) from 500 Hz to 2000 Hz.	74
Figure 5.5 Homogeneity results of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.....	75
Figure 5.6 Surface acoustic impedance of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.	76

Figure 5.7 Volume electrical conductivity and noise reduction coefficient of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.	77
Figure 5.8 Dielectric constant (a) and dielectric loss (b) of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.	77
Figure 5.9 Schematic illustration of (a) 3D overview of the open-cell porous foam; (b) P(VDF-TrFE)/MWCNT nanocomposite structure; (c) mechanisms for converting sound energy to electricity with local piezoelectric effect and electrical energy to thermal energy through resistive loss.....	78
Figure 5.10 Electrical impedance measurements for the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.	80
Figure 6.1 a) XRD patterns and b) ATR-FTIR spectra of open-cell PVDF and PVDF/KNN-nanofiber composite foams. The unmarked peaks are common for both α and β phases.....	85
Figure 6.2 SEM images and pore size distribution histograms of the open-cell (a) PVDF, (b) PVDF/3 wt.% KNN-nanofibers, and (c) PVDF/5 wt.% KNN-nanofiber composite foams.	86
Figure 6.3 DSC (a) heating and (b) cooling curves of open-cell PVDF and PVDF/KNN-nanofiber composite foams.....	87
Figure 6.4 Sound absorption coefficient of open-cell PVDF and PVDF/KNN-nanofiber composite foams, with the inset showing low-frequency absorption coefficient between 500 and 2500 Hz.....	88
Table 6.1 Noise reduction coefficient (NRC) of the open-cell PVDF/KNN-nanofiber composite foams with different KNN-nanofiber concentration.	89

Figure 6.5 Dielectric constant of the open-cell PVDF/KNN-nanofiber composite foams.	90
Figure 6.6 Three-dimensional graphs of vibration data of the KNN nanofibers under the electric sine wave driving (10 V amplitude at 1 kHz) measured with LSV under substrate clamping conditions for KNN nanofiber webs. The central protruded area is the electrically excited nanofibers under the top Au electrode (diameter size of 0.25 mm), whereas the flat adjacent area is the nanofibers without the top electrode.....	91
Figure 6.7 Schematic illustration of (a) PVDF/KNN-nanofiber composite structure, and (b) mechanisms for converting sound energy to electricity with local piezoelectric effect and electrical discharging to thermal energy through the opposite piezoelectric effect.	92
Figure 7.1 Sound absorption coefficient of open-cell P(VDF-TrFE)/7 wt.% MWCNT nanocomposite foam and PVDF/5 wt.% KNN-nanofiber composite foam. .	98
Figure 7.2 Sound absorption coefficients of piezo-PLLA, nonpiezo-PDLLA, in comparison with several commercial sound absorbers (20 mm in thickness).	100
Figure 7.3 SEM images and pore size distribution histograms of the open-cell (a) PLLA and (b) PDLLA foams.	100

Abbreviations

ANC	Active Noise Control
ATR	Attenuated Total Reflectance
$(\text{CH}_3\text{CH}_2\text{O})_5\text{Nb}$	Niobium Ethoxide
CH_3COONa	Sodium Acetate
CH_3OOK	Potassium Acetate
CO_2	Carbon Dioxide
Sc- CO_2	Supercritical Carbon Dioxide
DMA	Dynamic Mechanical Analysis
DMF	N,N-dimethylformamide
DSC	Differential Scanning Calorimetry
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
KNN	Potassium Sodium Niobate
MWCNTs	Multi-walled Carbon Nanotubes
NRC	Noise Reduction Coefficient
P(VDF-TrFE)	Poly(vinylidene fluoride-co-trifluoroethylene)
PDLA	Poly(_D -lactide)
PDLLA	Poly(_{D,L} -lactide)
PLA	Poly(lactic acid)
PLLA	Poly(_L -lactide)
PU	Polyurethane
PVDF	Poly(vinylidene fluoride)
PVP	Polyvinylpyrrolidone
XRD	X-ray Diffraction

Chapter 1

Introduction

This chapter presents a brief background and an overview of the thesis. The world is facing a growing noise pollution problem that is grown rapidly with expanding in technological advancements and increasing population. Open-cell foams are well-known as the most usable sound absorption systems; however, sound materials need further research to improve their current performance specifically at low-frequency range. In this thesis, the aim is to develop piezoelectric open-cell polymer and nanocomposite foams with controlled morphology, structure, and composition that are suitable for high-performance airborne sound absorption applications. In this chapter, a brief introduction concerning the noise and noise absorption techniques is stated followed by the introduction of the problems and challenges involved in the field of sound absorption. Therefore, the answers on how to resolve these problems, as well as the scope and objectives of the thesis will be discussed. Then, the organization of the thesis will be explained. Lastly, the major findings and outcomes of this doctoral thesis are summarized.

1.1. Problem Statement

Among the various environmental issues, noise pollution has been increasing over the past years. Many factors can determine the quality of life. One of the most vital factors determining the livability in high population density areas is noise level. It was reported that prolonged exposure to high noise levels for a period of time gradually causes hearing damage, such as a temporary or permanent hearing loss. [1] Thus, noise pollution has become a crucial problem with an increasing extent affecting the quality of peoples' lives. Noise experienced by people can be generated from various sources such as industrial machines, traffic road, and too many others. The noise often creates living environments and workplaces abhorrent. [2] Despite the increase of regulations and the efforts of scientists who have worked strenuously in order to minimize noise pollution, the noise levels have increased 12 dB(A) in the urban areas within the last 20 years and available designs these days do not fully eliminate the noise that is generated or transmitted. [3] Although extensive research has been done to beat the noise by scientists as well as acousticians, existing solutions are not effective in eliminating the noise issues in many cases, and there is plenty of work needed to improve the solution.

Three techniques of noise mitigation have been used as follows: (1) active, (2) passive, and (3) hybrid. [4-6] Neither active noise control nor passive noise control can work effectively at low cost over a broadband frequency as mentioned in **Figure 1.1**, due to the physical limits associated with each technique. [7] For instance, the use of passive methods to attenuate low frequency noise is often impractical since considerable extra bulk and weight are required, [8], while active noise control becomes more complicated and costly at high frequency. In the next section, the working principles of each method will be discussed, as well as the advantages and disadvantages of using each one.

Figure 1.1 Effectiveness of active and passive noise techniques at different frequency. [7]

1.1.1 Active Noise Control

Active noise control (ANC) is used when passive noise mitigation methods are ineffective to be applied. As such, this is particularly the situation for low-frequency noise environments. ANC is a technique with a purpose to reduce the noise level by introducing additional noise using one or more secondary noise sources. [9] ANC can be applied by introducing an anti-phase wave through secondary sources. The secondary sources are interconnected via an electronic system that uses a signal processing algorithm. Basically, ANC techniques are very effective and necessary at the frequency below 200 Hz. [10] ANC systems can be categorized by mechanisms of their control. First, feedforward control is where a coherent reference noise input is sensed before it propagates past the canceling speaker. Next, feedback control is where the active noise controller attempts to cancel the noise without the benefit of an upstream reference input. [11, 12]

At present, the feedforward ANC systems are the main used techniques. Feedforward ANC systems can be classified into two categories, as shown in **Figure 1.2**:

- Broadband feedforward control with an input sensor.
- Narrowband feedforward control with a non-acoustic input sensor.

Figure 1.2 (a) Broadband feedforward ANC system and (b) narrowband feedforward ANC system. [13]

Because the incoming noise characteristics vary over time, the system needs to adapt in order to deal with these differences. The adjustment of the signal is achieved using filters, which use different methods to reduce the error signal. [13] These filters become more complicated when they adapt more efficiently to noise sources. Thus, such systems become impractical to be implemented in environments with noise at different frequencies.

1.1.2 Passive Noise Control

For many years, the passive noise technique has been used to cope with noise problems, focusing mainly on the energy absorption from a source and ultimately convert it into heat. [13] This method utilizes such mechanism as sound absorptive material, enclosures, and noise barriers. Passive noise control technique excels on hybrid and active noise control techniques in wider applications as that it does not need an external source of electrical energy. [7] This advantage gives the passive noise control technique preference over any other approaches, in terms of cost. The passive noise control approach provides efficient attenuation performance mainly in the mid to higher frequency range, but it does not provide adequate reductions at low frequencies, which is the major drawback. [7] The process of converting sound energy into heat can be done basically using three materials:

(1) porous materials, [14] (2) micro-perforated panels, [15, 16] and (3) diaphragmatic absorbers. [15]

Absorption of acoustic energy depends on the sound wave frequency that is governed by the law of linear response. The linear response law dictates that the energy dissipation is a quadratic function of the rate of absorption. Thus, at low frequency, the absorption rate is low, and therefore intrinsically all materials have a very weak absorption of the low-frequency sound. Thus, due to the limitations of porous materials at low-frequency, other methods have been evolved to overcome this problem.

Porous materials reduce noise level through disseminating the sound energy and transforming it into heat. The porous material is a group of solids that contains cavities, channels, or voids through which the sound waves can pass, so the intensity of sound waves is brought down. [14] Sound absorbing materials can be classified into two classes based upon its macroscopic configurations, as shown in **Figure 1.3**.

Figure 1.3 Schematic cross-section of a porous solid material. [14]

The first type is called open pore, which has interconnected, and continuous channels are connected to the ambient environment. The second type is called closed pore. [14] Another classification of porous absorption material based on their microscopic structure as follows: 1) cellular, 2) fibrous, or 3) granular, [14] as illustrated in **Figure 1.4**.

Figure 1.4 Three main types of porous absorption materials. [14]

Noise control using porous absorption materials works through the friction process inside the pores. This friction creates viscous and thermal effects that cause the dissipation of the undesired acoustical energy. When sound waves propagate in porous materials, they experience a different situation from what they experience when they propagate through the atmosphere in many respects. For example, porous materials are highly dispersive and dissipative due to viscous and thermal diffusion processes occurring as the sound waves interact with the porous frame. [15] Because of these interactions, viscous and thermal boundary layers are formed. Within these layers, viscous and thermal diffusion have considerable influence. The thickness of the formed boundary layers is inversely dependent on the frequency. Furthermore, the pore size of porous materials is too small to enable the emergence of an ambient or turbulent flow.

The friction of the fluid across the solid produces heat that can be transferred from the solid frame to the fluid. An impact of pressure waves inside a pore can dissipate energy through the solid frame as a vibration. The air particles in the pores subjected to periodic compression and decompression, which is accompanied by a fluctuation change in temperature. In the low-frequency region, the viscous boundary layer may be of a similar size with the pores. In this case, viscous losses are high and dominant. Also, as the pore size increases, the air particles in the pores are subject to periodic compression and decompression, which is associated with a fluctuation, change in temperature. If the porous

material is a heat conductor, heat exchange in each half of the period will take place, making the air compressed isothermally, and the materials absorbed the sound by energy loss caused by heat exchange.

On the other hand, at high frequency, the thickness of the viscous boundary layer is much smaller than the pore size; hence, the viscous loss will be very few. Because of the irregularity of the pore structure that leads to a nonlinear airflow propagation causes a momentum loss in the direction of wave propagation. In general, at a higher frequency, the adiabatic process of compressing air takes place that produces heat loss due to friction when the sound wave crosses the irregular pores. [18] As mentioned earlier, porous absorbing materials have low absorption performance at low frequency and can only be overcome by increasing the porous absorption thickness. [19] This is the essential drawback of using porous materials for noise control because it needs a large thickness of the porous materials, and this is the impractical solution.

Other passive noise control techniques have been developed in such cases. One example that can be used is diaphragmatic absorber panels. As opposed to what happens in porous materials, these diaphragmatic absorbers are used to improve sound absorption at lower audible frequencies. [20] Diaphragmatic absorbers are usually flexible panels of wood or compressed wood mounted over an air gap. When the sound waves hit the panel, it will resonate at a frequency determined by the elastic stiffness of the panel and the dimension of air space. Other sound waves of the same frequency (or frequencies) getting close to the panel, therefore are also dampened. Diaphragmatic absorbers are used basically to absorb low-frequency sounds; accordingly, it is called traps. [17] In principle, this concept can also be applied to absorb high-frequency sounds. Due to its working principle, the diaphragmatic absorber can be modeled as a simple spring-mass system. Consequently, it has a specific resonance frequency at which it will operate efficiently. [8]

Due to the limitations of both porous materials and diaphragmatic absorbers, micro-perforated panels have been developed to cope with such constraints. The micro-perforated panel absorber is thin, and it can cover certain bandwidth, which is relatively sufficient for

wideband sound absorption applications by implementing many resonators in the same phase to absorb efficiently. However, the resonant frequency of the micro-perforated panel moves to the mid-high frequency range when the aperture is down to 0.1 mm. Consequently, the low-frequency absorption performance is abated. [21] The effectiveness of each passive control approach is illustrated in **Figure 1.5**.

Figure 1.5 Typical variation of a sound-absorbing coefficient for different passive noise absorbers. [21]

1.1.3 Hybrid Noise Control

Hybrid noise control technique has been developed for obtaining both active and passive noise control techniques advantages in order to achieve a wide band of noise absorption. [22] One of the most important advantages of hybrid noise control is that it needs less external energy than active noise control, but also the dependence on external energy can make it impractical in some applications. [23]

One design to note comprises piezoelectric polymer film (PVDF) embedded in porous absorption foam. [24] This method is called active hybrid noise control. The design of hybrid system takes the advantages of foam for passive noise absorption at the high-frequency range, and the PVDF is employed as an acoustic actuator to boost the low-frequency absorption of the foam. Precisely, it uses active noise control in the low-frequency region and the capability of the passive noise control for the mid and high

frequencies. Active hybrid control panels are available in two configurations, a) an active hybrid single panel (AHSP) and b) an active hybrid double panel (AHDP), as illustrated in **Figure 1.6**.

Figure 1.6 Schematic diagram of active hybrid panels of (a) AHSP and (b) AHDP. [25]

Another configuration in which a piezoelectric shunt damping has been used on panel structures to convert a structure from an active noise radiator to a weak radiator, this approach is called passive hybrid panels that require a simple and inexpensive shunt circuit, as illustrated in **Figure 1.7**. The goal of using passive hybrid panels was to decrease the thickness of porous materials used for absorbing the low-frequency noise. [25]

Figure 1.7 Schematic diagram of a passive hybrid panel. [25]

Based on the discussion above, high-performance sound absorption materials are needed. Among the various types of sound-absorbing materials, piezoelectric-based materials are promising, mainly due to effective electromechanical coupling.

In order to introduce a new airborne sound absorption mechanism and improve airborne sound absorbing performance, several approaches were investigated. Among the various strategies studied, piezoelectric foams with local piezoelectric properties, and composite formation with conductive multi-walled carbon nanotubes (MWCNTs) and piezoelectric potassium sodium niobate (KNN) nanofibers have yielded auspicious results.

1.2. Motivation

The motivation of this work arises in order to make the noise go away by introducing the local piezoelectric effect of open-cell polymeric foams for enhancing the performance of the noise mitigation applications.

Sound absorption became a subject of importance for both noise mitigation and interior acoustics optimization because of the strong revival in advanced technologies that led to increasing the noise level tremendously. Among the various environmental issues, noise pollution has been growing over the past years, especially in many developed urban areas. Active, passive, and hybrid noise mitigations are commonly used approaches for noise cancellation. [25, 26] The dissipation of sound in the audible range transmitting medium, such as air, is quite minimal and consequently, the noise mitigation approaches had emerged starting with W. C. Sabine around 1895 when he studied for the first time the relation between reverberation in a room and its sound absorption. [27]

Absorption of acoustic energy depends on the sound wave frequency that is governed by the linear-response law because the sound is associated with minimal air displacement velocities. [28, 29] The linear response law dictates that the frictional forces and fluxes to be both linearly proportional to the rate of dissipation, [30, 31] thus, the absorption rate of low-frequency sound is low. Intrinsically, almost all materials have a weak absorption of

the sound energy, particularly below 2 kHz. Due to the limitations of porous materials at low frequency, other complicated methods have been evolved to overcome this problem, including the use of acoustic metamaterials [32, 33], and sonic crystals. [34] Furthermore, conventional sound-absorbing materials possess fixed absorption spectra that can only be modified by changing the sample thickness that must be within a quarter of the sound-wavelength or through inventing a new approach for enhancing the low-frequency sound absorption performance. [34]

The use of piezoelectric materials for noise control technologies passed by enormous advancements. Lead zirconate titanate (PZT) piezoelectric ceramics have been utilized as films for suppression of the mechanical vibration plates by Yang and Chui, [35] beams by Blanguernon et al., [36] and shell structures by Balamurugan and Narayanan. [37] Moreover, structural vibration-damping technologies have been deployed utilizing the piezoelectric effect, such as in the piezoelectric shunt damping and piezoelectric damping composites. [38] A smart foam consists of a passive layer bonded to one surface of an active piezoelectric composite while the other surface is bonded to the vibrating plate surface was proposed to achieve a broad frequency range of vibration and acoustic noise control. [39] Our team at IMRE has recently first introduced the concept of hybrid local-piezoelectric and electrical conductive functions in foam material to achieve high-performance airborne sound absorption, which is made of porous polar polyvinylidene fluoride (PVDF) mixed with conductive single-walled carbon nanotube (SWCNT). [40] However, a profound understanding of how the introduction of local piezoelectric effect to acoustical foams works and what are the associated complications could take place is not well developed yet. Hence, in this thesis, open-cell foams of PVDF homopolymer, and P(VDF-TrFE) copolymer, and their composites with polar phases, local piezoelectric effect and conductivities were produced and evaluated comparably for airborne sound absorption investigations.

1.3. Objectives and Scope

The Ph.D. project aims to:

- (1) Explore the potential role of local piezoelectric effect of polymeric porous materials for airborne sound absorption.
- (2) Understand the energy conversion and loss mechanisms in piezoelectric porous polymeric materials and their contributions to airborne sound absorption.

These goals have been achieved by fabricating innovative open-cell piezoelectric polymeric foams for sound absorption evaluation, as well as investigating the link between material structure such as morphology and pore size with macroscopic properties. Additionally, how the local piezoelectric effect of polymeric foams can affect the noise absorption performance is examined, by a series of design and evaluation to identify the contribution of local piezoelectricity. This work will lead to material and technology for broadband noise absorption applications.

1.4. Dissertation Overview

Chapter 1 provides the motivation and significance of research on sound absorption materials and explains the problem statement in this field. Based on this motivation, the objective and scope of the thesis are established. Finally, this chapter summarizes the organization, and the main outcomes of the thesis.

Chapter 2 reviews the recent literature concerning the fields of open-cell foam fabrication approaches, sound absorption principles, significant acoustic properties of a medium and available characterization techniques, as well as the basic knowledge about piezoelectric materials is presented, followed by an explanation of the essential properties of porous materials that determine the sound absorption performance.

Chapter 3 discusses the principles underlying the fabrication, and characterization techniques employed and the methods of data analysis. The fabrication technologies for open-cell foams and its nanocomposites are also summarized.

Chapter 4 presents the strategy for the preparation of open-cell poly(vinylidene fluoride) foams with the polar phase for enhanced airborne sound absorption.

Chapter 5 elaborates the fabrication and performance of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams with local piezoelectric and conductive effects for airborne sound absorption.

Chapter 6 elaborates the fabrication and performance of enhanced airborne sound absorption effect in PVDF/KNN-nanofiber composite foams.

Chapter 7 summarizes the whole thesis and sheds light on the reconnaissance work, which can be carried out in the future. Extended ideas based on the hypothesis and experimental results are also included.

1.5. Findings and Outcomes

In this thesis, novel open-cell piezoelectric polymer foams were fabricated and applied in airborne sound absorption applications. This research leads to several original outcomes below:

1. Separating and identifying the contributions of local piezoelectric effect on airborne sound absorption in PVDF foams through comparable samples obtained by thermal treatment to enhance the polar β -phase content and thus local piezoelectric effect.
2. Building the models for analyzing the role of local piezoelectric and conductive effect in composite foams with enhanced airborne sound absorption performance.
3. Tailoring the conductivity percolation threshold of P(VDF-TrFE)/MWCNT nanocomposite foams to achieve the electrical impedance matching condition for maximizing characteristic piezoelectric damping effect for optimal broadband airborne sound absorption.

4. Incorporating the piezoelectric KNN-nanofibers with positive piezoelectric coefficient $+d_{33}$ into the PVDF matrix with negative piezoelectric coefficient $-d_{33}$ in order to facilitate the electrical discharge process inside the foam, which could enhance the energy dissipation with the opposite charges generated through the piezoelectric effects in the two phases with opposite polarity and hence the airborne sound absorption.

References

- [1] A. Garcia, A. M. Garcia, F. Baixauli, P. Boix, and A. Marcos, *Occupational Hygiene*, **1997**, 4, 47-54.
- [2] E. Donald, *Basic Acoustics*, Harper and Row, New York: Harper & Row, **1987**.
- [3] H. V. Fuchs, *Applied acoustics: concepts, absorbers, and silencers for acoustical comfort and noise control: Alternative solutions -- Innovative tools -- Practical examples*. Springer, Berlin, **2013**.
- [4] W-H. Chen, F-C Lee, Chiang D-M, *Sound & Vibration*, **2000**, 237, 337–55.
- [5] Z. Azkorra, G. Pérez, J. Coma, L. F. Cabeza, S. Bures, J. E. Álvaro, A. Erkoreka, and M. Urrestarazu, *Appl. Acoust.*, **2015**, 89, 46–56.
- [6] M. J. Jafari, M. R. Monazam, and M. Kazempour, *Journal of Environmental Health Science and Engineering*, **2018**, 16, 289–297.
- [7] C. M. Harris, *Handbook of Acoustical Measurements and Noise Control*, 3rd Ed. McGraw-Hill, New York, **1991**.
- [8] X. Sagartzazu, L. Hervella-Nieto, and J.M. Pagalday, *Arch. of Comp. Meth. in Eng.*, **2008**, 15, 311-342.
- [9] S. M. Kuo and D. R. Morgan, *Proceedings of the IEEE*, **1999**, 87, 943-973.
- [10] J. Landaluze, I. Portilla, J.M. Pagalday, A. Martinez, and R. Reyero, *Control Eng Pract.* **2003**, 11, 1423-1431.
- [11] H. F. Olson and E. G. May, *J. Acoust. Soc. Am.* **1953**, 25, 1130–1136.
- [12] H. F. Olson, *J. Acoust. Soc. Am.*, **1956**, 28, 966–972.
- [13] F. A. Everest, *Master handbook of acoustics*, New York: McGraw-Hill Companies, **2002**.
- [14] J. P. Arenas and M. J. Crocker, *Sound & Vibration*, **2010**, 44, 12-17.

- [15] D. Maa, *J. Acoust. Soc. Am.* **1998**, 104, 2861-2866.
- [16] H. V. Fuchs and X. Zha, *Acta Acust united Ac.* **2006**, 92, 139-146.
- [17] J. P. Arenas and F. Ugarte, *Appl. Acoust.* **2016**, 114, 10-17.
- [18] V. E. Ostashev and D. K. Wilson, *Acoustic in Moving Inhomogeneous Media*, 2nd Ed. CRC Press, Taylor & Francis Group, LLC. **2016**.
- [19] J. F. Allard and N. Attala, *Propagation of sound in porous media: modelling sound absorbing materials*, 2nd Ed. Hoboken, N.J: Wiley, **2009**.
- [20] R. Del Rey, J. Alba, J. P. Arenas, and V. J. Sanchis, *Appl. Acoust.* **2012**, 73, 604-609.
- [21] X. H. Duan, H. Q. Wang, Z. B. Li, L. K. Zhu, R. Chen, D. Y. Kong, and Z. Zhao, *Appl. Acoust.* **2015**, 88, 84–89.
- [22] C. A. Gentry, *J. Acoust. Soc. Am.* **1997**, 101, 1771-1778.
- [23] C. R. Fuller, C. Guigou, and C. A. Gentry, *Proc. SPIE*, **1996**, 2721, 26-37.
- [24] C. Guigou, C. R. Fuller, *Sound & Vibration*, **1999**, 220, 541-557.
- [25] J. Kim and Y.-C. Jung, *J. Acoust. Soc. Am.* **2006**, 120, 2017-2025.
- [26] X. Sagartzazu, L. Hervella-Nieto, J. M. Pagalday, *Arch. Comp. Meth. Eng.* **2008**, 15, 311-342.
- [27] T. D. Northwood, *J. Acoust. Soc. Am.* **1983**, 73, S41.
- [28] M. Yang, S. Y. Chen, C. X. Fu, P. Sheng, *Mater. Horiz.* **2017**, 4, 673-680.
- [29] J. P. Arenas and M. J. Crocker, *Sound & Vibration*. **2010**, 44, 12-17.
- [30] M. O'Donnell, E. T. Jaynes, J. G. Miller, *J. Acoust. Soc. Am.* **1981**, 69, 696-701.
- [31] J. Mei, G. Ma, M. Yang, Z. Yang, W. Wen, and P. Sheng, *Nat. Commun.* **2012**, 3, 756-761.
- [32] Z. Liu, X. Zhang, Y. Mao, Y. Y. Zhu, Z. Yang, C. T. Chan, and P. Sheng. *Science*, **2000**, 289, 1734-1736.
- [33] S. A. Cummer, J. Christensen, and A. Alù, *Nat. Rev. Mater.* **2016**, 1, 16001-16013.
- [34] M. D. Guild, V. M. García-Chocano, W. Kan, J. Sanchez-Dehesa, *J. Appl. Phys.* **2015**, 117, 114902-114914.
- [35] S. M. Yang, J. W. Chiu, *J. Comp. Struct.* **1993**, 25, 381-386.
- [36] A. Blanguernon, F. Léné, and M. Bernadou, *Smart Mater. Struct.* **1999**, 8, 116-124.
- [37] V. Balamurugan and S. Narayanan, *Smart Mater. Struct.* **2001**, 10, 173-180.

- [38] M. Sumita, H. Gohda, S. Asai, K. Miyasaka, A. Furuta, Y. Suzuki, K. Uchino, and D. Makrom. *Chem. Rap. Comm.* **1991**, 12, 657-661.
- [39] W. Akl and A. Baz, *Inter-Noise and Noise-Con Conf. and Conf. Proc.* **2002**, 5, 731-739.
- [40] M. Rahimabady, E. C. Statharas, K. Yao, M. S. Mirshekarloo, S. Chen, and F. E. H. Tay, *Appl. Phys. Lett.* **2017**, 111, 241601-241605.

Chapter 2

Literature Review

This chapter presents an overview of the literature and puts the research work within its context. The models that are being used to describe and predict the behavior of porous absorbing materials and the relevant parameters will be addressed. Moreover, the basics of piezoelectricity, PVDF homo-polymer, and its copolymers will be discussed. Additionally, the production techniques used to produce polymer foams will be presented.

2.1. Acoustic Properties of Porous Absorbing Materials

Porous absorbing materials also called fluid-saturated porous materials mainly comprise two phases: a) solid phase, which is essentially the skeleton of media; and b) fluid phase, which is basically the air inside the pores, but also other fluids can exist. For the solid phase, there are also different types of skeletons, such as continuous in the case of porous ceramics, or non-continuous in the case of granular materials. Understanding the acoustic properties of the absorbing materials enables us to describe the behavior of these materials, tailor properties of such materials, and thus apply the materials in various sound control applications. [1, 2] Due to the complexity of the structure of porous materials, to achieve a comprehensive description of porous sound absorbers, the following parameters should be defined: (1) liquid properties, (2) solid "skeleton" of the material, and (3) the coupling parameters that correlate the solid and liquid. To get a deep understanding regarding the dissipation mechanisms during sound absorption process, a complete description of these properties is of extreme importance.

2.1.1 Properties of the Fluid Phase

Attention regarding the fluid part comes because the sound wave propagation mainly happens in the liquid phase. The liquid properties can be stated as follows:

- 1) Volume mass (ρ): the parameter representing the mass of a body per unit of volume and generally expressed in kg/m^3 .
- 2) The ratio of specific heats (γ): the parameter representing the quotient of specific heat at constant pressure (C_p) and specific heat at constant volumes (C_v), given by **Equation (2.1)**.

$$\gamma = C_p/C_v \quad (2.1)$$

- 3) The speed of sound (c): the speed at which pressure waves travel in the medium when entropy remains constant, given by **Equation (2.2)**.

$$c = \sqrt{\frac{\partial \hat{p}}{\partial \rho}}(\rho_o, s_o) \quad (2.2)$$

- 4) Prandtl number (P_r): the quotient between kinematic viscosity and thermal diffusivity, given by **Equation (2.3)**.

$$P_r = \frac{\eta/\rho}{\kappa/\rho C_p} = \frac{\rho C_p}{\kappa} \quad (2.3)$$

where κ is the thermal conductivity, η is the dynamic viscosity.

2.1.2 Properties of the Skeleton

The characteristic properties of the solid phase "skeleton" have significant importance because the foam skeleton is what introduces the additional friction that leads to extra energy loss. The open cell porous materials skeleton can be adequately described using the three elastic properties: [3] Young's modulus (E), shear modulus (G), and Poisson's ratio (ν). The case of a harmonic excitation must be taken into consideration. Thus these three properties are complex and frequency-dependent due to the skeleton's material viscosity. As a result, to characterize these materials, dynamic tests need to be done. [4]

2.1.3 Properties that Define Coupling between the Fluid and Skeleton

These parameters related to the concentration of fluid, mainly air, and the way of its distribution in the porous medium, are called "acoustical" parameters. These coupling properties determine the degree of interaction between the fluid and the skeleton.

2.1.3.1 Porosity ϕ

The porosity of a porous material is the relative fraction, of air contained within the material by volume. [5] It is defined as the ratio of the voids volume V_f in the porous material over its total volume V_t .

$$\phi = V_f/V_t \quad (2.4)$$

The porosity can be measured simply based on the Boyle-Mariotte's law. The working principle is to decrease the volume of a chamber in which a material sample is placed. The piston generates a variation in pressure from which is deduced the air in the sample. The schematic diagram of a porosimeter is depicted in **Figure 2.1**.

Figure 2.1 Schematic diagram of a porosimeter. [1]

By using Boyle-Mariotte's law:

$$(V_f + V_{ext})p_0 = (V_f + V_{ext} + \Delta V)(p_0 + \Delta p) \quad (2.5)$$

$$V_f = -\left(\frac{p_0 + \Delta p}{\Delta p} \Delta V + V_{ext}\right) \quad (2.6)$$

Once the sample's air volume is determined, porosity can be calculated using **Equation (2.4)**. It is essential to mention that in sound absorption applications, only the open pores are considered since the closed pores add to the stiffness of the foam. [6, 7]

2.1.3.2 Flow Resistivity σ

Flow resistivity, "also called static airflow resistivity," [8] considered as one of the most significant parameters in the understanding of the sound-absorbing behavior in porous materials, is identified by **Equation (2.7)**.

$$\sigma = \frac{\Delta P}{Ql} \quad (2.7)$$

where P is the pressure drop across the material, Q the volume that flows per unit surface and per unit time and l the thickness of the sample, in the international system of units, its dimension is N.s.m^{-4} . In the case of sound absorption materials, the flow resistivity has a range of values between 10^3 and 10^6 N.s.m^{-4} . Flow resistivity can be measured experimentally using a resistometer that is illustrated in **Figure 2.2**, according to ASTM C522 standard test method. The pressure drops before and after passing the sample is then measured with a differential manometer. The flow resistivity can be determined from the slope of the pressure versus flow per unit surface and unit time curve.

Figure 2.2 Schematic diagram of the resistometer. [1]

2.1.3.3 Tortuosity α_∞

The tortuosity (or twistiness) is a quantity that takes into account the irregular shape of the pore. Tortuosity is a measure of the “non-straightness” of the pore structure of the porous material. Thus, the more complicated path, the more time a wave will be in contact with the wall of pores. Thus, much more sound energy will be dissipated. The easiest way to determine tortuosity is to assume that the elastic material possessing cylindrical pores has an inclination angle of ϕ with respect to the direction of the thickness of the material. [2] In this case, the tortuosity is determined using the following Equation:

$$\alpha_\infty = \frac{1}{\cos 2\phi} \quad (2.8)$$

Experimentally, one of the methods used to measure tortuosity is by saturating the sample with an electrically conductive fluid and measure the electrical resistivity of the saturated sample (r_s) and compare it to the resistivity of the fluid alone (r_f). Then the tortuosity is calculated using the following Equation:

$$\alpha_\infty = \phi \frac{r_s}{r_f} \quad (2.9)$$

2.1.3.4 Viscous Characteristic Length Λ

The viscous characteristic length is the parameter that accounts for viscous effects at high frequencies and is defined by **Equation (2.10)**. [8]

$$\frac{2}{\Lambda} = \frac{\int_A v^2(r_w) dA}{\int_V v^2(r) dV} \quad (2.10)$$

where $v(r_w)$ and $v(r)$ are the microscopic phase velocity of the non-viscous fluid on the pore wall and in the bulk of the pore, respectively.

2.1.3.5 Thermal Characteristic Length Λ'

Thermal characteristic length is the parameter that accounts for the thermal changes between the solid phase and fluid phase at high frequencies range. [8] Thermal characteristic length is defined using **Equation (2.11)**.

$$\Lambda' = 2 \frac{V_f}{A_i} \quad (2.11)$$

where V_f is the fluid volume and A_i is the surface area.

2.2. Acoustic Modeling of Porous Absorbing Materials

In order to improve the acoustic performance of porous absorbing materials, the relationship between different structural characteristics and acoustic behavior should be studied. The theoretical prediction of the acoustic properties of porous materials is difficult because of the complex cell structure of these materials. Two cases must be differentiated to characterize porous materials. [2]

First, the case in which the skeleton of the foam remains motionless, which called the rigid frame case. This assumption is valid when the density of the saturating fluid is much less than the density of the foam or when the viscous permeability of the porous media is quite high. Consequently, the skeleton of the foam cannot be excited by the energy of the sound wave. Thus, the only wave that travels in the material is the fluid-borne wave. [2]

However, the presence of a motionless skeleton case needs a modification; accordingly, the compressibility and the mass density of the saturating fluid will be complex and frequency-dependent. Several models have been published to describe the sound wave propagation in rigid frame porous media. [5] Because these foams are saturated with air, the thermal losses would not be neglected. Thus, six parameters (porosity, viscous, thermal permeability, tortuosity, viscous, and thermal characteristic lengths) are required to understand the acoustic behavior of isotropic porous materials.

In the second case, when sound wave energy is sufficient to make the structure of the foam excite and then vibrate, and this requires the use of the Biot theory [9, 10]. Therefore, the complex mass density, complex compressibility, and mechanical properties of the polymer that forms the foam are required to describe the acoustic behavior of porous media. By adding these four parameters to the six parameters needed by the rigid frame model, a full description of the isotropic porous media can be achieved using Biot theory. [11]

The propagation of sound in acoustic porous media can be classified into three categories: 1) diphasic models, 2) equivalent fluid models, and 3) equivalent solid models. The diphasic models consider the wave propagations and their interactions in both solid phase and fluid phase of a porous material. These models are the most comprehensive to describe the vibroacoustic or structural-acoustic interaction of porous media. However, they need more parameters to be used. Motionless skeleton models can be classified into three classes of models in order to find expressions of dynamic density $\tilde{\rho}$ and dynamic compressibility $\tilde{K}$. These models are analytical models, empirical models, and semi-phenomenological models. Furthermore, different motionless skeleton models can be seen in **Figure 2.3**. [12]

Figure 2.3 Propagation models assuming a motionless skeleton. [13]

2.3. Piezoelectricity

2.3.1 Piezoelectric Effect

Piezoelectricity is a coupling property that correlates the mechanical and electric behaviors of a specific category of materials. This coupling property refers to the fact that the mechanical strain and the electric field influence each other; changing one changes the other, and vice versa. These phenomena can be classified as a piezoelectric response. The local piezoelectric effect is just the similar effective mechanical to electrical energy conversion mechanism occurring locally, which is not feasible to be measured over macro-scale using conventional characterization method. Too many approaches can be used to describe and derive piezoelectric effect and all other related effects such as piezomagnetism, ferroelectricity, pyroelectricity, and paramagnetism. Thermodynamics theory can be used successfully to derive the piezoelectric effect in general [14-16]. An energy approach can be followed because of the resultant equations are very complicated due to a large number of parameters.

Consider a piece of solid with temperature θ and entropy σ — the stress T_j and the strain S_j , where $j=1, 2, \dots, 6$. The electric field in the solid is E_n , the displacement field is D_n , the magnetic field is H_n , and the magnetic intensity is B_n , where $n=1, 2, 3$. For a small general transformation of the state of the solid, the change in energy is

$$dU = T_j dS_j + E_n dD_n + H_n dB_n + \theta d\sigma \quad (2.12)$$

From the expression for dU , the natural independent variables of the energy are S_j , D_n , B_n , and σ can be defined. However, the appropriate independent variables are typically T_j , E_n , H_n , and θ . For example, for constant temperature, it is essential to have θ as an independent variable so that $d\theta$ can be set to be equal to **zero**. Thus, Gibbs's function can be considered using the Legendre transformation that motivates the connection between the internal energy and Gibbs free energy. A Legendre transform is a mathematical technique that can convert from a function of a set of variables to the second function with a conjugate set of variables.

$$G = U - T_j dS_j + E_n dD_n + H_n dB_n + \theta d\sigma \quad (2.13)$$

Taking the perfect differentiation of G , and using the expression for dU , yields

$$dG = -S_j dT_j + D_n dE_n + B_n dH_n + \sigma d\theta \quad (2.14)$$

Now, this expression has the desired natural “canonical” variables, and this relationship is quite important because it is relating the constants of material in a single equation. Then, to derive the piezoelectric strain constant, suppose the magnetic intensity (B) and temperature (θ) are held constant, and take the second derivative of Gibbs function, will end up to

$$\partial^2 G / \partial T_j \partial E_m = \partial^2 G / \partial E_m \partial T_j \quad (2.15)$$

From here, the piezoelectric strain constant can be determined as follow $d = \partial S / \partial E$ “the rate of change of strain with respect to the electric field” has two alternative equivalent meanings:

- 1) How the strain changes with the electric field.
- 2) How the displacement field changes with stress.

And thus,

$$d_{mj}^{H\theta} = \left(\frac{\partial D_m}{\partial T_j} \right)_{H\theta E} = \left(\frac{\partial S_i}{\partial E_m} \right)_{H\theta T} \quad (2.16)$$

Applying the same process with other mixed derivatives yields other transduction constants with alternatives meanings such as:

Piezoelectric strain constant:
$$d_{mj}^{H\theta} = \left(\frac{\partial D_m}{\partial T_i} \right)_{H\theta E} = \left(\frac{\partial S_i}{\partial E_m} \right)_{H\theta T} \quad (2.17a)$$

Pyroelectric constant:
$$p_m^{TH} = \left(\frac{\partial D_m}{\partial \theta} \right)_{THE} = \left(\frac{\partial \sigma}{\partial E_m} \right)_{TH\theta} \quad (2.17b)$$

Piezomagnetic strain constant:
$$d_{mj}^{E\theta} = \left(\frac{\partial B}{\partial T_i} \right)_{E\theta H} = \left(\frac{\partial S_i}{\partial H_m} \right)_{E\theta T} \quad (2.17c)$$

Pyromagnetic constant:
$$i_m^{TE} = \left(\frac{\partial B_m}{\partial \theta} \right)_{TEH} = \left(\frac{\partial \sigma}{\partial H_m} \right)_{TE\theta} \quad (2.17d)$$

Magnetodielectric constant:
$$m_{mi}^{T\theta} = \left(\frac{\partial D_m}{\partial H_n} \right)_{T\theta E} = \left(\frac{\partial B_n}{\partial E_m} \right)_{T\theta H} \quad (2.17e)$$

Thermal expansion constant:
$$\alpha_i^{EH} = \left(\frac{\partial S_i}{\partial \theta} \right)_{EHT} = \left(\frac{\partial \sigma}{\partial T_i} \right)_{EH\theta} \quad (2.17f)$$

Elastic compliance constant:
$$s_{ij}^{EH\theta} = \left(\frac{\partial S_i}{\partial T_j} \right)_{EH\theta} \quad (2.17g)$$

Dielectric constant:
$$\epsilon_{mn}^{TH\theta} = \left(\frac{\partial D_m}{\partial E_n} \right)_{TH\theta} \quad (2.17h)$$

Magnetic permeability constant:
$$\mu_{ij}^{TE\theta} = \left(\frac{\partial B_m}{\partial H_n} \right)_{TE\theta} \quad (2.17i)$$

Specific heat:
$$C^{EHT} = \left(\frac{\theta \partial \sigma}{\rho \partial \theta} \right)_{EHT} \quad (2.17j)$$

The need for all these constants can be seen through expanding a dependent variable in terms of the independent variables T_j , E_n , H_n , and θ . For example, the change in the strain due to changes in these independent variables is:

$$\begin{aligned} dS_i &= \left(\frac{\partial S_i}{\partial T_j} \right)_{EH\theta} dT_j + \left(\frac{\partial S_i}{\partial E_n} \right)_{H\theta T} dE_n + \left(\frac{\partial S_i}{\partial H_n} \right)_{E\theta T} dH_n + \left(\frac{\partial S_i}{\partial \theta} \right)_{TEH} d\theta \\ &= S_{ij}^{EH\theta} dT_j + d_{mj}^{H\theta} dE_n + d_{mj}^{E\theta} dH_n + \alpha_i^{EH} d\theta \end{aligned} \quad (2.17)$$

Over the range of stress, electric field, entropy, and temperature changes such that the coefficients are approximately constant, **Equation (2.18)** can be integrated. Assume that the equilibrium values of the variables are chosen to be zero, except temperature θ and entropy σ . A similar treatment can be carried out for D_m , B_m , and σ . The results are as follows:

$$S_i = S_{ij}^{EH\theta} T_j + d_{mj}^{H\theta} E_n + d_{mj}^{E\theta} H_n + \alpha_i^{EH} \Delta\theta \quad (2.18)$$

$$D_m = d_{mi}^{H\theta} T_j + \epsilon_{mn}^{TH\theta} E_n + p_m^{TH} \Delta\theta + m_{mn}^{T\theta} H_n \quad (2.19)$$

$$B_m = d_{ij}^{E\theta} T_j + \mu_{mn}^{TE\theta} H_n + i_m^{TE} \Delta\theta + m_{mn}^{T\theta} E_n \quad (2.19c)$$

$$\Delta\sigma = \alpha_i^{EH} T_j + p_n^{HT} E_n + i_n^{TE} dH_n + \frac{\rho}{\theta} C^{EHT} \Delta\theta \quad (2.19d)$$

Many of the coefficient in these equations are isothermal, due to the choice of θ as an independent variable. There is an exception in the case of acoustics; adiabatic constants are needed. However, it can be shown that the difference is either small or zero. To determine the equations with adiabatic coefficients; thus, the entropy is required to take the place of temperature as an independent variable.

Magnetic field effects are typically negligible in piezoelectric materials, and dielectric effects are generally negligible in piezomagnetic materials. Pyroelectric effects can be significant only in some piezoelectric materials so that magnetic and pyroelectric effects in piezoelectric materials will be neglected.

2.3.2 Piezoelectric Constitutive Relationship

When pyroelectric and all magnetic effects are ignored, the general boxed equations mentioned above will reduce to the piezoelectric relationships

$$S_i = S_{ij}^{EH\theta} T_j + d_{mj}^{H\theta} E_n \quad (2.20)$$

$$D_m = d_{mi}^{H\theta} T_j + \epsilon_{mn}^{TH\theta} E_n \quad (2.21)$$

For simplicity, these equations will go to:

$$S = s^E T + d_t E \quad (2.21a)$$

$$D_m = d T + \epsilon^T E \quad (2.21b)$$

It should be noted that the independent variables in these equations are the stress T and electric field E .

2.3.3 Piezoelectric Coupling Factor

Another significant parameter for a piezoelectric material is the coupling factor k_{eff} , which is defined as the relative energy that is transduced. [17, 18] The special case of piezoelectric transduction now is considered, which is between strain and electric field. For simplification, a piezoelectric sample considered with a uniform strain and electric field, which would occur for quasistatic changes. By integration of the following equation:

$$dU = T_j dS_j + E_m dD_m \quad (2.22)$$

where $T_i = c_{ij} S_j$ and $D_m = \epsilon_{mn} E_n$, the energy is calculated using **Equation (2.23)**.

$$U = \frac{1}{2} T_i S_i + \frac{1}{2} E_m D_m = \frac{1}{2} T S + \frac{1}{2} E D \quad (2.23)$$

Note that the terms here are analogous to the potential energy in a simple spring, which can be expressed as $U = FX/2$ where $F = KX$. The substitution of the above **Equation 2.21 (a, b)** in the vector-matrix form:

$$U = \frac{1}{2} T s^E T + E dT + \frac{1}{2} E \epsilon^T E = U_{elastic} + 2U_{mut} + U_{dielectric} \quad (2.24)$$

where the factor of 2 occurs in the second term because the energy U_{mut} is defined to be the energy transferred in one direction (electric to elastic, or elastic to electric), which is the same as the energy transferred in the other direction. Finally, the coupling factor is defined as the dimensionless quantity that is the mutual energy divided by the mean of dielectric energy as follows:

$$k = \frac{U_{mut}}{\sqrt{U_{elastic} U_{dielectric}}} = \frac{E dT}{\sqrt{(T s^E T)(E \epsilon^T E)}} \quad (2.25)$$

Finally, k is the piezoelectric coupling factor, which means the greater coupling factor, the greater is the relative energy that is transduced from one form to the other form, for example, gives a measure of the effectiveness of which mechanical energy is converted into electrical and vice-versa.

2.4. Piezoelectric Polymers

Piezoelectric and ferroelectric effects in polymeric materials were discovered for the first time in ferroelectric polyvinylidene fluoride (PVDF) by Kawai in 1969. [19] Since that

time, ferroelectric behavior in many other polymers have been discovered. [20-24] Also, the ferroelectric and piezoelectric polymers have attracted significant attention from the application point of view due to its significant characteristics such as flexibility, superior mechanical properties, low density, lightweight, low cost, low refractive index. Furthermore, its acoustic impedance much lower than those of ceramics materials. Moreover, polymeric materials exhibit higher dielectric breakdown strength, allowing them to withstand higher operating electric fields than ceramics. [24] Piezoelectric polymers, compared with the most other piezoelectric ceramics, show a lower piezoelectric strain coefficient d_{33} . However, the low value of permittivity of the polymers leads to high voltage constants values. [23] This means that they can be excellent in sensor applications. **Figure 2.4** shows a wide variety of devices based on piezoelectric polymers and manifests its importance in the modern technological age. [25]

Figure 2.4 Piezoelectric applications of piezoelectric polymers. [25]

Essentially, for real applications, the high piezoelectric performance of the polymers is necessary. In order to get high piezoelectric properties, it should form a remnant polarization. Among all polymers groups, there are four main groups are known to have ferroelectric properties and accordingly have also piezoelectric properties: 1) aliphatic and

aromatic polyurea, 2) PVDF and its copolymers, 3) vinylidene cyanide (VDCN) copolymers, and 4) odd-numbered nylons (Nylon 5, Nylon 7, Nylon 9 and Nylon 11). [26] Basically, to maintain the remnant polarization in these polymers, different mechanisms are used. For instance, in PVDF case, stabilization is occurring through injected or trapped charges formation at crystallites surface by oriented molecular dipoles. While in the odd-numbered nylons the stabilization is done by the formation of hydrogen bonds and the VDCN copolymers stabilized by using a poling process while the sample is cooled down. Among these polymers, at room temperature, PVDF shows the highest piezoelectric response but deteriorated with increasing temperature.

PVDF is the material that has been studied most extensively in the last 25 years because it has the highest piezoelectric response among all other piezoelectric polymers. An interesting advantage of PVDF has been found to remain ferroelectrically stable after many years. [27]

2.5. Ferroelectric Polyvinylidene Fluoride (PVDF)

Polyvinylidene fluoride (PVDF) is considered the most important ferroelectric polymer due to its unique and distinct properties as mentioned before. PVDF has four different polymorphs “crystal phases”, with different piezoelectric responses as illustrated in **Figure 2.5**.

Figure 2.5 Unit cell of (A) α -phase, (B) δ -phase, (C) γ -phase, and (D) β -phase. Schematic chain conformation of (E) α -phase and δ -phase, (F) γ -phase, and (G) β -phase. The green arrow indicates the direction of the dipoles. [28]

- 1) **α -phase:** This is the most stable phase at room temperature, α phase is formed when the polymer is cooled from the molten state. This is trans-gauche-trans-gauche nonpolar conformation distorted by the steric interaction between the two fluorine atoms. [29] This forms a paraelectric α phase that has no net polarization.
- 2) **β -phase:** This is the most significant phase for the sensing applications because it exhibits pyro-, ferroelectric and thus piezoelectric behavior. The conformation is all-trans so that the dipoles CF_2 are all oriented in the same direction. This is the origin of the spontaneous polarization.
- 3) **γ -phase:** This phase is characterized by a chain conformation TTTGTTTG that confers a low spontaneous polarization.
- 4) **δ -phase:** Applying a strong electric field greater than or equal to, 130 MV/m. [30] may cause 180° rotation of alternate chains, which leads to a polar, monoclinic form of α phase.

2.5.1 Production of PVDF β Phase

The β phase of PVDF is the most significant piezoelectric phase because it has the highest dipolar moment per unit cell. **Figure 2.6** summarizes the phase transitions of different PVDF crystalline phases. β -phase PVDF can be produced by a variety of means, such as mechanical stretching, high annealing temperature or application of the electric fields. [31]

Various methods can be used to achieve the β -phase PVDF, such as 1) mechanical stretching, 2) using polar solvents, 3) melt quenching, 4) introducing of hydrate salts, 5) blending with nanoparticles (such as ferrite, carbon nanotubes CNT or gold), and 6) using anodic aluminum oxide membrane (AAM) as a template.

Stretching α phase sample at a stretch ratio of about 3-5 can induce the formation of β phase. In the stretching process, the lamellae are oriented perpendicular to the draw direction so that the molecules are parallel to the draw direction. Hence, the β phase structure is formed. High annealing temperature of α phase leads to the formation of γ phase.

Figure 2.6 Phase transformation between the different crystalline phases of PVDF. [32]

2.6. Ferroelectric PVDF Co-polymer

It has been found that the physical properties of PVDF, such as Curie temperature (T_c), elastic modulus, the degree of crystallinity and electrical properties can exhibit significant improvements by grafting the polymer chain by an appropriate comonomer during the copolymerization process. Some of the produced PVDF copolymers out of this process include:

- Poly(vinylidene fluoride–trifluoroethylene) (P(VDF–TrFE)).
- Poly(vinylidenefluoride-trifluoroethylene-chlorotrifluoroethylene) (P(VDF-TrFE-CTFE)).
- Poly(vinylidenefluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)).
- Poly(vinylidene fluoride-chlorofluoroethylene) (P(VDF-CFE)).

- Poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE)).
- Poly(vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP)).

The distinguishing characteristic of this polymer is for being crystallized in the β phase directly from the molten state. Due to the excess amount of fluorine atoms in the P(VDF-TrFE), chains decrease the effect of the head-to-head and tail-to-tail defect. This effect enhances the degree of crystallinity of the P(VDF-TrFE) up to 80%, after annealing at 135 °C for approximately about one hour. Also, the concentration of the TrFE affects the produced phase. For instance, if its concentration higher than 18%, then the produced P(VDF-TrFE) will crystallize with the same chain conformation as the β phase. Further improvements can be achieved by applying mechanical stretching and Corona poling. [33] Based on the outstanding ferroelectric and piezoelectric properties of P(VDF-TrFE) diverse applications have been developed. However, the use of P(VDF-TrFE) in high-temperature environments is limited due to lower Curie temperature (T_c).

2.7. Polymer Foams

Polymer foam is a group of materials consisting of a solid matrix and pores of gases in the structure. Polymer foam can be found almost everywhere in our life, such as food packaging and the cushions of furniture and much more. The applications of polymer foams can be classified according to the density of foams. [34] High-density foams, whose density is about 75 % - 90 % of the un-foamed polymers, are mostly used in structural applications, such as cases of batteries, air-conditioner bases, and housing, where certain rigidity is required along with a reduction in weight. [34] While, low-density foams, whose density is about 10 % to 20 % of the un foamed polymers, are generally used in heat and sound absorption, vibration mitigation, and cushioning applications in the automotive industry, and construction applications. [34]

To fabricate polymeric foam, the use of blowing agents is one of the most commonly used methods. A blowing agent is a material that creates a gaseous phase in the polymer matrix structure. The blowing agents can be divided into physical and chemical blowing agents.

Blowing agent can combine with polymer melt during the continuous foam process, where polymers pass through saturation of gas and foam simultaneously, another method by adding it into the solid polymer with high pressure for a batch foam process where the polymers experience two separate steps: first is the saturation of foam agent and then the actual foam is formed. [35]

2.7.1 Physical Foaming Agents

During this process, no chemical reactions taking place to form the foams. Physical agents include either atmospheric gases or volatile liquids that evaporate under certain conditions. [34] Nitrogen, CO₂, helium, and argon are examples of gaseous blowing agents. Chlorofluorocarbons (CFCs), hydrocarbons such as butane and propane, and chlorinated hydrocarbons such as dichloromethane (DCM) are examples of volatile liquid blowing agents. [34] In industry, CFCs are the most used physical blowing agent; however, due to the ozone depletion layer by CFCs, it became illegal to be used in the US from the year of 2010, according to the Montreal Protocol. [36] Currently, inert gases such as nitrogen and CO₂ have attracted concerns because of their eco-friendly nature, more specifically CO₂ due to its higher solubility in polymers than that of nitrogen. [37]

2.7.2 Chemical Foaming Agents

Chemical foaming agents create gaseous phases by heat-induced decomposition process [43]. Chemical blowing agents are available in two types, exothermic and endothermic. Exothermic blowing agent produces heat during the chemical reaction to generate gases, while endothermic blowing agent needs heat to react. [43] The manufacturing of polyurethane (PU) foams is considered one example of using chemical foaming agents, in which the isocyanate group reacts with water to produce amine and carbon dioxide (CO₂). Using chemical foaming agents is particularly useful to produce foam thermoset polymers, for instance, polyurethane. Because of the conventional thermoset polymers cannot be processed after curing. Thus, the adding of chemicals in monomers enables foaming during curing. The disadvantage here is the chemical residue.

Summary

In this Chapter, the models that are being used to describe and predict the behavior of porous absorbing materials and the relevant parameters are addressed. These models are useful in the understanding of the energy dissipation mechanisms in sound-absorbing materials. Moreover, the basics of piezoelectricity, PVDF homo-polymer, and its copolymers are discussed. Additionally, the techniques commonly used to produce polymer foams are presented. The next chapters will address the experimental work for producing piezoelectric and non-piezoelectric porous foams, and discuss the preliminary experimental results.

References

- [1] X. Sagartzazu, L. Hervella-Nieto, and J. M. Pagalday, *Archives of Computational Methods in Engineering*, **2008**, 15, 311-342.
- [2] J. F. Allard and N. Attala, *Propagation of sound in porous media: modeling sound absorbing materials*, 2nd Ed. Hoboken, N.J: Wiley, **2009**.
- [3] C. Langlois, R. Panneton, and N. Atalla, *J. Acoust. Soc. Am.* **2001**, 110, 3032-3040.
- [4] C. R. Fuller, C. Guigou, and C. A. Gentry, Foam-PVDF Smart Skin for Active Control of Sound, *Proceedings of the SPIE*, **1996**, 2721: p. 26-37.
- [5] Y. Champoux, M.R. Stinson, and G.A. Daigle, *J. Acoust. Soc. Am.* **1991**, 89, 910-916.
- [6] T. J. Cox, P. D'Antonio, *Acoustic absorbers and diffusers: theory, design and application*. 2nd ed. Taylor & Francis. New York, **2009**.
- [7] N. Kino, T. Ueno, Y. Suzuki, H. Makino, *Appl. Acoust.* **2009**, 70, 595-604.
- [8] X. S. Amares, E. Sujatmika, T. W. Hong, R. Durairaj, and H. S. H. B. Hamid, *J. Phys.: Conf. Ser.* **2017**, 908, 012005-012014.
- [9] M. A. Biot, *J. Acoust. Soc. Am.* **1956**, 28, 168–178.
- [10] M. A. Biot, *J. Acoust. Soc. Am.* **1956**, 28, 179–191.
- [11] Melon, E. Mariez, C. Ayrault, and S. Sahraoui, *J. Acoust. Soc. Am.* **1998**, 104, 2622-2627.

- [12] L. Jaouen, F. Becot, and F. Chevillotte, *Inter-Noise and Noise-Con Conf. and Conf. Proc.* **2012**, 253, 725-730.
- [13] D. Johnson, J. Koplik, R. Dashen, *J. Fluid. Mech.* **1987**, 176, 379–402.
- [14] W. Nowacki, *Mathematical models of phenomenological piezoelectricity*, Banach Center Publications, **1985**, 15, 593-607.
- [15] A. A. Vives, *Piezoelectric Transducers and Applications*, 1st Ed. Springer, Berlin, Heidelberg, **1979**.
- [16] M. Ciarletta and A. Scalia, *Meccanica*, **1993**, 28, 303-308.
- [17] A. Safari and E. Akdogan, *Piezoelectric and Acoustic Materials for Transducer Applications*, Boston, MA: Springer US. **2008**.
- [18] J. Yang, *An Introduction to the Theory of Piezoelectricity*, 1st Ed, Springer US. **2005**.
- [19] H. Kawai, *Jpn. J. Appl. Phys.* **1969**, 8, 975-976.
- [20] L. Brown, J. Mason, M. Klinkenborg, J. Scheinbeim, and B. Newman, *IEEE Trans Ultrason Ferroelectr Freq Control.* **1997**, 44, 1049–1059. S. Tasaka, T. Shouko, and N. Inagaki, *Jpn. J. Appl. Phys.* **1992**, 31, L1086–L1088.
- [21] A. C. Jayasuriya, S. Tasaka, T. Shouko, and N. Inagaki, *Poly J.* **1995**, 27, 122–126.
- [22] S. Tasaka, N. Inagaki, T. Okutani, and S. Miyata, *Polymer*, **1989**, 30, 1639–1642.
- [23] J. S. Harrison and N. Langley, *Encyclopedia of Polymer Science and Technology*, Hoboken, NJ, USA: John Wiley & Sons, Inc. **2002**.
- [24] Z. L. Wang, *Adv. Fun. Mater.* **2008**, 18, 3553–3567.
- [25] B. Z. Mei, J. I. Scheinbeim and B. A. Newman, *Ferroelectrics*, **1993**, 144, 51-60.
- [26] R. B. Seymour and G. B. Kauffman, *Prod. Chem.* **1990**, 67, 763-765.
- [27] L. Zhu and Q. Wang, *N, Macromol.* **2012**, 45, 2937–2954.
- [28] G. Eberle, H. Schmidt, and W. Eisenmenger, *IEEE Transactions on Dielectrics and Electrical Insulation*, **1996**, 3, 634-646.
- [29] N. Suttle, *Mater. Des.* **1998**, 9, 318-324.
- [30] D. C. Bassett, *Developments in crystalline polymers-I*, 1st Ed, Applied Science Publishers, **1982**.
- [31] H. S. Nalwa, *Ferroelectric Polymers: Chemistry: Physics, and Applications*, 1st Ed, CRC Press. **1995**.

- [32] A. Lund, C. Gustafsson, H. Bertilsson, and R. W. Rychwalski, *Compos. Sci. Tech.*, **2011**, 71, 222-229.
- [33] J. L. Throne, *Thermoplastic foam extrusion: an introduction*, Hanser Gardner Publications, **2004**.
- [34] R. A Vaia, B. B. Sauer, O. K. Tse and E. P. Giannelis, *J Poly Sci Part B*, **1997**, 35, 59-67.
- [35] Guo, Z. *Experimental analysis of polymer nanocomposite foaming using carbon dioxide. Chemical and Biomolecular Engineering. Columbus, Ohio State University. Doctor of Philosophy (2008)*.
- [36] Lee, J. W. S. and C. B. Park, *Macromol Mater Eng.* **2006**, 291, 1233-1244.

Chapter 3

Experimental Methodology

In this chapter, experimental methods to fabricate various open-cell foams composites will be elaborated, including the rationale for selection of materials and processing methods. Prior to delving into result chapters, the description of preparation methods can provide understandings of the samples and experimental results in the project. Introduction to the characterization techniques will be presented to give a broader view of the applied techniques.

3.1. Rationale for Selection

In this project, poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoro ethylene (TrFE) were thoroughly selected for the fabrication of open-cell foams as airborne sound absorption materials. Cost-effective multi-walled carbon nanotubes (MWCNTs) were selected as a conductive filler of the P(VDF-TrFE) matrix in order to tailor the conductivity percolation threshold of the nanocomposite foams to achieve the optimum piezoelectric damping effect. Furthermore, potassium sodium niobate (KNN) nanofibers were selected as a piezoelectric filler of the PVDF matrix because it possesses significant large positive piezoelectric coefficient $+d_{33}$, in order to facilitate the electrical discharge process inside the fabricated foam. Sugar template method was selected in this work for fabricating PVDF and P(VDF-TrFE) composite foams because it is a straightforward and low cost method in the lab without complicated equipment or hazardous solvent required. In this method, water is utilized for the leaching process and the sugar particles can be removed leaving the PVDF and P(VDF-TrFE) composite skeletons with interconnected pores.

3.2. Experimental Methods

3.2.1 Materials

The materials and chemicals used in this work were poly(vinylidene fluoride) (PVDF) polymer with MW ~534,000 (Sigma Aldrich); poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) polymer with MW ~534,000 (Sigma Aldrich); N,N-dimethylformamide (DMF) (Merck); acetone (Merck); sugar; 2-methoxyethanol (2-MOE) (anhydrous, 99.8%) as the solvent in a dry nitrogen atmosphere; potassium acetate (CH_3OOK , A.C.S. reagent, 99+%); sodium acetate (CH_3COONa , reagent, 99+%); niobium ethoxide [$(\text{CH}_3\text{CH}_2\text{O})_5\text{Nb}$, anhydrous, 99.95%] and polyvinylpyrrolidone (PVP) powders (PVP360k); and MWCNTs (Mknano), with a carbon purity of > 95 wt.%, outer diameter of 8-15 nm, and length of 10-30 μm .

3.2.2 Method for Preparing Open-cell PVDF Foams

PVDF open-pore foams were prepared by the sugar template method. The solutions of PVDF were prepared by dissolving the PVDF polymer powder in the mixed solvent of DMF and acetone (50:50 in volume to volume ratio). The solutions were heated stirring (300 rpm) at 60 °C in a silicone oil bath for 12 h to dissolve the polymer completely. The PVDF foams were prepared by mixing the PVDF solution with a predetermined quantity of commercially available sugar to form a mixture like dough. The mixture was formed using the homemade mold, which has a suitable geometrical shape, and immediately dried in an oven at 100 °C for 1 h to remove excess solvents. Afterward, the sample was removed from the mold and leached in water for 96 hours for removing the sugar to obtain the porous structure. The samples were then annealed at 135 °C for 12 hours in an oven.

3.2.3 Method for Preparing Open-cell P(VDF-TrFE)/MWCNTs Nanocomposite Foams

Open-cell P(VDF-TrFE) foams were prepared by a sugar template method. The solutions were prepared by dissolving the P(VDF-TrFE) polymer powder in mixed organic solvent of DMF and acetone (50:50 in volume). MWCNTs (with concentrations of 0 wt.%, 3 wt.%, 5 wt.%, 7 wt.% and 9 wt.%) were dispersed in mixed DMF and acetone solvent and sonicated in ultrasonic bath. After that, both solutions were mixed, sonicated, and heated at 50 °C to obtain a homogeneous precursor solution. The foams were prepared by mixing the P(VDF-TrFE) or P(VDF-TrFE)/MWCNT precursor solutions with commercially available sugar to form a mixture dough. The mixture was formed using homemade molds which had a suitable geometrical shape and immediately dried in an oven at 100 °C to remove excess solvent and ensure complete drying. Then the samples were removed from the mold and leached (rinsed) in repeating cycles of hot water immersion to remove the sugar and obtain the foam with porous structure. The foam samples were then dried at 100 °C for 12 hours in an oven.

3.2.4 Method for Preparing Open-cell PVDF/KNN-nanofiber Composite Foams

3.2.4.1 Potassium Sodium Niobate (KNN)-nanofibers Preparation

The precursor of $K_{0.5}Na_{0.5}NbO_3$ (KNN) was prepared with 2-methoxyethanol (2-MOE) (anhydrous, 99.8%) as the solvent in a dry nitrogen atmosphere. Potassium acetate (CH_3OOK , A.C.S. reagent, 99+%), sodium acetate (CH_3COONa , reagent, 99+%), and niobium ethoxide [$(CH_3CHO)_5Nb$, anhydrous, 99.95%] were used as the starting chemicals. The solution was diluted with 2-MOE to obtain a concentration of 0.5 M, and then polyvinylpyrrolidone (PVP) powders (PVP360k) were added into the solution. The mole ratio of PVP to KNN was fixed at 1:1 (monomer: KNN). The KNN solution was loaded in a 3-mL plastic syringe capped with a 21-gauge stainless steel needle (inner diameter = 0.82 mm). A high voltage of 15 kV was applied to the needle through a DC power supply (Gamma High Voltage, AU-30P1-L220V, Japan). The solution was injected from the needle at a constant rate of 0.5 mL/h with a syringe pump (SP100IZ Syringe Pump, 789100W, U.S.A). A rotating cylinder (with a rotating speed of 1500 rpm) made of a metallic plate covered with an Al foil was grounded and used as the nanofiber collector substrate for obtaining the aligned nanofibers web. The obtained nanofibers were dried at 150 °C for 3 min, followed by prepyrolysis at 350 °C for 3 min, post-pyrolysis at 450 °C for 5 min, and final annealing in the furnace at 600 °C for 10 min with a heating rate of 8 °C /min.

3.2.4.2 PVDF Solution Preparation

PVDF solutions were prepared by dissolving the PVDF polymer powder in mixed organic solvent of DMF and acetone (50:50 in volume).

3.2.4.3 Method for Preparing Open-cell PVDF/KNN-nanofiber Composite Foams

Open-cell PVDF foams were prepared by a sugar template method. KNN-nanofibers (with concentrations of 0 wt.%, 3 wt.%, and 5 wt.%) were dispersed in mixed DMF and acetone

solvent and sonicated in ultrasonic bath. After that, both PVDF and KNN-nanofiber solutions were mixed, sonicated, and heated at 50 °C to obtain a homogeneous precursor solution. The foams were prepared by mixing the PVDF/KNN-nanofiber solutions with commercially available sugar to form a mixture dough. The mixture was formed using homemade molds which had a suitable geometrical shape and immediately dried in an oven at 100 °C to remove excess solvents and ensure complete drying. Then the samples were removed from the mold and leached (rinsed) in repeating cycles of hot water immersion to remove the sugar and obtain the foam with porous structure. The foam samples were then dried at 100 °C for 12 hours in an oven.

Figure 3.1 shows the processing flow chart for preparing PVDF/KNN-nanofibers composite foams.

Figure 3.1 Processing flow chart for preparing PVDF/KNN-nanofiber composite foams.

3.2.5 Charging of PVDF Foams

To promote aligned polar β -phase PVDF, the corona poling technique was used. During corona poling, the needle is elevated at a high enough potential to achieve a partial breakdown of the air around the needle. Then the air around it becomes ionized. These ions drift down towards the sample, which causes a charge build-up on the sample surface which in turn increases the surface potential. **Figure 3.2** illustrates the corona poling apparatus.

Figure 3.2 Corona poling apparatus.

3.3. Characterization

3.3.1 Fourier Transform Infrared Analysis (FTIR)

Fourier transform infrared (FTIR) analysis is a crucial tool to explore the structures of covalently bonded compounds by producing an infrared absorption spectrum that is like a fingerprint of the molecules. Depending on the element types and the nature of bonds, molecular bonds vibrate at different frequencies. For any given bond, there are several specific frequencies at which it can vibrate freely. According to the quantum theory, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to increase the frequency of molecular vibration is by exciting the bond by stimulating it to absorb light energy. The position and intensity of

absorption bands of material are specific to that material. The best-suited bands for the identification are those which can be classified to the carbon backbone of the molecule. [1] These types of absorption bands are often found in the easily accessible wavenumber range of about 1600 and 600 cm^{-1} , often called the “fingerprint region”. In this work, FTIR analysis (ATR mode) was carried out to identify the crystalline phases of PVDF prepared foams and to study the effect of electrical poling and thermal annealing treatments on that foams.

In this work, The FTIR spectra were collected by (FTIR Spectroscopy Spectrum 2000; Perkin Elmer), with scan recorded over a range of 1600–600 cm^{-1} at 4 cm^{-1} resolution.

3.3.2 X-ray Diffraction (XRD)

X-ray diffraction is a technique for characterizing the crystalline and non-crystalline phases of materials and dimensions of the unit cell for crystalline structures. Crystalline materials exhibit a long-range order since it is made of atoms arranged in a regular ordered pattern in three dimensions. The X-ray is generated by a cathode ray tube and filtered to produce monochromatic radiation which is focused on the sample. [2] If the crystalline sample possesses interplanar spacing (d), which satisfy the Bragg’s law:

$$n\lambda = 2d \sin \theta \quad (3.1)$$

where n is an integer, λ the wavelength of the X-ray. then constructive interference between elastically scattered X-ray beams will be observed at specific angle of 2θ as shown in **Figure 3.3**.

Figure 3.3 X-ray diffraction of a crystalline structure with interplanar spacing satisfying Bragg's law. [2]

By changing the angles of incident X-ray, a plot of diffracted X-ray intensity versus incident angles can be obtained for multiple possible diffraction angles within the crystal lattice. The possible diffraction angles depend on both the crystal lattice and the orientation of the crystalline domains. Hence, XRD can be utilized to investigate the crystal orientation of the sample.

In this study, the XRD system (D8-ADVANCE, Bruker AXS, GmbH, Karlsruhe, German) with X-Ray wavelength of $\lambda = 1.542 \text{ \AA}$ ($\text{Cu-K}\alpha$) was used

3.3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a class of electron microscopy techniques that images a sample by scanning it with a beam of electrons in a raster scan pattern. SEM enables observation and characterization of materials on widespread from a nanometer (nm) to micrometer (μm) scale. In SEM, a beam of highly energetic electrons is thermionically emitted from an electron gun fitted with a tungsten filament cathode. The sample area to be examined is bombarded with the finely focused electron beam and various electrons and quanta emitted which can be recorded by various detectors. The types of signals produced by the interaction of the electron beam with the sample include secondary electrons, backscattered electrons, characteristic X-rays, continuum X-ray, and

other photons of various energies. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and many other properties. [3]

In this work, the morphology of PVDF and P(VDF-TrFE) composite foams were examined with a scanning electron microscope (SEM 6360LA, JEOL).

3.3.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal characterization technique, which measures the change in the enthalpy of the materials because of their physical or chemical changes as a function of temperature. It is commonly used to measure specific heat capacity, phase transitions, and melting points. It measures the heat flow and it compares the rates of heat flow between a material and a known reference. Whenever a chemical or physical change happens in the material, heat is either absorbed or emitted. By recording the change in the heat flow, the system can then be analyzed. [4]

In this study, thermal studies of foams were performed by differential scanning calorimetry (DSC, Mettler Toledo) under dry N₂ environment.

3.3.5 Acoustic Impedance Tube

In this work, the acoustic impedance tube was used to determine the acoustic properties by measuring the sound absorption coefficient. Plane sound waves are generated in the tube by a sound source, and then the incident and the reflected components of the sound waves pressures are measured at two distinct locations nearby the sample to be measured using very sensitive and accurately calibrated microphones, as shown in **Figure 3.4**. The resulting frequency band is based on the distance between the microphone positions along with the diameter of the tube. The tube diameter used in this work is (29 mm in diameter) and the frequency range used was 500-6400 Hz. This test was done according to the ISO 10534-1:1996 standard test method for the absorption of sound absorption materials using

an impedance tube. [5] In this work, the standard impedance tube (4206 A, Bruel & Kjaer) was used to measure the sound absorption coefficients of all the porous materials.

Figure 3.4 Diagram of the impedance tube showing components of the acoustic wave. [5]

3.3.6 Dynamic Mechanical Analyzer

Dynamic mechanical analysis (DMA) is a technique that is used to determine the viscoelastic properties of a material as a function of temperature, time, or frequency. In this technique, a small deformation is applied to the manner in a cycling manner. The deformation can be under control stress or control strain. The results that can be obtained by this technique are the dynamic storage modulus, the dynamic loss modulus and the mechanical damping factor. The storage modulus is associated with the stiffness of the material, and it is related to the Young's Modulus. The dynamic loss modulus is associated with the internal friction of the material, and it is related to the molecular motions, relaxation process and morphology of the material. Thus the information that can be obtained is useful in understanding the dynamic mechanical behavior of a material in the molecular level. The study of the dynamic mechanical properties was done by Dynamic Mechanical Analyzer Q800 from TA instruments.

3.3.7 Electrical Characterization

3.3.7.1 Dielectric Characterization

Dielectric characterization is essential for the structure and properties studies of piezoelectric and ferroelectric materials. Under the external electric field, the dielectric response of ferroelectric materials results from the short-range motion of charge carriers. This separation of charges is called polarization. The dielectric constant is related to the polarization that can be achieved in the material.

In this work, effective parallel capacitance and loss factor measurements were done using (Agilent 4294A) impedance analyzer. The dielectric constant K can be calculated from C_p through the relationship $C_p = \frac{K\epsilon_0 A}{d}$.

where A is the area of the sample, d is the thickness of the sample, and ϵ_0 equals $(8.854 \times 10^{-12} \text{ F/m})$.

3.3.7.2 Piezoelectric Characterization

The piezoelectric response can be measured either by measuring the induced electrical charge under external mechanical force through the direct piezoelectric effect or by measuring the dilatation in response to the applied external electric field due to the inverse piezoelectric effect.

Laser scanning vibrometer has been applied successfully for the measurement of piezoelectric coefficient d_{33} of piezoelectric materials. [6] A suitable sample mounting is of decisive importance to suppress the bending of the substrate and to get the accurate piezoelectric strain values. In this work, a laser scanning vibrometer (LSV) system was used for the piezoelectric response measurements of the PVDF foams. The measurement of piezoelectric coefficient using LSV shows high reliability, high efficiency, and comprehensive information among all the other methods that are employed.

The LSV system (OFV-3001-SF6, PolyTech GmbH, Germany) consists of 1) a vibrometer scanning head, 2) a vibrometer controller, 3) a junction box and 4) a host computer. To produce the driving signal, a function generator (HP33120A) was used, which was amplified using a power amplifier (NF Electronic Instruments 4010). The vibration displacement and velocity can be measured based on the Doppler shift and optical interference. A sinusoidal signal of 100 V peak-to-peak at a frequency of 1 KHz was used to excite the samples.

References

- [1] P. R. Griffiths, J. A. De Haseth, *Fourier transform infrared spectrometry*. Vol. v. 83, New York: Wiley. **1986**.
- [2] O. H. Seeck, B. Murphy, *X-Ray Diffraction: Modern Experimental Techniques*. 1st Ed., Pan Stanford Publishing, **2014**.
- [3] J. Goldstein, D. E. Newbury, D. C. Joy, C. E. Lyman, P. Echlin, E. Lifshin, L. Sawyer, L., and J. R. Michael, *Scanning Electron Microscopy and X-Ray Microanalysis*. 3rd Ed., Springer. **2003**
- [4] G. W. H. Höhne, W. F. Hemminger, and H.-J. Flammersheim, *Differential Scanning Calorimetry*. 1st Ed., Springer, **2003**.
- [5] Deutsches Institut Fur Normung, E.V., *Acoustics - Determination of sound absorption coefficient and impedance in impedance tubes - Part 1: Method using standing wave ratio (ISO 10534-1:1996)*; English version of DIN EN ISO 10534-1. **2001**.
- [6] K. Yao, and F. E. H. Tay, *IEEE Trans Ultras on Ferroelectr Freq Control*. **2003**, 50, 113-116.

Chapter 4

Open-cell Poly(vinylidene fluoride) Foams with Polar Phase for Enhanced Airborne Sound Absorption¹

In this chapter, open-cell foams of simplified polyvinylidene fluoride (PVDF) homopolymer composition with and without piezoelectric effects, were produced and used comparably for airborne noise mitigation investigation. How the polar phase and the local piezoelectric effect would contribute to the airborne sound absorption was addressed.

¹ This section published substantially as (A. M. Mohamed, K. Yao, Y. M. Yousry, S. Chen, J. Wang, and S. Ramakrishna, Open-cell poly(vinylidene fluoride) foams with polar phase for enhanced airborne sound absorption. Appl. Phys. Lett. **113**, 092903 (2018). DOI: 10.1063/1.5048336).

4.1. Introduction

It is well known that sound absorption is related to various materials properties. Therefore, a complete characterization of the acoustic properties of a porous foam enables a good understanding of how the local piezoelectric property affects the absorption performance. However, this characterization is difficult to be achieved. By using piezoelectric materials, there is an opportunity to have a proof of concept about the effect of local piezoelectricity on sound absorption. To examine the contribution of the local piezoelectric effect; a series of samples with comparable morphology and structure, but with and without piezoelectric property should be obtained. For this purpose, thermal annealing processes applied to non-polar PVDF foams in order to induce polar nature in foams and keep the other properties unchanged. The samples were first prepared, as mentioned in Chapter 3 and cut into circular discs with dimensions of 10 mm in thickness and 29 mm in diameter. In order to choose the dimensions of the samples, essential things should be taken into account. The foams should be thick enough in order to be measured reliably for sound absorption in the acoustic impedance tube.

4.2. Results and Discussion

4.2.1 Crystal Phases

To assess the effect of local piezoelectric activity on the sound absorption performance, open-cell porous PVDF foams identical in all aspects except in their polar phase content are required. In this chapter, open-cell PVDF homopolymer foams prepared under the same conditions using a sugar template method with the mass ratio of PVDF: sugar = 1:9 were examined before and after thermal annealing at 140 °C for 2 h. For a valid comparison between a polar and non-polar foam, it was found that the appropriate annealing temperature and time for the PVDF foam was 140 °C and 2 hours, while lower temperature did not significantly enhance the β -phase content, and higher temperature dramatically changes the foam's morphology and porosity. Attenuated total reflection infrared (ATR-FTIR) spectroscopy technique was used to study the polar phases in the PVDF foams. **Figure 4.1** shows the ATR-FTIR spectra for the obtained PVDF foams. The characteristic

vibration bands designated to the polar β phase are at 840 cm^{-1} (CH_2 rocking and CF_2 asymmetrical stretching) and 1279 cm^{-1} (C-F stretching vibration), while in contrast, the characteristic bands associated with the non-polar α phase are at 766 cm^{-1} (CH_2 in-plane or rocking) and 976 cm^{-1} (CH_2 twisting). [1-5] As shown in **Figure 4.1**, both β and α phases exist in the open-cell PVDF foams, while the polar β phase is significantly enhanced after the thermal annealing. Thus, the annealed PVDF foam with higher polar β phase content should possess stronger local piezoelectric effect than the unannealed foam. Furthermore, the FTIR spectra show apparent overall crystallinity enhancement besides the increase of β -phase content in the annealed foam.

Figure 4.1 The ATR-FTIR spectra of the porous PVDF foams before and after thermal annealing. The unmarked peaks are common for both β and α phases.

X-ray diffraction (XRD) analysis at room temperature over a scan range from $2\theta = 10^\circ$ to 30° was also conducted to examine the crystalline phases of the obtained PVDF foams. The characteristic peaks of the polar β phase in the XRD patterns shown in **Figure 4.2** are at 20.2° , which corresponds to the (110)/(200) reflection. The peak at 18.3° is attributed to a reflection plane (100) of the non-polar α phase. [6] The diffraction intensity of the crystalline peaks at 20° increases after annealing, which indicates that annealing process promotes the formation of polar β phase, which is in good agreement with the FTIR results presented in **Figure 4.1**. Moreover, the average crystallite size of the polar β PVDF foams was calculated using Scherrer's equation: $D = \frac{K \cdot \lambda}{B \cdot \cos \theta}$, where D is the crystallite size, λ is

the wavelength of X-ray radiation (0.15406 nm), B is the full width at half maximum (FWHM) of the most intense diffraction peak, θ is the angle of diffraction, K is a constant (having the value 0.89). [7] β -phase crystallite size of open-cell PVDF foam before and after thermal annealing was about 4.69 nm and 5.236 nm, respectively. These results indicate that the thermal annealing process can increase the polar β -phase crystallite size of the PVDF polymer matrix.

Figure 4.2 XRD patterns of open-cell PVDF foams before and after thermal annealing.

4.2.2 Morphology and Mechanical Properties

Figures 4.3(a, b) and **4.3(c, d)** show the morphology and the respective pore size histogram of the PVDF foams before and after thermal annealing. The PVDF foams are highly porous with open-cell configuration, with pore size for both samples around 500 μm and below. The micrographs and pore size distribution histogram reveal that the thermal annealing process does not substantially affect the morphology, including pore size distribution of the PVDF foam.

Figure 4.3 SEM image and pore size distribution histogram of (a, b) unannealed, and (c, d) annealed open-cell PVDF foams.

The porosity of the PVDF foam was estimated using solvent saturation method. [7, 8] In this method, a dry sample is immersed in a solvent, usually water or alcohol, and the change in the original weight is monitored until a constant weight is achieved. Then the porosity is calculated using **Equation (4.1)**:

$$\phi(\%) = \left(\frac{(m_{sat} - m_d)/\rho_{solvent}}{V_a} \right) \quad (4.1)$$

where m_{sat} is the weight of the sample saturated with solvent, m_d is the dry weight, $\rho_{solvent}$ is the density of the used solvent, and V_a is the apparent volume. The porosity was adjusted by controlling the mass ratio of PVDF and sugar to be approximately 90 % in the prepared foam.

Figure 4.4 a) Dynamic stiffness, and b) damping factor ($\tan \delta$) of open-cell PVDF foams before and after thermal annealing.

As it is well known, stiffness and damping factor ($\tan \delta$) are important mechanical parameters affecting sound-absorbing properties. [9,10] To assess their effects, the dynamic stiffness and damping factor of open-cell PVDF foams were evaluated using dynamic mechanical analysis (DMA) technique. The dynamic stiffness and damping factor measurements of the prepared foams before and after thermal annealing is shown in **Figure 4.4(a, b)**, where no significant change is observed for the open-cell PVDF foams after the thermal treatment.

4.2.3 Sound-absorption Properties

Figure 4.5 presents the sound absorption coefficient in the frequency range of 500-6400 Hz of PVDF foams with a thickness of 10 mm before and after thermal annealing. The sound absorption coefficient shows a significant increase after the thermal annealing of the PVDF foams at 140 °C for 2 h, while the microstructure and the mechanical properties are maintained after annealing as shown in **Figures 4.3(a, b)**, **4.3(c, d)**, and **Figure 4.4(a, b)**. This improvement in sound absorption performance may be attributed to the increase of the polar β -phase content with local piezoelectric effect in the PVDF foams due to the thermal annealing treatment as shown in **Figures 4.1** and **4.2(a, b)**, respectively.

Figure 4.5 The sound absorption coefficient of the PVDF foams before and after thermal annealing.

Acoustic impedance does play a significant role in absorption of the sound energy. Improved impedance matching with air reduces reflection from the sound-absorbing structure, which facilitates that more sound energy is transferred to the structure. Thus acoustic impedance of the open-cell PVDF foams before and after thermal annealing was measured using the acoustic impedance tube, as shown in **Figure 4.6**, which shows the acoustic impedance did not change substantially after annealing process. Thus, the enhanced absorption coefficient should be attributed to the other extra energy dissipation mechanisms.

Figure 4.6 Surface acoustic impedance of the open-cell PVDF foams before and after annealing.

4.2.4 Electrical and Dielectric Properties

In an earlier report, [11] it was proposed that the optimized piezoelectric damping effect for mechanical structural vibration can be achieved if the resistance of the conductive phase R fulfills the condition of $R \sim 1/(\omega C)$. Connecting electrical resistivity with sound absorption, we can see how mechanical to electrical conversion could contribute to sound absorption in a piezoelectric foam. In this case, R denotes the electric resistance of the porous polar foam, C denotes the capacitance of piezoelectric part, and ω denotes the vibration frequency. As in the thesis, the matching resistivity of the piezoelectric polar foam does significantly contribute to the increase of the sound absorption, and so the contribution of local piezoelectric effect, as a mechanism of mechanical to electrical conversion is reasonably believed. The electrical resistivity of the open-cell PVDF foams has been further measured as shown in **Figure 4.7** and it was found that the electric resistivity was decreased after thermal annealing at 140 °C for 2 h. A downward peak around 3.7 kHz, which is very close to the maximum damping peak in the sound absorption coefficient measurement, further supports the interpretation, as shown in **Figure 4.5**. This observation is consistent with the result of how the variation of external resistive load affects the damping factor in the conventional piezoelectric shunt damping. [12] Thus, the local piezoelectric effect in combination with an appropriate matching electrical resistivity in the open-cell PVDF foams can further enhance the airborne sound absorption performance. It is very possible that maximum sound mechanical energy conversion to electric energy and to thermal energy can be achieved by introducing local piezoelectricity in porous polar foam and tuning the electrical resistivity using the appropriate thermal annealing process. It is well known that β phase, but not the α phase, has the piezoelectric effect.

Figure 4.7 Volume resistivity of the PVDF foams before and after thermal annealing.

After the annealing, the change in the crystalline phases of PVDF must affect the polarization and dielectric property of PVDF foam. [8] As shown in **Figure 4.8**, both the dielectric constant and dielectric loss of the PVDF foams increased after the thermal annealing, which could be an indication of the enhancement in the polar phase and polarization. The enhanced polar β phase and local polarization should improve the piezoelectric response, but it is not straightforward to clarify their relationship because of the challenge in measuring the local piezoelectric effect, particularly in the highly soft and porous foam samples. It should be noted that the open-cell PVDF foams have significantly lower dielectric constant than the solid PVDF counterpart due to the extremely porous structure. [13, 14]

Figure 4.8 Dielectric constant and dielectric loss of PVDF foams at room temperature before and after thermal annealing.

4.2.5 Converting the Sound Energy into Electrical Output Energy

To investigate the ability of both annealed and unannealed samples on converting the sound mechanical energy into electrical output energy, a homemade measuring setup was constructed to conduct the experimental measurement for both the annealed and unannealed foams after electrically poled using corona discharges under 60 kV for 3 mm-thick samples. **Figure 4.9** shows the setup used for measuring the output voltage response at different sound pressure levels. A loudspeaker of acoustic impedance tube was used in these measurements as a sound source in one side of the tube, while a microphone was used to measure the sound pressure level closely to the sample in the other side of the tube. The electrodes on the samples made of silver paste were collected to the oscilloscope through a low noise amplifier (1:1) to collect the generated electrical charges.

Figure 4.9 The setup for testing voltage response at different sound pressure levels of open-cell PVDF foams.

Figure 4.10 presents the output voltage versus various sound pressure level (SPL) at 700 Hz for both annealed and unannealed open-cell PVDF foams before and after electrical poling. Although both annealed and unannealed samples did not exhibit any substantial piezoelectric voltage response before poling, they did show a substantial difference in the output voltage after poling. Before electrical poling, the β -phase PVDF did not apparently

exhibit macroscopic piezoelectric behavior, because the local polarization is randomly aligned and the local piezoelectric effect cannot constructively contribute to macroscopic piezoelectric property over the entire material. The annealed PVDF foams showed larger piezoelectric output, which could be attributed to the enhancement of the polar β phase due to the thermal annealing (as shown in **Figures 4.1** and **4.2**, respectively) and the poling-induced polarization orientation. Without the polarization orientation, local polarization from the existence of β phase and local piezoelectric response should also exist although could not constructively generate a substantial observable overall output voltage due to the random polarization orientation. Nevertheless, even before poling, the annealed PVDF foam exhibited significantly improved noise absorption performance than the unannealed sample, indicating the content of polar β phase and local piezoelectric effect instead of the overall piezoelectric effect may have played a more critical role in noise absorption.

Figure 4.10 Voltage output at different sound pressure levels for open-cell PVDF foams before and after thermal annealing and electrical poling.

4.2.6 Mechanism for Energy Dissipation with Local Piezoelectricity

After taking into account the effects of local polarization and local piezoelectric response, **Figure 4.11** schematically illustrates the noise absorption mechanisms in open-cell PVDF foam. When the sound wave strikes open-cell porous material, the sound pressure wave penetrates deeply inside the materials, and the interactions between the fluid and solid occur causing energy transfer from the fluid to the solid structure. As a consequence, the mechanical energy in the sound wave of fluid is absorbed and eventually converted into

heat. In addition to the conventional visco-inertial, thermal and materials damping effects, the thin and polar struts of PVDF with polar β phase have at least another two effects: (1) the mechanical vibration excited by the sound wave is partially damped by being converted to electricity through the local piezoelectric effect and finally to thermal energy; and (2) the friction and viscous loss at the fluid-solid interface may be enhanced with the presence of electrical charges. Thus, the enhancement in the polar β phase and local piezoelectricity in the open-cell porous PVDF foam after annealing significantly improved the airborne sound absorption performance. Hence, open-cell PVDF polymer foam with high content of polar β phase has great potential for noise mitigation applications.

Figure 4.11 Schematic illustration of (a) an open-cell PVDF foam, and (b) mechanisms of acoustic energy absorption with polar β phase.

Conclusions

Open-cell foams of simplified PVDF homopolymer composition with different content of polar β phase were fabricated, and their airborne noise mitigation performance properties were investigated comparably. Thermal treatment was applied to the PVDF foams to enhance the polar β -phase content and thus local piezoelectric effect. The experimental results and theoretical analysis showed that the existence of polar phase and local piezoelectric effect significantly improved the sound absorption coefficient of PVDF polymer foams. In addition to the conventional visco-inertial, thermal and materials

damping effects, the thin and polar struts of PVDF foams with polar phase and local piezoelectric effect may further enhance the mechanical damping by converting the excited mechanical vibration to electricity through the local piezoelectric effect, and increasing the friction and viscous loss at the fluid-solid interface with the presence of electrical charges. Thus, the open-cell polymer foams with a high content of polar phase and local piezoelectric effect have great potential for passive airborne noise mitigation applications.

References

- [1] J. Humphreys, E. L. V. Lewis, I. M. Ward, E. L. Nix, and J. C. McGrath, *J. Poly. Sci. Part. B Polym. Phys.* **1988**, 26, 141-158.
- [2] N. C. Banik, F. P. Boyle, T. J. Sluckin, P. L. Taylor, *Phys Rev Lett.* **1979**, 43, 456–460.
- [3] F. Bauer, E. Fousson, Q. M. Zhang, L. M. Lee, *IEEE Trans. Dielectr. Electr. Insul.* **2004**, 11, 293-293.
- [4] M. G. Broadhurst, G. T. Davis, J. E. McKinney, and R. E. Collins, *J. Appl. Phys.* **1978**, 49, 4992-4997.
- [5] A. Salimi and A. Yousefi, *Poly. Test.* **2003**, 22, 699-704.
- [6] Li, X.; Lim, Y.; Yao, K.; Tay, F E. H.; Seah, K. H. *Phys. Chem. Chem. Phys.* **2013**, 15, 515-520.
- [7] P. Scherrer, *Nachr. Ges. Wiss. Goettingen. Math. Phys. Kl.* **1918**, 2, 98-100.
- [8] J. E. Unosson, C. Persson, and H. Engqvist, *J. Biomed. Mater. Res., Part B.* **2014**, 103, 62-71.
- [9] A. J. Lovinger, *Macromol.* **1982**, 15, 40-44.
- [10] I. M. Daniel, J. M. Cho, *Exp. Mech.* **2011**, 51, 1395-1430.
- [11] M. Rahimabady, E. C. Statharas, K. Yao, M. S. Mirshekarloo, S. Chen, and F. E. H. Tay, *Appl. Phys. Lett.* 2017, 111, 241601-241605.
- [12] L. Peng, B. Song, J. Wang, and D. Wang, *Adv. in Mate. Sci. and Eng.* **2015**, 2015, 1-6.
- [13] K. Uchino and T. Ishii, *J. Ceram. Soc. Jpn.* **1988**, 96, 863-867.

- [14] B. Zhao, C. Zhao, C. Wanga, and C. B. Park, *J. Mater. Chem. C*, **2018**, 6, 3065-3073.

Chapter 5

Open-cell P(VDF-TrFE)/MWCNT Nanocomposite Foams with Local Piezoelectric and Conductive Effects for Airborne Sound Absorption

In this chapter, piezoelectric open-cell foams of P(VDF-TrFE) and its nanocomposites with cost-effective MWCNTs were fabricated for airborne sound absorption investigations. P(VDF-TrFE) was selected because of its enhanced piezoelectricity with higher polar β -phase content in comparison with PVDF homopolymer. Analyses on the structure of the nanocomposite and hybrid local piezoelectric and conductive effects were conducted to understand the obtained outstanding airborne sound absorption performance.

5.1. Introduction

In this chapter, P(VDF-TrFE) polymer was selected for the fabrication of open-cell foams as airborne sound absorption materials with cost-effective multi-walled carbon nanotubes (MWCNTs) as a conductive filler in order to tailor the conductivity percolation threshold of the nanocomposite foams to achieve the optimum piezoelectric damping effect and hence high performance airborne sound absorption coefficient at lower and intermediate frequency range.

5.2. Results and Discussion

5.2.1 Crystal Phases

Figure 5.1(a) shows the attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectra for the obtained P(VDF-TrFE) foams with different concentrations of MWCNTs. The characteristic vibration bands designated to the polar β phase are at 840 cm^{-1} (CH_2 rocking and CF_2 asymmetrical stretching), 1288 cm^{-1} (C-F stretching vibration), and 1400 cm^{-1} (CH_2 wagging vibration), while the characteristic bands associated with the non-polar α phase are at 766 cm^{-1} (CH_2 in-plane or rocking) and 976 cm^{-1} (CH_2 twisting). [1] As shown in **Figure 5.1(a)**, both β and α phases co-exist in the open-cell P(VDF-TrFE) and its nanocomposite foams, whereas it is clear that β phase is dominant in P(VDF-TrFE)/MWCNT foams comprising 3 to 9 wt.% MWCNTs, and the amount of β phase increases with the MWCNTs. Furthermore, the FTIR spectra show that the crystallinity of P(VDF-TrFE) is slightly enhanced besides the increase of β -phase content.

X-ray diffraction (XRD) analysis at room temperature over a scan range from $2\theta = 10^\circ$ to 40° was also conducted to examine the crystalline phases of the obtained P(VDF-TrFE)/MWCNT foams. The characteristic peaks of the polar β phase in the XRD patterns shown in **Figure 5.1(b)** are at 20° and 35° , which correspond to the (110)/(200) and (020)/(101) reflections, respectively. The peak at 18.3° is attributed to a reflection plane (100) of the non-polar α phase. [2] The diffraction intensity of the crystalline peaks at 20° increases with adding more MWCNTs, which indicates that MWCNTs promotes the

formation of polar β phase, which is in good agreement with the FTIR results presented in **Figure 5.1(a)**. In contrast, the peak intensity of the non-polar α phase at 18.3° was reduced with increasing MWCNTs in the nanocomposites. The results here show that the MWCNTs with large specific surface areas dispersed in the polymer matrix can enhance the degree of crystallinity of the β phase, which could be attributed to the crystallization nucleation occurs at the interfaces between P(VDF-TrFE) and the MWCNTs. The local polarization and piezoelectric effects are expected to improve in the open-cell nanocomposite foams with increasing MWCNTs highly dispersed in P(VDF-TrFE) matrix.

Figure 5.1 a) ATR-FTIR spectra, and b) XRD patterns of open-cell P(VDF-TrFE) and P(VDF-TrFE)/MWCNT nanocomposite foams. The unmarked peaks are common for both α and β phases.

5.2.2 Morphology

Figures 5.2(a, b, c, d, and e) present the morphology and the pore size distribution histograms of the P(VDF-TrFE)/MWCNT nanocomposite foams with different amount of MWCNTs. The SEM micrographs and pore size distribution histograms reveal all the foams are highly porous with open-cell configuration, with pore size around $500\ \mu\text{m}$ and below. The incorporation of MWCNTs does not substantially affect the morphology and pore size of the P(VDF-TrFE) foams.

Figure 5.2 SEM images and pore size distribution histograms of the cross-section position of (a) P(VDF-TrFE), (b) P(VDF-TrFE)/3 wt.% MWCNT, (c) P(VDF-TrFE)/5 wt.% MWCNT, (d) P(VDF-TrFE)/7 wt.% MWCNT, and (e) P(VDF-TrFE)/9 wt.% MWCNT foams at different locations: A circumference surface, B top surface, and C cross-section. These images demonstrated that there is no substantial difference in the morphology or pore distribution among these foams.

The porosity of the P(VDF-TrFE)/MWCNT nanocomposite foams was determined using solvent saturation method. [3] In this approach, a dry sample was immersed in a solvent, ethanol in this work, and the change in the original weight was observed until a constant weight was reached. Then the porosity was calculated using **Equation (4.1)**.

The porosity was adjusted by controlling the mass ratio of P(VDF-TrFE) and sugar to be approximately $\approx 88\%$ in all the prepared foams.

5.2.3 Thermal Analysis

To gain insight into the effect of MWCNTs on the structure and properties of P(VDF-TrFE) foams, differential scanning calorimetry (DSC) measurements were conducted. **Figure 5.3(a)** shows DSC curves during heating of P(VDF-TrFE)/MWCNT nanocomposites. Endothermal peaks at 106.7 °C and 146.3 °C for P(VDF-TrFE) are attributed to the ferroelectric-paraelectric phase transition at Curie temperature (T_c) and the melting temperature (T_m), respectively. The melting temperature T_m of P(VDF-TrFE)/MWCNT nanocomposite foam is continuously increased from 146.3 °C for the pristine P(VDF-TrFE) foam to about 153.5 °C with 9 wt.% MWCNTs. Moreover, **Figure 5.3(b)** shows DSC cooling curves for P(VDF-TrFE)/MWCNT nanocomposites with different amount of MWCNTs. For the pristine P(VDF-TrFE) foam, three endotherm peaks are observed at 123.8 °C, 65.3 °C, and 58.8 °C, correlated to crystallization temperature (T_{cr}), and two phase-transition temperatures due to the coexistence of two ferroelectric phases, respectively. The crystallization temperature increases with increasing MWCNTs or crystallization occurs earlier during cooling of the melt with MWCNTs, which well supports that crystallization nucleation occurs at the interfaces between P(VDF-TrFE) and the MWCNTs. The effect of the added MWCNTs on the consistent shift of the peaks whether in heating or cooling curves, and the intensity increase of the peaks indicate that the MWCNTs are well dispersed in the nanocomposites and promote the crystalline structure, which is consistent with the FTIR and XRD results.

Figure 5.3 DSC (a) heating and (b) cooling curves of the open-cell P(VDF-TrFE) and P(VDF-TrFE)/MWCNT nanocomposite foams.

5.2.4 Sound-absorption Properties

Figure 5.4(a) presents the sound absorption coefficient in the frequency range of 500-6400 Hz for the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams with different MWCNT concentrations with a thickness of 20 mm. The sound absorption measurements were conducted using the standard impedance tube. The sound absorption coefficient shows a significant increase with the introduction of the increasing MWCNTs, while the porous morphology is maintained substantially as shown in **Figure 5.2**. The zoom-in plots in low-frequency range of 500 – 2000 Hz, as presented in **Figure 5.4(b)**, shows clearly that the MWCNTs in the open-cell P(VDF-TrFE)/MWCNT foams enhance the sound absorption in the relatively low-frequency range below 2000 Hz, which is highly valuable as it is usually challenging to absorb low-frequency noise with passive approach. However, it is further noted that the sound absorption coefficient drops significantly with excess MWCNTs. The sound absorption coefficient of open-cell P(VDF-TrFE)/7 wt.% MWCNT nanocomposite foam is the highest among all the P(VDF-TrFE) nanocomposite foams with 0, 3, 5, 7, and 9 wt.% MWCNTs.

A small resonance peak is noted at 680 Hz for the foam with 7 wt.% MWCNTs, which has the largest sound absorption coefficient. Smaller resonance peak around this frequency is also noted in the sample with the second largest sound absorption coefficient but not

significant in other compositions with relatively lower absorption. The analysis shows that this small peak is related to longitudinal mechanical resonance of the skeleton, with the frequency of 670 Hz for the foam with 7 wt.% MWCNTs as estimated according to **Equation (5.1)**:

$$f_s = \frac{1}{4e} \sqrt{E((1-\nu)/(1+\nu)(1-2\nu))/\rho_s} \quad (5.1)$$

where f_s is the skeleton resonance frequency, e is the thickness, E is the modulus of elasticity, ν is the Poisson's ratio of the skeleton, and ρ_s is the density of the solid material.

Figure 5.4 Sound absorption coefficient of open-cell P(VDF-TrFE) and P(VDF-TrFE)/MWCNT nanocomposite foams with different amount of MWCNTs (a) from 500 Hz to 6400 Hz, and (b) from 500 Hz to 2000 Hz.

Furthermore, the first large absorption peak occurs at 3950 Hz for the P(VDF-TrFE) foam matches well with the first acoustic resonance mode at 3969 Hz of the porous foam, as calculated according to **Equation (5.2)**:

$$f_r = \frac{nv}{2(L + 0.8d)} \quad (5.2)$$

where n is a positive integer (1, 2, 3...) representing the resonance node, L and d are the length and diameter of the foam respectively, v is the speed of sound in air (which is approximately 343 m/sec at 20 °C). The position of the first acoustic resonance absorption peak could be affected by many factors such as the mechanical and electrical impedances, dimension of the porous foams. The effects of all these parameters and the shift of the acoustic resonance peak will be discussed in details later.

Furthermore, an efficient way to examine the homogeneity of the fabricated samples was done by testing the sound absorption coefficient of the sample from both sides (front and back). The measured sound absorption results for both sides of the foams are presented in **Figure 5.5**, which show a high degree of homogeneity with the matching results from the front and back surfaces of the foams.

Figure 5.5 Homogeneity results of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.

The acoustic impedance was measured for the open-cell P(VDF-TrFE) samples with 0 and 7 wt.% MWCNT using impedance tube, as shown in **Figure 5.6**. The acoustic impedance did not show substantial change with the addition MWCNT annealing process. The

observed improvement in the sound absorption coefficient should be attributed to other extra energy dissipation mechanisms which are highly relevant to the local piezoelectric effect in combination with the appropriate matching electrical conductivity of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.

Figure 5.6 Surface acoustic impedance of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.

5.2.5 Electrical Conductivity

The experimental results show the electrical conductivity of the P(VDF-TrFE)/MWCNT nanocomposite foams increases significantly with the increasing concentration of the conductive MWCNT filler as presented in **Figure 5.7**. From 0 to 9 wt.% of MWCNTs in the composite foam, the conductivity increases from 3.3×10^{-11} to 3.0×10^{-4} (S/cm), nearly 7 orders of magnitude. A percolation behavior in electrical conductivity with MWCNT content is observed, with the percolation threshold around 7 wt.% of MWCNTs. According to the percolation theory, when the concentration of the MWCNTs is high enough to satisfy the percolation threshold, the conductive MWCNTs in the foam are connected with each other, forming a long-range three-dimensional conducting network, in which conductivity could be realized effectively with the electron transport via hopping and migration among

the MWCNTs. [4] Thus, electrical charges in the foam can be steadily dissipated near or above the percolation threshold.

Figure 5.7 Volume electrical conductivity and noise reduction coefficient of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.

Furthermore, with the addition of MWCNTs affecting the conductivity of the P(VDF-TrFE)/MWCNT nanocomposite foams and even the crystallinity of P(VDF-TrFE), it is found that the dielectric constant and loss of the P(VDF-TrFE)/MWCNT nanocomposite foams increase with increasing the MWCNT concentration, as presented in **Figure 5.8(a, b)**, and some reports in the literature. [5,6]

Figure 5.8 Dielectric constant (a) and dielectric loss (b) of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.

The noise reduction coefficient (NRC) was further calculated to identify a clear relationship between sound absorption performance and MWCNT concentration. The noise reduction coefficient is an average rating of how much sound energy a sound absorber can absorb in 250, 500, 1000, and 2000 Hz, which is calculated using **Equation (5.3)**:

$$NRC = \frac{\alpha_{250} + \alpha_{500} + \alpha_{1000} + \alpha_{2000}}{4} \quad (5.3)$$

As shown in **Figure 5.6**, increasing the concentration of MWCNTs until 7 wt.% significantly enhances NRC, while it drops significantly with increasing concentration of MWCNTs beyond 7 wt.%.

5.2.6 Theoretical Model

To summarize the investigation results above on the structure, morphology, and strong correlation between electrical conductivity and airborne sound absorption, a model on the P(VDF-TrFE)/MWCNT nanocomposite foam and its airborne sound absorption mechanism are schematically illustrated in **Figure 5.9**.

Figure 5.9 Schematic illustration of (a) 3D overview of the open-cell porous foam; (b) P(VDF-TrFE)/MWCNT nanocomposite structure; (c) mechanisms for converting sound energy to electricity with local piezoelectric effect and electrical energy to thermal energy through resistive loss.

As shown in **Figure 5.9(a, b)**, P(VDF-TrFE)/MWCNT nanocomposite has an open-cell porous structure, and polar β phase of P(VDF-TrFE) forms with interfaces to the MWCNTs. XRD and FTIR results showed that the MWCNTs promote crystallization of the polar β phase with local piezoelectric effect. The effect of the added MWCNTs on the thermal analysis peaks indicated that the MWCNTs are well dispersed in the nanocomposites for promoting the crystalline structure, which is consistent with the FTIR and XRD results.

The airborne sound pressure wave can penetrate deeply into the open-celled porous structure for realizing effective vibration interactions between the air and solid with mechanical energy transfer from the air to the thin solid structure. Here the thin struts of P(VDF-TrFE) polymer matrix are polar and possess a substantial local piezoelectric effect, particularly when it crystallizes into β phase. Thus, in addition to the well-known sound absorption mechanisms, such as fluid viscous and thermal losses, and visco-elastic structural damping effect, which commonly exist in common porous foams, the mechanical vibration or strain of P(VDF-TrFE) excited by the airborne sound wave can be converted to electrical charges through the local piezoelectric effect in the polar phase. Electrical discharge can happen through the conductive MWCNTs adjacent to the polar phase, so that the electrical energy can be converted into thermal dissipation. **Figure 5.9(c)** schematically illustrates the proposed additional noise absorption mechanism with the combined functions of the local-piezoelectric response of P(VDF-TrFE) and the electrical conductivity of the adjacent MWCNT filler in the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams. Further enhancement in sound absorption performance could be possible with the formation of electrical charges at the fluid-solid interface with potentially increasing friction losses.

It has been known that the optimum piezoelectric damping effect for mechanical structural vibration can be achieved when the external load R matches the condition of $R \sim 1/\omega C$, where C denotes the capacitance of the piezoelectric, and ω denotes the frequency. [7, 8] Therefore, we further measured the electrical impedance of the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams to examine the effect of impedance matching on the sound absorption performance. The addition of MWCNTs to P(VDF-TrFE) polymer

matrix significantly was found to decrease the electrical impedance of the foams due to the increased conductivity, as shown in **Figure 5.10**, which in turns affects the impedance matching condition.

Figure 5.10 Electrical impedance measurements for the open-cell P(VDF-TrFE)/MWCNT nanocomposite foams.

Further analysis revealed that the maximum sound absorption peak constantly shifts toward low frequency with increase of MWCNT concentration in the P(VDF-TrFE) matrix, which means an improvement of absorption at low frequency. This situation occurs until 7 wt.%, while with further increase in the concentration of MWCNTs beyond the percolation threshold concentration, the first large absorption peak shifts to a higher frequency with a much lower sound absorption coefficient compared to the foam of 7 wt.% concentration of MWCNTs, as shown in **Figure 5.4**. This shift of the first acoustic resonance absorption peak of the foam with 9 wt.% MWCNTs towards higher frequency can be explained from the impedance match and enhanced sound absorption at higher frequency, for smaller $l/\omega C$ to match with the smaller impedance of the foam with 9 wt.% MWCNTs. The shift of the sound absorption peak for the samples with 3, 5, and 7 wt.% of MWCNTs to lower frequency can possibly be understood with the significantly enhanced sound absorption particularly in the lower and intermediate frequency range attributed to the local piezoelectric effect, in contrast to that the conventional sound absorption mechanisms, such

as fluid viscous and thermal losses, and visco-elastic structural damping are typically more effective in high-frequency range.

Conclusions

Structural and thermal analyses showed that the MWCNTs were well dispersed in the P(VDF-TrFE) matrix and enhanced the degree of crystallinity of polar β phase, which improved the local piezoelectric effect with the interfaces between the polar phase P(VDF-TrFE) and MWCNTs. The electrical conductivity of the P(VDF-TrFE)/MWCNT nanocomposite foams increased significantly by nearly 7 orders of magnitude with the increasing concentration of the MWCNT up to 9 wt.%, with the percolation threshold in electrical conductivity observed near 7 wt.% of MWCNTs. The measurements in standard acoustic tube showed that introduction of appropriate amount of MWCNTs significantly enhanced the airborne sound absorption coefficient of P(VDF-TrFE) foam without poling, particularly in the lower and intermediate frequency range. This is attributed to the electrical energy generation through local piezoelectric effect of polar phase of P(VDF-TrFE) foam and charge dissipation through the conductive MWCNTs interfacing the polar phase. The experimental results clearly showed that the optimal sound absorption performance was obtained in the nanocomposite foams with conductive or resistive percolation threshold, near 7 wt.% of MWCNTs, where is promising for achieving impedance matching condition for maximizing characteristic piezoelectric damping. The experimental results and theoretical analysis indicated that the open-cell nanocomposite foam with polar phase and local piezoelectric effect, and electrical conductive percolation threshold has great potential for enhancing airborne sound absorption at lower and intermediate frequency range, and thus promising for noise mitigation applications.

References

- [1] Y. M. Yousry, K. Yao, S. Chen, W. H. Liew, S. Ramakrishna. *Adv. Electron. Mater.* **2018**, 4, 1700562-1700570.
- [2] X. Li, Y. Lim, K. Yao, F. E. H. Tay, K. H. Seah, *Phys. Chem. Chem. Phys.* **2013**,

- 15, 515-520.
- [3] J. E. Unosson, C. Persson, H. Engqvist, *J. Biomed. Mater. Res. Part B.* **2014**, 103, 62-71.
- [4] A. Agambayev, M. Farhat, S. P. Patole, A. H. Hassan, H. Bagci, K. N. Salama, *Appl. Phys. Lett.* **2018**, 113, 093505-093509.
- [5] A. J. Lovinger, *Macromol.* **1982**, 15, 40-44.
- [6] Z. J. Han and B. K. Tay, *J. Appl. Polym. Sci.* **2008**, 107, 3332-3336.
- [7] W. Wei and C. Huang, Z. Zhou, *J. Mod. Transp.* **2011**, 19, 143-146.
- [8] M. Sumita, H. Gohda, S. Asai, K. Miyasaka, A. Furuta, Y. Suzuki, and K. Uchino, *Macromol. Rapid. Commun.* **1991**, 12, 657-661.

Chapter 6

Enhanced Airborne Sound Absorption Effect in Poly(vinylidene fluoride)/(K_{0.5}Na_{0.5})NbO₃-nanofiber Composite Foams

In this chapter, open-cell poly(vinylidene fluoride)(K_{0.5}Na_{0.5})NbO₃ (PVDF/KNN) nanofiber composite foams were proposed and investigated for airborne sound absorption purpose. Structural and thermal analyses showed that the KNN nanofibers were well dispersed in the PVDF matrix and enhanced the degree of crystallinity of polar phase of PVDF. Significantly enhanced airborne sound absorption over a broad frequency range was observed in the PVDF/KNN-nanofiber composite foams, with increasing KNN nanofibers. One possible mechanism for the improved sound absorption with the piezoelectric KNN nanofibers with positive piezoelectric coefficient added in the PVDF matrix with negative piezoelectric coefficient is that electrical discharge could be facilitated for energy dissipation with the opposite charges generated through the piezoelectric effects in the two phases with opposite polarity. The experimental results show that the open-cell PVDF/KNN-nanofiber composite foams are promising for broadband airborne sound absorption application, and the analysis shed a light on the strategy in designing piezoelectric composite foam with high sound absorption performance.

6.1. Introduction

In this chapter, instead of conductive fillers, potassium sodium niobate (KNN) nanofibers with significantly larger piezoelectric coefficient were selected as the filler to be introduced to the porous PVDF matrix. KNN is known as one of the most competitive lead-free piezoelectric ceramic materials, [1, 2] and high piezoelectric coefficient of $d_{33(eff)}$, up to 98 pm V⁻¹ is obtained for KNN nanofibers. [1] In contrast, PVDF has a negative piezoelectric coefficient d_{33} . [3] It is very interesting to investigate how the KNN fillers with much stronger and opposite local piezoelectric effect impact the airborne sound absorption behaviors in the PVDF/KNN-nanofiber composite foams.

6.2. Results and Discussion

6.2.1 Crystal Phases

Figure 6.1(a) shows the X-ray diffraction (XRD) patterns of the KNN-nanofibers, and the open-cell PVDF composite foams with different concentrations of KNN-nanofiber filler (0, 3, and 5 wt.%). The XRD pattern of KNN-nanofibers shows sharp crystalline peaks at $2\theta = 22.2^\circ, 31.6^\circ, 45.2^\circ, 45.8^\circ, 51.1^\circ$ and 56.4° due to the characteristic planes (100), (110), (111), (200), (120) and (121), respectively, indicating the KNN-nanofibers possesses a perovskite crystal structure (ABO₃) according to the crystallographic indexing. [4, 5] For all of the open-cell PVDF/KNN-nanofiber composite foams, the peak at 18.3° is attributed to a reflection plane (100) of the non-polar α phase, whereas the peak at $2\theta = 20.1^\circ$ is assigned to the (110)/(200) reflection plane of β phase. The diffraction intensity of the crystalline peaks at 20.1° increases with adding more KNN-nanofibers, in addition to the presence of the diffraction peak at $2\theta = 35^\circ$, corresponding to the (020)/(101) reflection of β phase, which indicates that KNN-nanofiber promotes the formation of polar β phase and the overall crystallinity of the open-cell PVDF matrix.

The average crystal size of the polar β PVDF can be calculated using Scherrer's equation:

$$D = \frac{K \cdot \lambda}{B \cdot \cos \theta}, \text{ where } D \text{ is the crystallite size, } \lambda \text{ is the wavelength of X-ray radiation (0.15406}$$

nm), B is the full width at half maximum (FWHM) of the most intense diffraction peak, θ is the angle of diffraction, K is a constant (having the value 0.89). [6] β -phase crystallite size of pure open-cell PVDF foam is about 5.1 nm, and crystallite size of composite foams of 3 wt.% and 5 wt.% KNN-nanofibers concentrations are about 5.8 nm and 6.8 nm, respectively. These results indicate that the introduction of KNN-nanofibers can increase the polar β -phase crystallite size of the PVDF polymer matrix.

Figure 6.1(b) shows the attenuated total reflection–Fourier transform infrared (ATR-FTIR) spectra for the obtained PVDF foams with different concentrations of KNN-nanofibers (0, 3, and 5 wt.%). The characteristic vibration bands designated to the polar β phase are at 840 cm^{-1} (CH_2 rocking and CF_2 asymmetrical stretching), 1288 cm^{-1} (C-F stretching vibration), and 1400 cm^{-1} (CH_2 wagging vibration), while the characteristic bands associated with the non-polar α phase are at 766 cm^{-1} (CH_2 in-plane or rocking) and 976 cm^{-1} (CH_2 twisting). [7] As shown in **Figure 6.1(b)**, both β and α phases co-exist in the open-cell PVDF and its composite foams, whereas it is clear that β phase is significantly enhanced in PVDF/KNN-nanofiber foams comprising 3 to 5 wt.% KNN-nanofibers, and the amount of β phase increases with the KNN-nanofibers.

Figure 6.1 a) XRD patterns and b) ATR-FTIR spectra of open-cell PVDF and PVDF/KNN-nanofiber composite foams. The unmarked peaks are common for both α and β phases.

6.2.2 Morphology

Figures 6.2(a, b, and c) present the morphology and the pore size distribution histograms of the PVDF/KNN-nanofiber composite foams with different content of KNN-nanofibers. The SEM micrographs and pore size distribution histograms reveal that all the foams are highly porous with open-cell configuration, with pore size varies between 200 and 500 μm . The incorporation of KNN-nanofibers does not significantly affect the morphology and pore size of the PVDF foams. The porosity of the PVDF/KNN-nanofiber composite foams was determined using solvent saturation method. [8] In this approach, a dry foam was immersed in an ethanol solvent, and the change in the original weight was observed until a constant weight is reached. Then the porosity was calculated using **Equation (4.1)**.

The porosity was adjusted by controlling the mass ratio of PVDF and sugar to be approximately $\approx 90\%$ in all the prepared foams.

Figure 6.2 SEM images and pore size distribution histograms of the open-cell (a) PVDF, (b) PVDF/3 wt.% KNN-nanofibers, and (c) PVDF/5 wt.% KNN-nanofiber composite foams.

6.2.3 Thermal Analysis

Differential scanning calorimetry (DSC) measurements were conducted to investigate structure and properties of PVDF/KNN-nanofiber composite foams. **Figure 6.3(a)** shows DSC curves during heating of PVDF/KNN-nanofiber composites. Endothermal peak at 158 °C is observed for PVDF foams, attributed to the melting temperature (T_m) of the crystalline phase. The melting temperature T_m of PVDF/KNN-nanofiber composite foam is continuously shifted from 158 °C for the pure PVDF foam to approximately 174 °C with 5 wt.% KNN-nanofibers. This shift in melting temperature is possibly because the incorporation of KNN nanofibers in the PVDF matrix leads to the enhanced crystallinity as found from the XRD and FTIR results. Moreover, **Figure 6.3(b)** presents DSC cooling curves for PVDF/KNN-nanofiber composites with different amount of KNN-nanofibers. For the pure PVDF foam, an exothermal peak is observed around 128 °C, correlated to crystallization temperature (T_{cr}). The crystallization temperature increases with increasing KNN-nanofibers or crystallization occurs earlier during cooling of the melt with KNN-nanofibers. The effect of the added KNN-nanofibers on the shift of the peaks in heating and cooling curves and the intensity increase of the peaks indicate that the KNN-nanofibers are well dispersed in the composites and promote the crystalline structure, which is in a good agreement with the FTIR and XRD results.

Figure 6.3 DSC (a) heating and (b) cooling curves of open-cell PVDF and PVDF/KNN-nanofiber composite foams.

6.2.4 Sound-absorption Properties

The sound absorption coefficient for the open-cell PVDF/KNN-nanofiber composite foams with different KNN-nanofiber concentrations with a thickness of 20 mm was measured using the standard acoustic impedance tube. It is important to note that the measurement accuracy in the acoustic tube depends on the diameter of the acoustic tube and the spacing between the microphone positions, which is important to ensure only plane waves in the acoustic tube. Thus, the accurate results are those only between 500-6400 Hz for the selected acoustic tube. The sound absorption coefficient shows a significant increase in a broad frequency range of 500-6400 Hz with the introduction of the increasing KNN-nanofibers, as shown in **Figure 6.4**, while the porous morphology is maintained substantially with adding KNN-nanofibers as in **Figure 6.2**. It is further noted that the sound absorption coefficient of the open-cell PVDF/KNN-nanofiber composite of 5 wt.% concentration is the highest among all the PVDF composite foams with 0, 3, and 5 wt.% KNN-nanofibers. The zoom-in plots in low-frequency range of 500-2500 Hz, clearly shows that the KNN-nanofibers in the open-cell PVDF/KNN-nanofiber composite foams also enhance the sound absorption in the relatively frequency range, which is highly beneficial as it is commonly challenging to effectively absorb low-frequency airborne sound using the passive technique.

Figure 6.4 Sound absorption coefficient of open-cell PVDF and PVDF/KNN-nanofiber composite foams, with the inset showing low-frequency absorption coefficient between 500 and 2500 Hz.

A small mechanical resonance peak is noted at 860 Hz for the foam with 3 wt.% KNN-nanofibers. Smaller resonance peak around this frequency is only noted in the sample with the second largest sound absorption coefficient but not significant in other compositions. The analysis shows that this small peak is related to a longitudinal mechanical resonance of the skeleton, with the frequency of 870 Hz for the foam with 3 wt.% KNN-nanofiber as estimated according to **Equation (5.1)**.

The reason why this small resonance peak only appears in the foam of 3 wt.% KNN-nanofibers is not clear yet, and further theoretical investigations are needed.

We further calculated the noise reduction coefficient (NRC) to figure out the quantitative relationship between sound absorption performance and KNN-nanofiber concentration. The noise reduction coefficient is an average rating of how much a sound absorber can absorb in 250, 500, 1000, and 2000 Hz, which is calculated using **Equation (5.3)**.

As shown in **Table 6.1**, increasing the concentration of KNN-nanofibers until 5 wt.% significantly enhances NRC. However, further increasing KNN-nanofibers beyond 5 wt. % substantially degraded the mechanical property of the foam due to the brittleness of the ceramic KNN-nanofibers, which makes the foams fragile and not suitable for acoustic measurement and application.

Table 6.1 Noise reduction coefficient (NRC) of the open-cell PVDF/KNN-nanofiber composite foams with different KNN-nanofiber concentration.

<i>KNN-nanofibers (wt.%)</i>	0	3	5
<i>NRC</i>	0.25	0.30	0.37

6.2.5 Electrical and Piezoelectric Properties

The dielectric constant of the PVDF/KNN-nanofiber composite foams was measured, as shown in **Figure 6.5**. It can be observed that the dielectric constant of the PVDF/KNN-

nanofiber composite foams increases as the KNN-nanofiber weight percentage increases, as KNN ceramic has much high dielectric constant than the PVDF matrix. The dielectric constant of the PVDF/KNN-nanofiber composite foam with 5wt.% KNN-nanofiber loading is as high as 10 at 1 kHz, which is about four times higher than that of pure PVDF foam.

Figure 6.5 Dielectric constant of the open-cell PVDF/KNN-nanofiber composite foams.

With the high porosity, it is difficult to pole the composite foams and test their macro-scale piezoelectric properties. Here the piezoelectric properties of KNN-nanofibers were investigated before mixing with PVDF. The macroscopic piezoelectric properties of KNN-nanofibers were evaluated using a laser scanning vibrometer (LSV), which is an efficient approach in determining the effective piezoelectric longitudinal strain coefficient. [9] During the measurement, a unipolar ac signal of 10 V in amplitude at 1 kHz was applied to the KNN-nanofiber web with top Au electrode and bottom Al electrode. **Figure 6.6** presents a three-dimensional vibration data of the nanofiber film under the electric driving. The central protruding portion is the electrically excited area under the top electrode, and the surrounding flat region is the KNN-nanofiber film not covered by the top electrode. As the displacement profile of the top electrode area is not flat, the average displacement values were used in determining the dilation or strain of the KNN-nanofiber film. The effective piezoelectric strain coefficient ($d_{33(eff)}$) of the nanofiber film is determined to be 80 pm V^{-1} , which is much larger than that of PVDF, usually -30 pm/V^{-1} . [10]

Figure 6.6 Three-dimensional graphs of vibration data of the KNN nanofibers under the electric sine wave driving (10 V amplitude at 1 kHz) measured with LSV under substrate clamping conditions for KNN nanofiber webs. The central protruded area is the electrically excited nanofibers under the top Au electrode (diameter size of 0.25 mm), whereas the flat adjacent area is the nanofibers without the top electrode.

6.2.6 Theoretical Model

To investigate the correlation between local piezoelectric effect and airborne sound absorption process, a physical model on the PVDF/KNN-nanofiber composite foam and its airborne sound absorption mechanisms are schematically illustrated in **Figure 6.7**.

Figure 6.7 Schematic illustration of (a) PVDF/KNN-nanofiber composite structure, and (b) mechanisms for converting sound energy to electricity with local piezoelectric effect and electrical discharging to thermal energy through the opposite piezoelectric effect.

As schematically illustrated in **Figure 6.7(a)**, PVDF/KNN-nanofiber composite has an open-cell porous structure. Based on the XRD and FTIR results, KNN-nanofibers enhance formation of the polar β phase with local piezoelectric effect. The addition of KNN-nanofibers would increase the dipole density in the PVDF/KNN-nanofiber composite foams. The airborne sound wave can penetrate deeply into the open-cell porous structure for realizing effective vibration interactions between the air and solid with mechanical energy transfer from the air to the thin solid structure. Here the thin struts of polar PVDF/KNN-nanofiber possess substantial local piezoelectric effect. Thus, in addition to the well-known sound absorption mechanisms, such as fluid viscous and thermal losses, and visco-elastic structural damping effect, which commonly exist in porous foams, the mechanical vibration or strain of PVDF/KNN-nanofiber composite foam excited by the airborne sound wave can be converted to electrical discharge through the local piezoelectric effect of PVDF and KNN nanofibers.

When the composite is excited by the airborne sound waves, induced stress will affect both PVDF matrix and KNN-nanofibers simultaneously, which causes generation of electrical charges in both, but may often with the opposite polarity because of the opposite polarity of piezoelectric effect between PVDF and KNN, as illustrated in **Figure 6.7(b)**. As a result, the electrical discharge will take place at the interfaces between opposite dipoles of PVDF

and KNN nanofibers, so that the electrical energy converted from the mechanical energy could be dissipated as thermal energy. **Figure 6.7(b)** schematically illustrates the proposed additional noise absorption mechanism with the combined effects of the local negative piezoelectric response of PVDF and the local positive piezoelectric response of the adjacent KNN-nanofiber filler in the open-cell PVDF/KNN-nanofiber composite foams. In addition, KNN nanofibers may reflect the impinging sound waves back to the polymer matrix, thereby allowing the polar foam skeleton to absorb more mechanical energy.

Conclusions

Structural and thermal analyses showed that the KNN nanofibers, which exhibited large positive longitudinal piezoelectric coefficient d_{33} , were well dispersed in the PVDF matrix and enhanced the degree of crystallinity of polar β phase, which has negative d_{33} value. Acoustic measurements showed that introduction of the KNN-nanofibers significantly enhanced airborne sound absorption over a broad frequency range in the PVDF/KNN-nanofiber composite foams, at least up to 5 wt.%. One possible mechanism for the improved sound absorption with the piezoelectric KNN nanofibers with positive piezoelectric coefficient added in the PVDF matrix with negative piezoelectric coefficient is that electrical discharge could be facilitated for energy dissipation with the opposite charges generated through the piezoelectric effects in the two phases with opposite polarity. The experimental results show that the open-cell PVDF/KNN-nanofiber composite foams are promising for broadband airborne sound absorption application, and the analysis shed a light on the strategy in designing piezoelectric composite foam with high sound absorption performance.

References

- [1] Y. M. Yousry, K. Yao, X. Tan, A. M. Mohamed, Y. Wang, S. Chen, and S. Ramakrishna, *ACS Appl. Mater. Interfaces* **2019**, 11, 23503-23511.
- [2] K. S. Ramadan, D. Sameoto, S. Evoy, *Smart Mater. Struct.* **2014**, 23, 033001-033027.

- [3] I. Katsouras, K. Asadi, M. Li, T. B. van Driel, K. S. Kjær, D. Zhao, T. Lenz, Y. Gu, P. W. M. Blom, D. Damjanovic, M. M. Nielsen, and D. M. de Leeuw, *Nat. Mater.* **2016**, 15, 78-84.
- [4] A. Salimi and A. Yousefi, *Polym. Test.* **2003**, 22, 699-704.
- [5] B. L.A. Farmer, J. Hopfinger, and J. B. Lando, *J Appl. Phys.* **1972**, 43, 4293-4303.
- [6] P. Scherrer, *Nachr. Ges. Wiss. Goettingen. Math. Phys. Kl.* **1918**, 2, 98-100.
- [7] Y. M. Yousry, K. Yao, S. Chen, W. H. Liew, S. Ramakrishna, *Adv. Electron. Mater.* **2018**, 4, 1700562-1700569.
- [8] J. E. Unosson, C. Persson, and H. Engqvist, *J. Biomed. Mater. Res. Part B.* **2014**, 103, 62-71.
- [9] K. Yao and F. E. H. Tay, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control.* **2003**, 50, 113-116.
- [10] S. Chen, K. Yao, F. E. H. Tay, C.L. Liow, *J. Appl. Phy.* **2007**, 102, 104108-104113.

Chapter 7

Discussion and Future Work

In this chapter, the main findings and outcomes of the thesis are briefly summarized. Three different types of open-cell composite foams were fabricated, and the experimental results showed excellent performance in airborne noise absorption. The thesis also paves the way toward a novel airborne sound absorption technology, by enhancing the energy conversion processes through local piezoelectric effect in polymer foams for enhancing airborne sound absorption. Finally, the recommendations for future works and outlook are proposed.

7.1. General discussion

Open-cell piezoelectric foams are investigated for understanding the contribution of the electromechanical conversion mechanism to airborne noise absorption, particularly local piezoelectric effect in porous polar materials. The objectives are to explore the potential of deploying the local piezoelectric effect in polymeric materials for airborne noise absorption and to understand the energy conversion and loss mechanisms. This has been accomplished through experimentally fabricating and testing innovative open-cell piezoelectric polymeric foams, as well as analyzing the link between materials' composition and structure with sound absorption properties.

The conclusion of this work follows:

- In PVDF homopolymer system, the effect of piezoelectric property of open-cell PVDF homopolymer foams on airborne sound absorption was investigated with dedicatedly designed samples with different content of polar β -phase content and local piezoelectric response. The polar β -phase content and thus local piezoelectric effect was enhanced in the open-cell PVDF foams by dedicated thermal annealing, without substantially changing the samples' structural and mechanical property. The measurement results showed that the airborne sound absorption performance of the open-cell PVDF foams significantly improved with the increase of polar β -phase content and effective local piezoelectric effect. The further analyses on the experimental results showed that the local piezoelectric effect of the PVDF foams provided an additional sound absorption mechanism by converting the mechanical energy into electricity through the local piezoelectric effect, and also possibly increasing the friction and viscous loss at the fluid-solid interface with the presence of electrical charges. The study on open-cell PVDF foams suggests that effective local piezoelectric effect can be introduced in porous materials to enhance their airborne sound absorption performance.

- For P(VDF-TrFE)/MWCNT nanocomposite foams, structural and thermal analyses showed that the MWCNTs were well dispersed in the P(VDF-TrFE) matrix and enhanced the degree of crystallinity of polar β phase, which improved the local piezoelectric effect with the interfaces between the polar phase P(VDF-TrFE) and MWCNTs. The electrical conductivity of the P(VDF-TrFE)/MWCNT nanocomposite foams increased significantly by nearly 7 orders of magnitude with the increasing concentration of the MWCNT up to 9 wt.%, with the percolation threshold in electrical conductivity observed near 7 wt.% of MWCNTs. The acoustic measurements showed that the introduction of appropriate amount of MWCNTs significantly enhanced the airborne sound absorption coefficient of P(VDF-TrFE) foam without poling, particularly in the lower and intermediate frequency range. This is attributed to the electrical energy generation through local piezoelectric effect of polar phase of P(VDF-TrFE) foam and charge dissipation through the conductive MWCNTs interfacing the polar phase. The experimental results clearly showed that the optimal sound absorption performance was obtained in the nanocomposite foams with conductive or resistive percolation threshold, near 7 wt.% of MWCNTs, where is promising for achieving impedance matching condition for maximizing characteristic piezoelectric damping. The analyses of the experimental results and theoretical analysis proved that the open-cell nanocomposite foam with polar phase and local piezoelectric effect, and electrically conductive percolation threshold has great potential for enhancing airborne sound absorption at lower and intermediate frequency range, and thus promising for noise mitigation applications.
- For PVDF/KNN-nanofiber composite foams, structural and thermal analyses showed that the KNN nanofibers, which exhibited large positive longitudinal piezoelectric coefficient d_{33} , were well dispersed in the PVDF matrix and enhanced the degree of crystallinity of polar β phase, which has negative d_{33} value. Acoustic measurements showed that introduction of the KNN-nanofibers significantly enhanced airborne sound absorption over a broad frequency range in the PVDF/KNN-nanofiber composite foams, at least up to 5 wt.%. One possible

mechanism for the improved sound absorption with the piezoelectric KNN nanofibers with positive piezoelectric coefficient added in the PVDF matrix with negative piezoelectric coefficient is that electrical discharge could be facilitated for energy dissipation with the opposite charges generated through the piezoelectric effects in the two phases with opposite polarity. The experimental results show that the open-cell PVDF/KNN-nanofiber composite foams are promising for broadband airborne sound absorption application, and the analysis shed a light on the strategy in designing piezoelectric composite foam with high sound absorption performance.

Based on the results of Chapters 5 and 6, combining both open-cell P(VDF-TrFE)/MWCNT and PVDF/KNN-nanofibers composite foams, with their respective performance as shown in **Figure 7.1**, may produce a functionally graded foam, for absorbing airborne sound over a further widen frequency range.

Figure 7.1 Sound absorption coefficient of open-cell P(VDF-TrFE)/7 wt.% MWCNT nanocomposite foam and PVDF/5 wt.% KNN-nanofiber composite foam.

Finally, in order to make the comparison valid, all the composite foams were fabricated using the sugar template method and the fabrication parameters were optimized to verify that the mechanical and morphological properties are substantially similar. Since the mechanical (mechanical stiffness, damping factor ($\tan \delta$), acoustic etc.) and morphological (pore size, roughness, etc.) properties affect the sound absorption property, therefore these properties were measured using DMA and SEM, respectively.

In addition, the local piezoelectric effect and piezoelectric phase were evaluated using FTIR and XRD techniques. Furthermore, the sound absorption coefficient for all composite foams was measured using a standard impedance tube. Finally, when the structure and other properties are kept unchanged expect the local piezoelectric effect, we can investigate the effect of local piezoelectric properties of the prepared composite foams on the enhancement in sound absorption performance.

7.2. Recommendations and Future Work

As it is known that one of the biggest challenges in mechanism investigation is the separation of the different absorption mechanisms in one material, and this challenge becomes more difficult when the local piezoelectric effect is introduced to the porous absorber materials. Future research should be focused on more effectively separating the thermal, viscous, and damping effects in order to identify quantitatively the exact impact of the local piezoelectricity on the airborne sound absorption performance. An improved understanding of the absorption mechanisms and their respective frequency spectra will assist in the design and creation of suitable airborne sound-absorbing foams for the targeted practical applications.

Furthermore, the fabrication and improvement strategy for sound absorption using bio-based open-cell poly (lactic acid) (PLA) foams can be explored. Poly (lactic acid) (PLA) is a highly versatile, biodegradable, and biocompatible thermoplastic polymer, as a aliphatic polyester derived from 100% renewable resources such as corn and sugar cane. [1-3] Since PLA is a chiral molecule, PLA has different stereo forms, such as poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(D,L-lactide) (PDLLA). PLLA, as a chiral polymer in which molecules with asymmetric carbon atoms have a helical orientation, exhibits shear piezoelectricity, while PDLLA has no shear piezoelectric effect in nature.

Through a preliminary study, highly porous open-cell PLA and PDLLA foams were fabricated using supercritical carbon dioxide (Sc-CO₂) as a physical foaming agent. PLA foams of two different stereoisomers were characterized and tested for the frequency range

of 500 - 6400 Hz using acoustic impedance tube. The effect of local piezoelectric properties of the processed PLA polymeric foams on passive sound absorption performance was examined. **Figure 7.2** shows the sound absorption coefficient for the prepared foams, in comparison with various commercially available sound absorbers. With all the porous samples having the same thickness of 20 mm, it was found that the sound absorption coefficient of PLLA piezoelectric foam is significantly higher than those of open-cell PDLLA foams, and commercial polyurethane and melamine acoustic foams.

Figure 7.2 Sound absorption coefficients of piezo-PLLA, nonpiezo-PDLLA, in comparison with several commercial sound absorbers (20 mm in thickness).

Moreover, **Figure 7.3(a, b)** shows the morphology of both PLLA and PDLLA. Both are highly porous with comparable morphology and pore size.

Figure 7.3 SEM images and pore size distribution histograms of the open-cell (a) PLLA and (b) PDLLA foams.

The application potential of deploying local piezoelectric effect of biodegradable piezoelectric open-cell polymeric foams for improving passive airborne sound absorption and noise mitigation needs further study.

References

- [1] M. S. Lopes, A. L. Jardini, and R. M. Filho, *Chemical Engineering Transactions*, **2014**, 38, 331-336.
- [2] M. Murariu, A-L. Dechief, R. Ramy-Ratiarison, Y. Paint, J-M. Raquez, and P. Dubois, *Nanocomposites* **2015**, 1, 71-82.
- [3] R. E. Drumright, P. R. Gruber, and D. E. Henton, *Adv. Mater.* **2000**, 12, 1841-1846.

Publications

Journal papers

- [1] **A. M. Mohamed**, K. Yao, Y. M. Yousry, J. Wang, and S. Ramakrishna, *Enhanced airborne sound absorption using Poly(vinylidene fluoride)/(K_{0.5}Na_{0.5})NbO₃-nanofiber composite open-cell foams*. (Accepted in ***J. Appl. Polym. Sci.***)
- [2] **A. M. Mohamed**, K. Yao, Y. M. Yousry, J. Wang, and S. Ramakrishna, *Open-cell P(VDF-TrFE)/MWCNT Nanocomposite Foams with Local Piezoelectric and Conductive Effects for Airborne Sound Absorption*. (Submitted)
- [3] E. C. Statharas, K. Yao, M. Rahimabady, **A. M. Mohamed**, L. Zhang, and F. E. H. Tay, *Ferroelectret Polyethylene Foams with Effective Piezoelectric Property for Enhanced Sound Absorption*. (Submitted)
- [4] Y. M. Yousry, K. Yao, X. Tan, **A. M. Mohamed**, Y. Wang, S. Chen, and S. Ramakrishna, *Structure and High Performance of Lead-Free (K_{0.5}Na_{0.5})NbO₃ Piezoelectric Nanofibers Crystallized at Lowered Temperature*, ***ACS Appl. Mater. Interfaces***. 26, 23503 (2019).
- [5] E. C. Statharas, K. Yao, L. Zhang, R. Salloum, **A. M. Mohamed**, and F. E. H. Tay, *Theoretical analysis on hybrid local piezoelectric and conductive effect on sound absorption performance of porous poly(vinylidene fluoride)*, ***Mater. Res. Exp.*** 6, 086204 (2019).
- [6] E. C. Statharas, K. Yao, M. Rahimabady, **A. M. Mohamed**, and F. E. H. Tay, *Polyurethane/poly(vinylidene fluoride)/MWCNT composite foam for broadband airborne sound absorption*, ***J. Appl. Polym. Sci.*** 136, 47868, (2019).
- [7] **A. M. Mohamed**, K. Yao, Y. M. Yousry, S. Chen, J. Wang, and S. Ramakrishna, *Open-Cell Poly(vinylidene fluoride) Foams with Polar Phase for Enhanced Airborne Sound Absorption*, ***Appl. Phys. Lett.*** 113, 092903, (2018).

Conference presentations

- [1] **A. M. Mohamed**, K. Yao, J. Wang, and S. R. Puniredd, *Biodegradable Piezoelectric Polymeric Foam for Acoustic Absorption*, Joint ISAF-ICE-EMF-IWPM-PFM meeting 2019. July 14 - 19, 2019, EPFL Lausanne Switzerland. (*Poster Presentation*)

- [2] **A. M. Mohamed**, K. Yao, J. Wang, E. C. Statharas, *Airborne Sound Absorption Using Open-Cell P(VDF-TrFE)/MWCNT Nanocomposite Foam*, 10th International Conference on Materials for Advanced Technologies (ICMAT), June 23th - 28th, 2019, Singapore. (*Oral Presentation*)

- [3] **A. M. Mohamed**, K. Yao, J. Wang, and E. C. Statharas, *Open-Cell PVDF Foams with Piezoelectric Properties for Noise Absorption*, (IFAAP) Joint Conference, May 27 - 1 June 2018 Hiroshima, Japan. (*Poster presentation*)