Unique filler dispersion and physical properties of polyurethane/multi-walled carbon nanotubes composites

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**UNIQUE FILLER DISPERSION AND PHYSICAL PROPERTIES
OF POLYURETHANE/MULTI-WALLED CARBON
NANOTUBES COMPOSITES**

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ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

2017

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OF POLYURETHANE/MULTI-WALLED CARBON
NANOTUBES COMPOSITES**

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Interdisciplinary Graduate School
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A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

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

2017/05/18

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Abstract

The objective of this study is to develop high performance multi-walled carbon nanotubes (CNTs) based electromagnetic interference (EMI) shielding materials, via building strong fundamentals and gaining new insights of the mechanism. This study focus on the relationship between CNTs dispersion and EMI shielding properties of composites, as well as investigating the influences of matrix type and composite processing.

This study began with the investigation on the effects of types of polyurethane (PU) (i.e., thermoplastic and thermoset) on CNTs dispersion and EMI shielding effectiveness (SE) of composites. By investigating the composites from these two types of PU, it was observed that CNTs could be well dispersed in thermoset system. In fact, ‘island-structure’ formed in thermoplastic PU due to the serious CNTs aggregation. By contrast, CNTs formed a connected network in thermoset PU. Further study confirmed that the sequence of adding CNTs into thermoset PU influenced the dispersion of CNTs, which was attributed to the different interaction between monomers and CNTs. Since contributions for EMI SE of CNTs composites arise from dielectric polarization and conductive network, the EMI SE of composites is closely related to CNTs dispersion at the same CNTs loading.

CNTs based composites exhibit EMI shielding performances contributed by their enriched electrons in CNTs. The states of electrons (i.e., free or confined) in CNTs is also related to their dispersion states in matrix, which is supported by Pendry model and Maxwell-Wagner two-layer structure model. Plasma frequency is an intrinsic property of materials, which is again affected by the dispersion state. Moreover, one of the most important parameters in composites, i.e., complex permittivity, is frequency dependent and related to the plasma frequency of CNTs according to Lorentz-Drude Model. In this work, the CNTs

dispersion was correlated to the complex permittivity of composites, which could be obtained directly. The oscillation of complex permittivity vs frequency was quantified and employed to evaluate CNTs dispersion. The proposed method was systemically verified in terms of its accuracy, sensitivity and applicability.

Surface modification is an effective method to improve the comprehensive properties of CNTs based composites. In this study, the method of polymer encapsulation was used to modify CNTs, in which polydopamine (PDA) was coated on CNTs through self-oxidation polymerization of dopamine (DA). It was proven by Raman spectra that the PDA modification could retain the CNTs intrinsic structure. Moreover, the presence of PDA coating enhanced the mechanical property of PU/PDA-CNTs composites, which was attributed to the enhanced interfacial interaction between PDA-CNTs and PU matrix, which could effectively transfer load from polymer matrix to CNTs. However, because of the insulation property of PDA, the electrical conductivity of PU/PDA-CNTs composite decreased. As a consequence, the EMI SE decreased and the contribution for EMI SE of composites was mainly from the conductivity of CNTs themselves, rather than the conductive network.

This thesis concluded the outcomes and findings of this study, and also proposed the future work based on these conclusions, including the incorporation of magnetic particles, enhancement of mechanical properties, and decreasing amount of solvents used during the process of composite preparation.

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Table of Contents

Abstract.....	i
Acknowledgements	iii
Table of Contents	v
Table Captions.....	xi
Figure Captions.....	xiii
Abbreviations	xxi
 Chapter 1 Introduction.....	 1
1.1 Problem Statement	2
1.2 Objectives and Scope	4
1.3 Dissertation Overview	5
1.4 Findings and Outcomes.....	7
References.....	8
 Chapter 2 Literature Review	 11
2.1 EMI shielding.....	12
2.1.1 Basic plane wave shielding theory.....	13
2.1.2 Transmission-Line equations	15
2.1.3 Experimental EMI shielding effectiveness	18
2.2 EMI shielding solutions	19
2.2.1 EMI shielding enclosure and gaskets.....	19
2.2.2 Composite materials for EMI shielding.....	20
2.3 Carbon nanotubes (CNTs).....	22

2.3.1	Introduction.....	22
2.3.2	Physical properties	23
2.3.3	Dispersion and functionalization of CNTs.....	25
2.3.4	Polymer/CNTs composites for EMI applications	30
2.4	Polyurethane (PU).....	33
2.4.1	Reaction of isocyanate	33
2.4.2	Reactants for PU fabrication	34
2.4.3	PU classification	35
	References.....	35

Chapter 3 Experimental Methodology.....45

3.1	Introduction.....	46
3.2	CNTs dispersion method.....	46
3.2.1	Raw CNTs without treatment.....	46
3.2.2	Raw CNTs with surfactants	46
3.2.3	Polydopamine treated CNTs (PDA-CNTs)	47
3.3	Synthesis method	48
3.3.1	Basic reactions of polyurethane (PU)	48
3.3.2	Composites with Raw-CNTs.....	49
3.3.3	Composites with PDA-CNTs.....	51
3.4	Characterization	51
3.4.1	Fourier Transform Infrared Spectroscopy (FTIR)	51
3.4.2	Scanning Electron Microscopy (SEM)	52
3.4.3	Transmission Electron Microscopy (TEM)	53
3.4.4	Raman spectroscopy	54
3.4.5	Direct Current (DC) Conductivity	55
3.4.6	EMI shielding performances.....	57
3.4.7	Tensile test.....	61
3.4.8	Differential Scanning Calorimetry (DSC)	61
3.4.9	Thermogravimetric Analysis (TGA).....	62

References.....	63
-----------------	----

Chapter 4 Matrix Identification and Processing of Polyurethane Composites.....67

4.1 Introduction.....	68
4.2 Materials and methods	69
4.2.1 Materials	69
4.2.2 Matrix identification	70
4.2.3 The effect of processing of PU/Raw-CNTs composites on EMI shielding properties.....	71
4.2.4 Characterization	72
4.3 Results and discussion	73
4.3.1 Matrix identification	73
4.3.2 Microstructure and DC conductivity of PU/Raw-CNTs composites	75
4.3.3 EMI shielding effectiveness of PU/Raw-CNT composites.....	79
4.3.4 Mechanism.....	82
4.3.5 Thermal behaviors and mechanical properties of PU/Raw-CNTs composites.....	85
4.4 Conclusions.....	87
References.....	88

Chapter 5 The Study of CNTs Dispersion by Electromagnetic Signals91

5.1 Introduction.....	92
5.2 Materials and methods	95
5.2.1 Materials	95
5.2.2 Preparation of PU/Raw-CNTs composites.....	96
5.2.3 Preparation of thermoplastic polyurethane (TPU)/surfactant-CNTs composites (i.e., PVP, Span® 80 and Triton X-100)	96
5.2.4 The verification of the new method by 0D and 2D fillers	97
5.2.5 Characterization	98

5.3	Theoretical background	99
5.3.1	Lorentz-Drude Model	99
5.3.2	Maxwell-Wagner model.....	105
5.3.3	Nicholson-Ross-Weir (NRW) technique.....	107
5.4	Results and discussion	108
5.4.1	Changing the sequence of adding CNTs into matrix	108
5.4.2	The effect of surfactants incorporation on CNTs dispersion	110
5.4.3	The maximum loading of CNTs.....	111
5.4.4	The dispersion of conductive fillers with different dimensions.....	113
5.5	Conclusions.....	114
	References.....	114

Chapter 6 The Mussel-inspired Strategy towards the High Performance Polyurethane (PU)/Carbon Nanotubes (CNTs) Composites for EMI Shielding Application.....119

6.1	Introduction.....	120
6.2	Materials and methods	122
6.2.1	Materials	122
6.2.2	The fabrication of PU/CNTs composites	122
6.2.3	Characterization	123
6.3	Results and discussion	124
6.3.1	Modification of CNTs by PDA coating.....	124
6.3.2	EMI shielding properties of PU/CNTs composites.....	128
6.3.3	CNTs dispersion states of PU/CNTs composites	131
6.3.4	Mechanical property of PU/CNTs composites.....	134
6.4	Conclusions.....	135
	References.....	136

Chapter 7 Conclusions and Future Work.....139

7.1	Outcomes of this project	140
-----	--------------------------------	-----

7.1.1	Polymer matrix identification and processing of composites	140
7.1.2	The study of CNTs dispersion by electromagnetic signals	142
7.1.3	CNTs treated by Polydopamine (PDA-CNTs)	143
7.2	Future work	144
7.2.1	Incorporation of magnetic particles	145
7.2.2	Improvement of mechanical properties	146
7.2.3	Decreasing the amount of solvents	147
	References	148

Table Captions

Table 2.1 Common EMI sources and receptors	12
Table 2.2 Reduction in signal strength.....	19
Table 2.3 The comparison of various techniques for CNTs dispersion	28
Table 2.4 Summary of the polyurethane by ASTM classification	35
Table 4.1 The thermal behaviors of PU/Raw-CNTs composites	86

Figure Captions

Figure 1.1 Illustration of correlation of CNTs dispersion and EMI shielding performance	4
Figure 2.1 EM radiation spectrum	13
Figure 2.2 Plane wave analogy: (a) conventional transmission line and (b) plane wave, in which the electric and magnetic field perpendicular to each other	14
Figure 2.3 Reflection of EM waves at (a) single interface and (b) double interfaces showing multiple re-reflections. The vertical solid line stands for interface.....	16
Figure 2.4 The structures of SWCNT and MWCNT [17]	23
Figure 2.5 The construction of a nanotube from a single graphene sheet by rolling up the sheet along the wrapping vector	25
Figure 2.6 The pictures of (a) three-roll calander and (b) schematic of its working mechanism	26
Figure 2.7 Pictures of (a) shear mixer and (b) extruder.	27
Figure 2.8 General strategies for chemical functionalization of CNTs (A: direct functionalization and B: defect functionalization).....	30
Figure 3.1 Synthesis procedure for the preparation of PDA-CNTs [4]	47

Figure 3.2 Basic reaction of isocyanate chemistry	48
Figure 3.3 Preparation of PU by diol and diisocyanate	48
Figure 3.4 The side reaction of isocyanate groups with water.....	49
Figure 3.5 Synthesis procedure for the preparation of (a) TPU/Raw-CNTs and (b) PU/Raw-CNTs composites	50
Figure 3.6 The schematic diagram of FTIR principles	52
Figure 3.7 Schematic of a SEM	53
Figure 3.8 Recommendations of resistivity meters for the measurements of materials with various resistivities.....	56
Figure 3.9 The digital photos of resistivity meters (a) for high resistivity (Hiresta series) and (b) for low resistivity (Loresta seres).....	56
Figure 3.10 The calculation of surface resistivity and volume resistivity for ring electrode. The RCF is the abbreviation of the term of Resistivity Correction Factor. It is given by the supplier. In this project, the used probe has RCF _s 10.09 and RCF _v 0.273, respectively	57
Figure 3.11 The calculation of surface resistivity and volume resistivity for four-probe electrode.....	57
Figure 3.12 Schematic of EMI shielding [26].....	58
Figure 3.13 The schematic illustration of EMI shielding tester.....	60

Figure 3.14 The experimental setup for the EMI shielding performance of composites.....	60
Figure 3.15 The sample size of composites for tensile test according to ASTM D 638-V	61
Figure 3.16 The cartoon picture of DSC measurement	62
Figure 3.17 Instrumentation of TGA	63
Figure 4.1 The illustration of PU/Raw-CNTs composites fabrications: (a) NCO/Raw-CNTs composites and (b) OH/Raw-CNTs composites	71
Figure 4.2 ASTM 4935 D99 measurement setup and specimen.....	73
Figure 4.3 Cryo-fracture surfaces of (a) TPU/Raw-CNTs 5, (b) TPU/Raw-CNTs 10, (c) PU/Raw-CNTs 5 and (d) PU/Raw-CNTs 10.....	74
Figure 4.4 EMI shielding properties of TPU/Raw-CNTs and PU/Raw-CNTs composites.....	75
Figure 4.5 Surface morphologies of (a) NCO/Raw-CNTs 5, (b) NCO/Raw-CNTs 10, (c) OH/Raw-CNTs 5 and (d) OH/Raw-CNTs 10 composites	77
Figure 4.6 The DC conductivity of PU/Raw-CNTs composites.....	78
Figure 4.7 (a) Total SE and (b) the contribution of absorption and reflection shielding mechanism of PU/Raw-CNTs composites	80

Figure 4.8 The (a) real part (ϵ') and (b) imaginary part (ϵ'') of complex permittivity of composites, and the contribution of (c) AC conductivity and (d) dielectric polarization to EMI SE	82
Figure 4.9 Cartoons of CNTs reinforced polymer composites containing various dispersed CNTs	83
Figure 4.10 The proposed mechanism of crack formation	84
Figure 4. 11 The DSC curves of of PU/Raw-CNTs composites.....	86
Figure 4.12 Young's moduli of PU/Raw-CNTs composites	87
Figure 5.1 (a) Theoretical model of Maxwell-Wagner two layer capacitor and its equivalent circuit, and the equivalent circuits of composites at (b) uniform CNTs dispersion and (c) poor CNTs dispersion. R is the resistivity of single nanotube and CP is capacitance of insulating polymer outside CNT, respectively. R_i ($i=1, 2, 3, 4, 5, \dots$) correspond to the resistivity of CNTs agglomerates with various amount of nanotubes	95
Figure 5.2 ASTM 4935 D99 measurement setup and specimen.....	99
Figure 5.3 The cartoon illustration of the harmonic oscillator	100
Figure 5.4 Lorentz oscillator model	101
Figure 5.5 A periodic structure of thin wires infinitely arranged in cubic lattice. The value of a and r might be a few millimeters and micrometers, respectively	104

Figure 5.6 Maxwell-Wagner two-layer structure and its equivalent circuit ...	105
Figure 5.7 The flow chart of the development of this method.....	106
Figure 5.8 Real permittivity of NCO/Raw-CNTs composites and OH/Raw-CNTs composites	109
Figure 5.9 Real permittivity of TPU/surfactant-CNTs composites	110
Figure 5.10 Cryo-fracture surfaces of (a) TPU/Raw-CNTs 5, (b) TPU/PVP-CNTs 5, (c) TPU/Span 80-CNTs 5 and (d) TPU/Triton 100-CNTs 5 composites	111
Figure 5.11 (a) Real permittivity and (b) standard deviation of NCO/Raw-CNTs composites. The red star is the theoretical standard deviation of NCO/Raw-CNTs 10, while the orange heart are the experimental standard deviations of OH/Raw-CNTs 5 and OH/Raw-CNTs 10, respectively	112
Figure 5.12 Real permittivity and standard deviation of (a) PU/Carbon black composites and (b) PU/rGO composites.....	113
Figure 6.1 Schematic illustration for the preparations of PDA-CNTs.....	125
Figure 6.2 (a) FTIR spectra and (b) TGA curves of raw CNTs, PDA-CNTs and pure PDA	125
Figure 6.3 TEM images of (a) raw CNTs and (b) PDA-CNTs. Arrows show the PDA coating wrapped on the nanotubes. The high magnified images with a scale bar at 10 nm were given for better clarity	126

Figure 6.4 Raman spectra of raw CNTs and PDA-CNTs	127
Figure 6.5 EMI SE of the as-fabricated PU/CNTs composites.....	129
Figure 6.6 The (a) imaginary part (ϵ'') of complex permittivity of composites, and (b) AC conductivity and (c) the contribution of dielectric polarization to EMI SE.....	131
Figure 6.7 SEM pictures of the cryo-fracture surfaces of (a) PU/Raw-CNTs 10 composite and (b) PU/PDA-CNTs 10 composite	132
Figure 6.8 (a) The real permittivity and (b) its standard deviation of PU/Raw-CNTs and PU/PDA-CNTs composites	133
Figure 6.9 Schematic illustration for network formation of PU/PDA-CNTs composites.....	134
Figure 6.10 (a) Representative stress-strain curves and (b) Young's modulus of PU/CNTs composites.....	135
Figure 7.1 The proposed PDA structure	145
Figure 7.2 Schematic of the preparation of CNTs-PDA-Fe ₃ O ₄ [18]	146
Figure 7.3 Schematic structures of (a) dendrimers, and (b) hyperbranched polymers. D: dendritic units; T: terminal units; L: linear units	147
Figure 7.4 The scheme of the preparation of composite enhanced by different mechanisms: (a) conventional composites-phase separated, (b) intercalated composites and (c) exfoliated composites [24].....	147

Figure 7.5 Schematic illustration showing the reaction of oxazolidine with moisture.....	148
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Abbreviations

PU	Polyurethane
CNTs	Carbon Nanotubes
PDA	Polydopamine
GO	Graphene Oxide
PVP	Polyvinyl Pyrrolidone
DMF	Dimethylformamide
PTFE	Polytetrafluoroethylene
IPD	Interparticle Distance theory
SE	Shielding Effectiveness
DP	Dielectric Polarization
SD	Standard Deviation
T _g	Glass Transition Temperature
FTIR	Fourier Transform Infrared Spectroscopy
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
DSC	Differential Scanning Calorimetry
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
TGA	Thermogravimetric Analysis
EMI	Electromagnetic Interference
VNA	Vector Network Analyzer
NRW	Nicholson-Ross-Weir Technique
CVD	Chemical Vapor Deposition
I	Transmits Electrical Current
V	Voltage
η	Impedance
σ	Electrical Conductivity

σ_{DC}	Direct Current Conductivity
σ_{AC}	Alternating Current Conductivity
ϵ	Complex Permittivity
ϵ'	Real Permittivity
ϵ''	Imaginary Permittivity
μ	Permeability
E	Electric Field
H	Magnetic Field
p	Transmission Coefficients
q	Reflection Coefficients
δ	Skin Depth
T	Transmittance
R	Reflectance
A	Absorbance

Chapter 1

Introduction

This chapter states the trend of EMI shielding materials development and existing problems, which motivate this project. Motivated by the outstanding problems, a series of objectives are proposed. This chapter gives the overview of this dissertation, i.e., correlating the CNTs dispersion states and EMI shielding properties, developing a new method to evaluate CNTs dispersion and some preliminary work for further enhancement of EMI shielding performances. Finally, the outcomes of this project is summarized.

1.1 Problem Statement

With the rapid development of indispensable electronic devices and communication instruments, e.g., satellites, radars and wireless LAN, the issue associated with electromagnetic interference (EMI) such as adverse effect on the performance of other equipment and human health have been attracting scientists' attention. Metals are the first choice to be used in EMI shielding applications, attributed to their excellent electrical conductivity and ability of heat diffusivity. However, the drawbacks of metals limit their applications, e.g., susceptible for corrosion, high density, high cost and so on. Compared to conventional metal-based EMI shielding materials, polymer-matrix composites containing conductive fillers are attractive candidates for the substitution of metal shielding materials, arising from their easy processability, low cost and low density. [1]

There is an increasing trend for carbon-based composites to be studied as the shielding materials instead of metallic materials because of their lightweight, high stability to chemical corrosion and processing advantages. [2-11] It is well recognized that the electrical conductivity enhances the EMI shielding and polymer composites with high conductivity exhibit superior EMI shielding effectiveness (SE). [12] The high conductivity, high aspect ratio and low cost of multi-walled carbon nanotubes (CNTs) make polymer/CNTs composites easily achieve high conductivity at low CNTs loading. [13-16] Attributed to these advantages, CNTs act as an ideal option to achieve high performance EMI shielding materials. In order to fully release their potentials, some functional groups are introduced onto CNTs, e.g., -COOH, [17] -NH₂ [18] and -NCO [19], which could effectively debundle the CNTs agglomerates and create the bridge between tubes and matrix. Although majorities of literature reported improved EMI performance of composites when the fillers dispersion in matrix is enhanced, the relationship of CNTs dispersion and EMI shielding properties

was not clearly understood because most of the reports are based on phenomenological evidences. In this thesis, attempts are made to go beyond the literature and to discover the theoretical basis.

The observation of CNTs dispersion in matrices still mainly relies on the scanning electron microscope (SEM) and transmission electron microscopy (TEM) at the current stage, which is only capable of investigation at the microscopic level. Additionally, the specimen preparation of SEM and TEM is destructive, complicated and non-representative. Another drawback of using SEM and TEM is the difficulty of evaluating dispersion at high filler loading, as the filler cannot be distinguished as individually dispersed or aggregated through morphological observation.

According to the EMI theory, both the permittivity and the permeability of composites determine the EMI shielding performances. The incorporation of as-received CNTs could only improve the permittivity of composites. Some researcher reported that they incorporated magnetic particles onto CNTs, which could further improve the EMI shielding performances, attributed to the contribution from magnetic particles to permeability of composites. [7] Generally, the incorporation of magnetic particles to CNTs was achieved by indirect approach, which involved CNTs treatment. [20] Polymer encapsulation is one of effective methods, which not only retains the CNTs intrinsic structure, but provides the possibility for secondary modification of CNTs. However, the effect of polymer encapsulation on EMI shielding performances was still unclear. Therefore, the preliminary work that the intermediate layer of polydoamine (PDA) as linkage of CNTs and magnetic particles was done in this thesis.

1.2 Objectives and Scope

The objective of this project was to develop high performance CNTs-based EMI shielding materials as well as have a better understanding the mechanism. Firstly, CNTs dispersion was correlated to EMI shielding properties, as shown in **Figure 1.1**. Generally, there are three states of CNTs in matrix, i.e., (1) all of CNTs perfectly disperse in matrix, (2) all of CNTs exist in the form of aggregates and (3) a mixture of individual nanotube and CNTs agglomerates. These three dispersion states were affected by polymer matrix and processing method of composites. The relationship of CNTs dispersion with EMI shielding properties of composites was systematically studied.

Figure 1.1 Illustration of correlation of CNTs dispersion and EMI shielding performance

Moreover, it could be seen from **Figure 1.1** that at the same CNTs loading, the amount of interfaces between CNTs and matrix is determined by the CNTs dispersion state. The better dispersion, the more interfaces created. Furthermore, the better dispersion state of CNTs in insulating polymer, the less free electrons in CNTs. [21-23] All these phenomena will determine the one of intrinsic parameters in composites, i.e., complex permittivity. Based on some classical theoretical models that describes the complex permittivity, we tried to

find a quantitative way to evaluate the CNTs dispersion. This method and calculation method will be discussed in details, which will be also verified by experimental data.

With the established method, the surface treatment of CNTs was also studied. Since surface treatment is widely employed to improve the comprehensive properties of composites for many applications, for example, the incorporation of magnetic particles and improvement of mechanical properties.

To summarize, all these studies aim to obtain a clear and deep understanding on the EMI shielding mechanism, which will be employed to guide the design of high performance EMI shielding materials in future.

1.3 Dissertation Overview

The thesis addresses the matrix identification, the processing of PU/CNTs composites, the surface modification of CNTs and the quantitative analysis of CNTs dispersion.

Chapter 1 states the motivation for this project and its significance in the field of EMI shielding. In this chapter, the trend of shielding materials development and existing problems are briefly described. Based on these analyses and understanding, a series of works are proposed, associated with the expectation and hypothesis.

Chapter 2 summarizes the background and the research progress of EMI shielding materials. It first gives the theory of EMI shielding, the current solutions for EMI shielding and the future trend for EMI shielding materials. In this chapter, the current studies on EMI shielding are reviewed in detail, including the fillers treatment, the fabrication process of shielding material, the

structural design of EMI shielding barriers. This chapter also reviews the challenges in the field of EMI shielding.

Chapter 3 elaborates the theoretical induction of all experiments and characterizations involved in this thesis. The principles of experiment design and purposes of characterization are expounded. Moreover, the experimental details are also briefly introduced in this chapter.

Chapter 4 correlates the CNTs dispersion and EMI shielding properties of composites. The CNTs dispersion was carried out in thermoplastic PU and thermoset PU, resulting in the different CNTs dispersion. As a consequence, the EMI shielding properties of composites exhibited obvious differences. Moreover, the effect of processing of sequences of CNTs on EMI shielding properties of composites and their dispersion were systematically studied. This chapter explored the experimental parameters for further studies and made a complimentary understanding to literatures

Chapter 5 elaborates the method for the evaluation of CNTs dispersion. In this part, three theoretical models were introduced in detail and correlated to the resonance phenomenon of conductive fillers in polymer matrix. Then, the method utilizing the oscillation of the real part of permittivity was used to distinguish the fillers dispersion state. By combining SEM technique, the developed method was fully verified, including various fillers with different dimensions. It was found that this method could be employed to distinguish the efficiency of surfactants, and also to measure the maximum filler's loading.

Chapter 6 elaborates the effect of CNTs surface treatment on EMI shielding properties and mechanical properties of composites. Although PDA treatment resulted in decreased EMI shielding properties, it could be further employed as intermediate layer for secondary modification. The preliminary result gives a

guideline for further development.

Chapter 7 draws together the threads of the thesis. According to the outcomes of this project, further studies are proposed, including: (1) the incorporation of magnetic particle for further improvement of EMI shielding performances; (2) the enhancement of the mechanical properties for composites; (3) decreasing the amount of solvents using during the processing.

1.4 Findings and Outcomes

This research focuses on the development of high performance EMI shielding materials and leads to several novel outcomes:

(1) Identified the matrix type and studied the effect of sequence of adding CNTs into composites on the EMI shielding properties of composites. Attributed to the method of in-situ polymerization, uniform CNTs dispersion was achieved in thermoset PU. Moreover, it was found that the CNTs dispersion was prone to the processing sequence of CNTs into PU in thermoset system, in which polyisocyanurate part exhibited higher efficiency for CNTs dispersion than polyol part. The relationship of CNTs dispersion and EMI shielding properties was detailed discussed.

(2) The new method to evaluate CNTs dispersion was developed, which was strongly supported by three theoretical models. Complex permittivity of composites was correlated to the resonance phenomenon of conductive fillers which was influenced by their dispersion states. This developed method was verified by several cases, e.g., composites by changing processing method, composites with the aid of various surfactant and statistical analysis. It was found that this method can be employed to not only distinguish the efficiency of surfactants, but also estimate the maximum filler loading.

(3) The modification of CNTs by PDA through self-oxidation polymerization of DA was beneficial for their further modification. The modification of PDA retained the intrinsic structure of CNTs. The influences of PDA modification on PU/PDA-CNTs composites were investigated, including mechanical and EMI shielding performances. It was found that the mechanical properties of PU/PDA-CNTs composite were increased compared with that of PU/Raw-CNTs composite, attributed to the presence of reactive groups in PDA coating. However, the EMI shielding properties of PU/PDA-CNTs composites were decreased, resulting from the intrinsically insulating PDA.

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Chapter 2

Literature Review

This chapter gives the theoretical background of the EMI shielding, the current solutions for EMI shielding and the future trend for EMI shielding materials. In this part, the progress of studies on the EMI shielding materials are fully investigated, including the fillers treatments, fabrication process of shielding materials, as well as the existing limitations in current stage.

2.1 EMI shielding

In recent years, the EMI shielding has been widely recognized as an area of materials or structure designs protecting the interference among electronic devices. Interference is defined as EM energy which causes the degradation of electronic devices, and will be referred to as EMI. The interference always occurs between EM energy in the form of EM wave and electronic component, or receptor, which is susceptible to that particular amplitude and frequency. **Table 2.1** gives some common sources and receptors of EMI.

In general, EMI can be classified in two ways, radiated and conducted, according to the type of propagation path involved. Radiated interference happens when an EM source emits energy, e.g., radio frequency (RF) signals, which travel in the medium of atmosphere. The interfered part may be the receptor in the same system, or a completely electrically isolated component. By contrast, the conducted interference occurs when the EM wave propagates from one unit to the other along the medium. The conducted interference could be easily controlled by filters. In this dissertation, the radiated interference will be the research targets, since the wireless devices in both the industrial and domestic field become more popular in our daily life.

Table 2.1 Common EMI sources and receptors

EMI sources	EMI receptors
Televisions and radios	Aircraft navigation systems
Electric motors	High frequency equipment
Engine ignition systems	Electronic measuring equipment
Paging systems	Radio and television receivers
Power tools	Mobile telephones

Moreover, the electrical devices as the source of EM energy radiate EW waves

travelling in all directions. At any point the wave consists of an electric field and a magnetic field which perpendicular to each other and to the direction of propagation. The EM radiation spectrum is illustrated in **Figure 2.1**.

Figure 2.1 EM radiation spectrum

The EM wave theory is not new. The basic equations were systematically formulated by Maxwell, Faraday and others, in order to describe the relation between electric and magnetic fields.

To assist in the understanding of the shielding behavior and further designing the shielding materials or structures, some classic theories are introduced below:

2.1.1 Basic plane wave shielding theory

Conventional two-wire transmission line transmits electrical current (I) and voltage (V) can be described in **Figure 2.2a**. And the distributed series impedance (η) and shunt admittance (Y) per unit length are complex constants.

$$\begin{aligned}\frac{dV}{dx} &= -\eta I \\ \frac{dI}{dx} &= -YV\end{aligned}\tag{1}$$

As mentioned above, the EM wave is a transverse wave, which refers to the wave with an electric field and a magnetic field perpendicular to each other and to the direction of propagation. In **Figure 2.1b**, the electrical constants of electrical conductivity, magnetic permeability and dielectric constant are σ , μ and ϵ , respectively. They are linked by the Eq. (2):

$$\begin{aligned}\frac{dE}{dx} &= -j\omega\mu H \\ \frac{dH}{dx} &= -(\sigma + j\omega\epsilon)E\end{aligned}\quad (2)$$

Figure 2.2 Plane wave analogy: (a) conventional transmission line and (b) plane wave, in which the electric and magnetic field perpendicular to each other

The wave impedance is a useful concept to link the factors involved in EMI shielding theory. The intrinsic impedance of sheet materials is: [\[1\]](#)

$$\eta = \sqrt{\frac{j\omega\mu}{\sigma + j\omega\mu}} \quad (3)$$

For air, the electrical conductivity is negligible, thus the impedance of air (η_0)

$$\eta_0 = \sqrt{\frac{\mu}{\epsilon}} \quad (4)$$

When the EM wave travels along sheet materials, it follows a function, which is described as propagation constant:

$$\gamma = \alpha + j\beta = \sqrt{j\omega\mu(\sigma + j\omega\epsilon)} \quad (5)$$

α, β are the attenuation constant and phase constant, respectively.

There are two extreme cases are considered. For metallic sheet,

$$\gamma \approx \sqrt{j\omega\mu\sigma} = (1+j)\sqrt{\pi\mu f\sigma} \quad (6)$$

and, in air

$$\gamma \approx \sqrt{-\omega^2\mu\epsilon} = j\omega\sqrt{\mu\epsilon} \quad (7)$$

It is apparent that $\alpha=0$ in air and in metal

$$\alpha = \beta = \sqrt{\pi\mu f\sigma} \quad (8)$$

2.1.2 Transmission-Line equations

If the impedance (η_t) at $x = t$ in the plane where the wave propagates mismatches that of sheet material (η), reflection occurs at the boundary or interface (**Figure 2.3a**). At this plane, let E^i, H^i be the incident electric and magnetic fields; E^r, H^r the reflected fields, and E^t, H^t the transmitted fields. Since the fields are continuous across the plane [1]

$$E^i + E^r = E^t \quad H^i + H^r = H^t \quad (9)$$

The reflected wave travels back to the source impedance for a sheet with a matched impedance at the plane $x = 0$, thus

$$E^i = \eta H^i, \quad E^r = -\eta H^r \text{ and } E^t = \eta_t H^t \quad (10)$$

When (2) are substituted in (1), we can obtain for reflection coefficients

$$q_E = \frac{E^r}{E^i} = \frac{n-1}{n+1}, \quad n = \frac{\eta_t}{\eta}$$

$$q_H = \frac{H^r}{H^i} = \frac{1-n}{n+1} = -q_E \quad (11)$$

and for transmission coefficients

$$p_E = \frac{E^t}{E^i} = \frac{2n}{n+1} = 1 + q_E$$

$$p_H = \frac{H^t}{H^i} = \frac{2}{n+1} = 1 + q_H \quad (12)$$

The net transmission coefficient is the product of the two transmission coefficients when two mismatched interfaces are considered as in a plane:

$$p = p_E = p_H = p_E(0) \cdot p_E(t) = p_H(0) \cdot p_H(t) = \frac{4n}{(n+1)^2} \quad (13)$$

When considering the re-reflections (**Figure 2.3b**), the transmission coefficients across the plane are [\[1\]](#):

$$T = p(1 - qe^{-2\gamma t})^{-1}e^{-\gamma t} \quad (14)$$

where the two parameters are expressed as below:

$$p = p_H = \frac{4n}{(n+1)^2}$$

$$q = q_H = \frac{(n-1)^2}{(n+1)^2} \quad (15)$$

where n is the ratio of characteristic impedances η_t/η , and η_t is the impedance of the incident wave inside the materials. It is worth noting that the transmission coefficient and reflection coefficient from multi-reflection model have the same formula with those from single reflection (**Figure 2.3**).

Figure 2.3 Reflection of EM waves at (a) single interface and (b) double interfaces showing multiple re-reflections. The vertical solid line stands for interface

By definition total shielding effectiveness (SE) is

$$\begin{aligned}
 SE_T &= -20 \log_{10}|T| \\
 &= 20 \log_{10} \left| \frac{(1 - qe^{-2\gamma t})e^{\gamma t}}{p} \right| \\
 &= 20 \log_{10}|e^{\gamma t}| - 20 \log_{10}|p| + 20 \log_{10}|1 - qe^{-2\gamma t}| \\
 &= SE_A + SE_R + SE_M
 \end{aligned} \tag{16}$$

in which the reflection loss, absorption loss and multi-reflection loss are: [2, 3]

$$SE_R = -20 \log_{10}|p| = 20 \log_{10} \frac{|n+1|^2}{4|n|} \tag{17}$$

$$SE_A = 20 \log_{10}|e^{\gamma t}| = 8.686\alpha t \tag{18}$$

$$SE_M = 20 \log_{10} \left| 1 - \frac{(n-1)^2}{(n+1)^2} e^{-2\gamma t} \right| \tag{19}$$

where the parameters α , n and γ are defined as following equations, t is the thickness of the sheet materials.

$$\alpha = \omega \sqrt{\frac{\varepsilon\mu\sqrt{1+\tan^2\delta}-1}{2}} \tag{20}$$

$$\beta = \omega \sqrt{\frac{\varepsilon\mu\sqrt{1+\tan^2\delta}+1}{2}} \tag{21}$$

$$n = \sqrt{\frac{\mu\varepsilon\sqrt{1+\tan^2\delta}\pm 1}{2}} + i\sqrt{\frac{\mu\varepsilon\sqrt{1+\tan^2\delta}\mp 1}{2}} \tag{22}$$

$$\gamma = \omega \sqrt{\frac{\mu\varepsilon\sqrt{1+\tan^2\delta}-1}{2}} + i\omega \sqrt{\frac{\mu\varepsilon\sqrt{1+\tan^2\delta}+1}{2}} \tag{23}$$

For good conductor ($\sigma \gg \omega\varepsilon$), the Eq. 17 and 18 simplify to: [4, 5]

$$SE_R = 39.5 + 10 \log \frac{\sigma}{2\pi f\mu} \tag{24}$$

$$SE_A = 8.686t\sqrt{\pi f\sigma} \tag{25}$$

Another importance concept in EMI shielding theory is skin effect. It describes the depth where the EM field drops to 1/e of the incident value, designated as δ .

For good conductor, it can be given by: [4]

$$\delta = \frac{1}{\sqrt{\pi f\mu\sigma}} \tag{26}$$

2.1.3 Experimental EMI shielding effectiveness

However, the basic equations from the EMI theories are seldom used in real applications, resulting from the complicated calculations. Experimentally, shielding is measured using instrument called Vector Network Analyzer. Vector network analyzer (VNA) can provide magnitude as well as phases of various signals. The incident and transmitted wave in a two port VNA can be mathematically represented by complex scattering parameters (S-parameters), i.e., S_{11} , S_{21} , S_{22} and S_{12} . These S-parameters are conveniently correlated to reflectance (R), absorbance (A) and transmittance (T) (shown in **Eq. 24-26**), which are further used to calculate the EMI SE. [6-8] Moreover, the output attributes of complex permittivity and permeability are from the input S-parameters by Nicholson-Ross-Weir technique. [9, 10]

$$R = |S_{11}|^2 = |S_{22}|^2 \quad (24)$$

$$T = |S_{12}|^2 = |S_{21}|^2 \quad (25)$$

$$A = 1 - R - T \quad (26)$$

Then, the experimental EMI SE can be achieved from the R, A and T:

$$SE_{Total} = -20 \log_{10}|T| \quad (27)$$

$$SE_A = -10 \log_{10}|1 - R| \quad (28)$$

$$SE_R = -10 \log_{10}|T/(1 - R)| \quad (29)$$

Furthermore, the SE of a shielding material also could be defined to be the ratio between incoming power (P_i) and outgoing power (P_o) of the electromagnetic wave:

$$SE_{Total} = -10 \log_{10}|P_o/P_i| \quad (30)$$

Thus, the shielding effectiveness can be converted to percentages of power shielded, shown in **Table 2.2**.

Table 2.2 Reduction in signal strength

SE / dB	Power reduction / %
10	90
20	99
30	99.9
40	99.99
50	99.999
60	99.9999

2.2 EMI shielding solutions

2.2.1 EMI shielding enclosure and gaskets

The EMI barriers include physical barriers like filters and geometrical barriers, in which the conductive shielding enclosures are one of most common geometrical barriers. The selection of shielding materials would determine the choice of production technique. First of all, the electrical and mechanical properties must be taken into account, as the enclosure should meet the EMI requirements as well as the mechanical protection for interior components. From this point of view, metal materials with high conductivity and enough strength are highly desired. In practical, the design of EMI enclosure should also consider the necessary discontinuities for installment of EMI enclosure. It means that the enclosure should be divided into several parts, which makes the accessibility of the equipment inside (emitter or receiver) easy. However, the presence of doors, side panels, and input/output panel openings results in the leakage of EM wave.

Thus, the gaskets have been used to seal the enclosure, which improve the conductivity to minimize the leakage. There are slight differences between enclosure materials and gaskets materials, since the design of gaskets have to

consider two types of forces: compression and shear. The materials could be used to fabricate gaskets including metals, flexible graphite gaskets and conductive filler enhanced polymers. The selection of gaskets materials should be dependent on their working environment.

2.2.2 Composite materials for EMI shielding

As mentioned above, metal is best choice for EMI shielding attributed to their excellent electrical conductivity and strong strength. However, metallic materials also have some disadvantages, such as high density, high cost, difficult molding and easy corrosion or oxidation.

Polymer matrix composites containing conductive fillers become attractive for EMI shielding applications, which complement the drawbacks of metallic materials. [11] In addition, the most of polymers are electrically insulating and do not contribute to the shielding, therefore, certain amount of conductive fillers are needed to form a conductive network, which could meet the requirement of EMI shielding.

For a general shielding composite material, low filler loading to reach excellent shielding effectiveness is desirable, because the strength and ductility of a composite will be decreased with increasing filler contents, especially for the cases of absence of filler-matrix bonding. Moreover, the processability (viscosity) of composite is also related to the filler contents.

Usually, the conductive fillers include metal based and carbon based. The metal based fillers (e.g., nickel, silver and copper) are in the form of flakes, fibers and spheres. The selection of fillers is also concerning the oxidation resistance and cost of metal fillers. For example, nickel is more stable than copper due to its better oxidation resistance. The resulted oxide film will be detrimental to

shielding effectiveness, resulting from the high resistivity of oxide film. Moreover, the fabrication of metal reinforced composite is influenced by the intrinsic properties of metal fillers. The density of metal is significantly higher than polymer or solvents, leading to the obvious precipitation and bad dispersion.

Carbon-based fillers are ideal to substitute the uses of metal fillers, in which both continuous and discontinuous fillers have been intensively studied. Carbon fibers as continuous fillers can not only enhance the EMI shielding effectiveness, but also improve the mechanical and physical properties of the carbon fiber reinforced composites. [12] Because the network of conductive carbon fiber spreads the whole shielding materials, carbon fiber reinforced materials usually exhibit the abilities of electrostatic dissipation and EMI shielding. Carbon fibers consist of crystalline and amorphous carbons and they are generally developed from pitch or polyacrylonitrile (PAN) as precursors. Their crystallinity plays major roles in determining the electrical and EMI properties of final composites.

Compared with shielding materials with continuous fillers, composites with discontinuous fillers are essentially decided by some factors, e.g., the type of fillers, the shape, size and aspect ratio of fillers. [13] The percolation threshold is a useful concept for this type of composites, at which the long-range conductive network form in bulk composites. Only when the filler content is above on percolation threshold, the composites exhibit satisfied EMI shielding properties, because of the presence of conductive network. It is found that the composites enhanced by fillers with high aspect ratio and high conductivity have a much lower percolation threshold. [14] The attractive fillers are CNTs and graphene.

Considering the capacity of CNTs production and the high filler concentration required for EMI shielding associated with the cost of fillers, CNT become more attractive candidates for polymer composites with high EMI shielding properties, compared with graphene.

2.3 Carbon nanotubes (CNTs)

2.3.1 Introduction

CNTs were discovered as a byproduct of fullerene synthesis by Iijima in 1991. [15] Remarkable progress has been made in the past years, attributed to their miracle properties from their special structures. CNTs are long cylinders of three-coordinated carbon, slightly pyramidalized by the curvature from sp^2 hybridized graphene. [16] As a perfect tube, both ends should be capped by hemi-fullerenes, no dangling bonds left. With several decades of developments, some types of CNTs, i.e., single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multiwall carbon nanotubes (MWCNTs), have been produced. The MWCNT consists of many nested cylinders, while SWCNT has only one cylinder. The structures of these two CNTs are illustrated in **Figure 2.4**. As expected, the more perfect structure is, the more expensive cost is. Thus, MWCNTs are much more popular with industries. Compared with SWCNTs, MWCNTs have two advantages, i.e., more stiff and easy manufacturing. So far, the large-scale syntheses of MWCNTs are promoted by enhance chemical vapor deposition (CVD) processes, while only the Rice HiPco process exhibits potential to be scaleable for SWCNTs manufacture.

Figure 2.4 The structures of SWCNT and MWCNT [17]

2.3.2 Physical properties

Attributed to their special structures, the unique properties of CNTs could be easily observed. The macroscopic nanotubes exhibit attractive properties, including mechanical properties, thermal properties, electronic properties and magnetic and superconducting properties. Theory does a reasonable job to predict and rationalize the properties of single nanotubes, and the relationships between structure and properties have been studied as well. [18, 19] It is found that applications for CNTs will benefit from their multi-functionality, such as excellent electricity and low thermal expansion, while also possessing a stiff character.

The excellent mechanical properties are attributed to the strength of sp^2 carbon- sp^2 carbon bonds. According to the literature, the individual CNT illustrates a remarkable response of “bend and don’t break” even under large transverse deformation. Moreover, once the applied force is removed, a straight tube is recovered according to the simulations and experiments. [20, 21]

The Young’s modulus and strength of CNTs are highly dependent on the growth method and subsequent processing, resulting in the variable and uncontrolled defects on CNTs structure. The Young’s modulus of individual

nanotube was estimated as 1.0 to 1.8 TPa from TEM through the observation of the amplitude of their intrinsic thermal vibrations. [22] Furthermore, the bending modulus (23 to 32 GPa) of MWCNTs produced by pyrolysis was obtained by TEM based bending tests. [23]

The thermal conductivity of CNTs has also received considerable attention. [24] The thermal conductivity of ~3000 W/m K for MWCNTs [25] and ~2000 W/m K for SWCNTs [26] from experimental studies were reported. However, the quantitative measurement of thermal conductivity of individual nanotube remains challenging, [27] since the direct measurement of thermal conductive properties of individual nanotube is extremely restricted by technological difficulties and experimental measurements in nano-scale [28-31]. All these limitations result in the significantly scattered values for thermal conductivities of CNTs in the range of 2000 to 6000 W/m K. The mechanism of thermal transportation in CNTs is assumed to be that of phonon conduction. The phonon conduction is determined by several parameters; for example, number of phonon active modes, boundary surface scattering, the length of free path for the phonons and inelastic Umklapp-scattering. [32, 33]

Electrical conductivity is another property that triggers the CNT related studies. One monolayer of graphene has two energy bands crossing at the Fermi energy, thus, the system is at the transition between metal-insulator. Therefore, the electronic ground state in graphene could be described as a zero-gap semiconductor (or a metal with infinitesimal density of states at the Fermi energy). Then, the CNTs are a form of rolled graphene at the symmetry-breaking transition, depending on the orientations of wrapping (shown in **Figure 2.5**). [34-36]

The electrical properties of CNTs are determined by their rolling helicity. Similarly, the direct measurement of electrical properties of individual nanotube

is rather challengeable. Electron transportation in SWCNTs is uniform in nature, while that transportation in MWCNTs is more complex due to the presence of cylinders of different helicity. The electrical properties are susceptible to the defects and doping by other elements. [37]

Figure 2.5 The construction of a nanotube from a single graphene sheet by rolling up the sheet along the wrapping vector

2.3.3 Dispersion and functionalization of CNTs

As discussed, much literature has suggested that CNTs are ideal materials for some applications (e.g., thermal management, electrostatic dissipation and so on), but great challenges for the fabrication of high performance CNTs based materials involve the issues of CNTs dispersion and processing of composites. Thus, the enhancement of composites by CNTs is only a fraction of their potential and their superb properties have not yet fully realized in finished products. To solve these problems, great efforts have been made in the last two decades. There is much literature reporting on the methods for CNTs dispersion. [38-40]

Ultrasonication is an effective method to isolate CNTs in liquid media, including solvents and polymer solution (melt) with low viscosity. The

commonly used ultrasonication is usually achieved by ultrasonic bath or ultrasonic probe/horn. The principle of this technique is that alternative compression (high pressure) and rarefaction (low pressure) cycles are created by the propagation of sound waves in liquid media. Large amount of small vacuum bubbles (or voids) in liquid media are generated during rarefaction, followed by the violent collapse of these bubbles during compression, associated with high local temperatures. However, sonication is aggressive when the treatment is too long or under high power, resulting in the generation of CNTs defects or shortening issues. [41, 42] It is reported that graphene layers of CNTs could be destroyed completely and the CNTs could be converted into amorphous carbon nanofibers in extreme cases.

Moreover, the uses of strong mechanical forces can also deagglomerate CNTs bundles, for example, calendaring process, ball milling, and stir and extrusion. Calendaring is suitable to disperse, homogenize viscous materials through shear forces created by rollers. This method has been widely used in the dispersion of color pigments for lacquers and cosmetics. [43, 44] This method also has its limitation. The minimum gap between the rollers is 1-5 μm , which is much larger than the diameter of CNTs and comparable to the length of CNTs. It is suggested that this method is better for disentangling larger agglomerated CNTs into smaller ones, although individual CNTs may be disentangled out from the agglomerates.

Figure 2.6 The pictures of (a) three-roll calender and (b) schematic of its working mechanism

Ball milling utilizes high local pressure created by tiny and rigid balls to grind CNTs clusters. [45] Sometimes chemicals are used during ball milling of CNTs to enhance dispersity via a chemo-mechanical method effect. For example, amino functionalization of CNTs was obtained by ball milling at the presence of ammonium bicarbonate. [46]

Stirring is a common technique to mix CNTs with liquid media, for example polymer solution or monomers. The shear forces are highly dependent on the geometry of the propeller (i.e., size and shape) and speed control. A relative fine dispersion of CNTs could be achieved by intensive stirring. [47] Extruder is an effective tool to disperse filler in thermoplastic polymer or mix different polymer matrices. The shear forces are supplied by two screws which rotate at a controlled speed. The shear forces can be tuned by changing the diameter of screws and rotation directions. Due to the high energy input, this method is used for producing the polymer/CNTs composites at high CNTs loadings. [48]

Figure 2.7 Pictures of (a) shear mixer and (b) extruder.

Table 2.3 compares the effectiveness and influences of dispersion techniques on CNTs. Typically, the combination of multiple techniques is much more effective, e.g., ultrasonication plus ball milling, and ultrasonication plus extrusion [46, 49, 50]

Although so many techniques have been employed to disperse CNTs in polymer matrices, the raw CNTs still have not performed up to their expectation. The carbon atoms on CNTs walls are chemically stable, associated with the sp^2 hybridization, therefore, the interaction (π - π) between nanotubes is much stronger than that between CNTs and polymer matrix, resulting in the presence of CNTs aggregates in obtained composites. In order to weaken the interaction, physical and chemical functionalization of CNTs have been intensively studied, which are also known as non-covalent and covalent methods, respectively. [51, 52]

Table 2.3 The comparison of various techniques for CNTs dispersion

Techniques		
	Damage to CNTs	Controlling factors
Ultrasonication	Yes	Power, time, mode, type of sonicator
Calendering	No	Rotation speed, gap between adjacent rolls
Ball milling	Yes	Rotation speed, time, ball size, ratio of CNTs and balls
Shear mixing	No	Mixing speed, time, geometry of propeller
Extrusion	No	Configuration and rotation speed of screw, time, temperature

Chemical functionalization is popular in many applications, since functional groups could be introduced onto CNTs walls, which could be covalently linked with polymer matrix or secondary modifications. The general strategies for CNTs chemically functionalization is summarized in **Figure 2.8**. In details, the chemical functionalization consists of direct side wall functionalization and defect functionalization. Direct functionalization (**Figure 2.8A**) is achieved by the substitution of sp^2 carbon by other atoms (sp^3), which possess high chemical reactivity, e.g., fluorine. [53-56] Also the reactions of cycloaddition are possible to be employed, such as Diels-Alder reaction [57], chlorination, bromination,

[58] hydrogenation [59] and azomethine ylides [60]. Defect functionalization is usually achieved with the aid of strong acid, i.e., HNO_3 , H_2SO_4 or the mixture of them at certain ratio. [61] Sometimes strong oxidants are employed to facilitate the defect creation, e.g, KMnO_4 [62], ozone [63] and reactive plasma [64]. These functional groups have intensive chemistries, which could be further converted to other groups or polymer chains through chemical reactions, such as polymer grafting [65], esterification [66], silanation [67], thiolation [68], alkylation and arylation [69]. This approach extremely broads the applications of CNTs, since the types of functional groups could be easily tuned according to host solvents or matrices.

However, chemical methods have two disadvantages: (1) defects creation associated with CNTs shortening and disruption of π electron system, resulting in the detrimental change of properties of CNTs; (2) harsh chemicals are involved in the procedures, which are harmful to environment and safety of operators. Physical functionalization as an alternative method has been developed widely. Polymers with aromatic rings could be used to obtain CNTs suspensions through the interactions of polymer wrapping or π - π stacking. The types of polymer include poly(phenylene vinylene) [70], polystyrene [71] and so on. Besides polymers, another physical functionalization is the usage of surfactants, which could form micelles above a critical micelle concentration (CMC) to prevent the re-aggregation of CNTs. [72] The surfactants studied in literatures include non-ionic surfactants (e.g., polyoxyethylene lauryl ether and Triton X-100) [73, 74], anionic surfactants (e.g., sodium dodecylsulfate and sodium dodecylbenzenesulfonate) [75, 76] and cationic surfactants (e.g., dodecyl tri-methyl ammoniumbromide and cetyltrimethylammounium 4-vinylbenzoate) [77, 78].

Figure 2.8 General strategies for chemical functionalization of CNTs (A: direct functionalization and B: defect functionalization)

2.3.4 Polymer/CNTs composites for EMI applications

Due to their intrinsic structure and aspect ratio, composites with CNTs exhibit lower percolation threshold than carbon black. [79] Associated with the lower cost compared with graphene, CNTs have been paid much more attentions. The EMI shielding effectiveness of CNTs-based composites is influenced by several factors, e.g., CNTs types, concentrations, dispersion state and types of host matrix.

Huang and coworkers [80] studied that effect in SWCNTs reinforced epoxy. Three types of SWCNTs were produced using arc-discharge method. By controlling the composition of the carrier gas, long-SWCNTs and short-SWCNTs could be obtained, in which arc vaporization using 100% of He as carrier gas produced the long-SWCNTs while arc vaporization using 90% of He and 10% of CO₂ as carrier gas produced the short-SWCNTs. Short-SWCNTs were annealed in N₂ atmosphere to increase the graphitic perfection of the

CNTs. It was found that the EMI SE and conductivity of composites were related to the aspect ratio and wall integrity. For example, the conductivity of $0.15 \text{ S}\cdot\text{cm}^{-1}$ for the composite with 15 wt% of annealed-SWCNTs was higher than that of $0.04 \text{ S}\cdot\text{cm}^{-1}$ for the composite using short-SWCNTs (same loading). However, both composites from annealed-SWCNTs and short-SWCNTs exhibited lower conductivity than that ($0.20 \text{ S}\cdot\text{cm}^{-1}$) for the composite with 15 wt % of long-SWCNTs. In terms of EMI performance, the EMI SE of the composites with 15 wt% of long-SWCNTs and annealed-SWCNTs were 25 and 21 dB at 10 GHz, respectively. By contrast, the EMI SE of the composite with 15 wt% of short-SWCNs was 16 dB. Thus, high aspect ratio and better surface integrity of CNTs result in better conductivity and higher EMI shielding performance. This conclusion is supported by other researchers. [81, 82]

The processing conditions also affect the EMI shielding performances of composites through varying the dispersion and alignment of CNTs. [83, 84] Arjmand et al. compared the two CNTs composites from injection molding and compression molding. The results showed that the injection-molded composites with higher degree of alignments have higher resistivity and percolation threshold compared with compression-molded composites. [84] The mechanism of CNTs-based shielding materials was explained by Al-Saleh and Sundararajan. [7] Both theoretical and experimental shielding properties of as-prepared Polypropylene (PP)/CNTs were discussed. It was found that dominating mechanism to shield EM wave was adsorption. Regardless the CNTs loading and the thickness of shielding plate, the net shielding by reflection was lower than that by absorption. For example, the shielding by absorption was 62%-84% of the overall shielding for PP/CNTs composites with EMI SE above 10 dB. Moreover, the shielding by reflection was affected by conductivity and thickness of composites as well as the CNTs concentration.

The CNTs dispersion is a hot topic since CNTs was firstly discovered. Melt mixing, solution mixing and in-situ polymerization have been employed to fabricate CNTs-based polymeric composites. Due to the high shear forces from the screws, the CNTs tend to align in the same direction with the flow, resulting in the anisotropic structure of CNTs filled composites. Thus, the composites exhibited structure-dependent EMI shielding performances. [85, 86] On the contrary, in-situ and ex-situ (solution mixing) method could achieve isotropic CNTs dispersion state in composites. Yuen and coworkers compared the Poly (methyl methacrylate) (PMMA)/CNTs composites made from these two processing methods. [87] It was concluded that a lower electrical resistivity and lower percolation threshold (~ 0.25 wt%) could be achieved by in-situ method compared with on ex-situ method (~ 0.74 wt%). According to the SEM observation, the CNTs adhered better to PMMA matrix in composites by in-situ method, which was attributed to the formation of chemical bonding between PMMA with CNTs by free radical reaction. The dispersion of CNTs can also be improved by CNTs surface treatment, e.g., Friedel-Craft acylation, [88] amine and carboxyl acid functionalization [89].

Moreover, the presence of ferromagnetic Fe metal catalyst in CNTs was found by Kim et al. to be useful for EMI SE improvement, attributed to the magnetic permeability from Fe. [90] For example, the EMI SE of raw CNTs-PMMA (20 wt%) composites was measured to be ~ 20 dB, while that of purified CNTs-PMMA composites with the same CNTs loading was only around 7 dB in the measured frequency range. Similarly, the impurity of nickel in CNTs was used for enhancing EMI shielding applications. [91] In some cases, the magnetic particles were deliberately introduced onto CNTs, in order to obtain better EMI shielding properties. For example, nickel coated CNTs [92] and Fe@Fe₃O₄ decorated CNTs [93, 94].

So far, many types of polymer matrices have been used as host matrices for EMI shielding applications, including polyurethane, [95] polystyrene, [96] epoxy, [97] polyacrylate, [98] poly vinylalcohol, [4, 99] polyaniline, [100, 101] poy (ϵ -caprolactone) [102] and so on.

2.4 Polyurethane (PU)

Polyurethanes are a broad class of polymers, which have one common aspect-urethane groups (-NHCO-O-). The urethane groups are usually generated from isocyanate group via the reaction of nucleophilic addition by hydroxyl compounds. [103] An isocyanate having two isocyanate groups is named as diisocyanate, which is well-known in polyurethane industries. The diisocyanates are manufactured by treating amines with phosgene as shown below: [104]

2.4.1 Reaction of isocyanate

Attributed to the significant industrial and academic importance of PU, the chemistry of isocyanates has been studied extensively. Isocyanate groups are extremely reactive chemicals, which could create several different products with hydroxyl and amine functional substances through nucleophilic addition reactions. The presence of oxygen and nitrogen atoms makes the carbon atom more positive character, resulting in the high reactivity. Even, the isocyanates can react with urethanes and produce allophanates. In addition, isocyanate groups could polymerize via self-addition reactions, resulting in uretidione rings, isocyanurate or carbodiimide. [105] The basic reactions of isocyanates are shown in **Scheme 1**.

Scheme 1. Basic reactions of isocyanates with various reactants [106]

2.4.2 Reactants for PU fabrication

Isocyanates used to prepare PU can have aromatic or aliphatic structures. In general, aliphatic polyisocyanates contribute better oxidative and ultraviolet stabilities to PU than aromatic ones. [107] It is worth noting that the diisocyanate exhibits high toxicity and can seriously threaten operators' health. Herein, the polyisocyanurates from trimerization of diisocyanates are developed to replace the uses of diisocyanate, [108] as hardener or cross-linker. An isocyanurate ring is created after trimerization, which contains three nitrogen atoms and three carbonyl groups. The introduction of isocyanurate rings is beneficial for the thermal stability and UV resistance of PU materials, [109, 110] leading to the spread applications of polyisocyanurate in industry.

The component of polyol can be polyether-based, acrylic-based, polyester-based, polycarbonate-based, or mixture of these. A huge list of polyols could be found in industrial markets, depending on the requirements of final products. Sometimes, catalysts are employed to accelerate reactions at lower temperatures. Also there are many effective catalysts are available. Most often used catalysts are organo tin compounds, [111] tertiary amines, [112] tetravalent tin compounds [113].

2.4.3 PU classification

For coating application, six PU coating types are classified by ASTM D16 Standard. [114] **Table 2.4** gives the summary of PU coating classification.

Table 2.4 Summary of the polyurethane by ASTM classification

Types		Characteristics	Curing Mechanism	Polymer
One package	Pre-reacted	Products of unsaturated drying oil modified with isocyanate	Oxidation of drying oil and evaporation of solvent	Drying oil modified with isocyanate
	Moisture cured	Free isocyanate	Atmosphere moisture reacting with isocyanate	Polyol
	Heat cured	Blocked isocyanate	Unlock the isocyanate and react with polyol	Prepolymer adduct blocked by certain agents
	Non-reactive lacquer	Polyurethane solution	Solvent evaporation	Thermoplastic polyurethane
Two package	Catalyst	Prepolymer and catalyst	Residual isocyanate reacting with moisture	Prepolymer terminated with isocyanate
	Polyol	Polyol and isocyanate	Reaction between polyol and isocyanate	Polyol

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Chapter 3

Experimental Methodology

In this chapter, the experimental methods and techniques are described. This project involves a broad range of basic reactions in the process of material fabrications as well as characterization methods to evaluate the performances of the as-prepared composites. Understanding the principles of interaction between fillers and matrix for design of proper experiment methods and the mechanism is beneficial for the development of the targeted materials.

3.1 Introduction

This project focuses on the development of high performance CNTs based EMI shielding materials. The great challenges of fabrication of CNTs based shielding materials include CNTs dispersion and limited techniques for evaluation of CNTs dispersion. Thus, both of these two problems were addressed in this project. Firstly, the influences of polymer matrices on CNTs dispersion and EMI shielding properties were studied, following by the effects of processing. Then, a new method to evaluate the CNTs dispersion was developed based on several classical models through monitoring the differences in dielectric permittivity. The details of these models will be elaborated in chapter 5.

3.2 CNTs dispersion method

3.2.1 Raw CNTs without treatment

According to the literature, the most effective method to get a relative homogeneous CNTs suspension is ultrasonication, since the probe sonicators are generally aggressive due to their high power, [1, 2], the technique of ultrasonic bath was chosen in this project. The CNTs concentration in solvent was fixed at 0.5 mg/ml, aiming at fully isolating nanotubes and wetting of CNTs surfaces.

3.2.2 Raw CNTs with surfactants

For the CNTs dispersion by surfactants, a two-step method was employed in this project. The raw CNTs suspension was prepared following the method described in **section 3.2.1**. Then the surfactant solution (dissolved in the same

solvent prior to the incorporation) was further incorporated into the raw CNTs suspension, followed by another 1 h of ultrasonication.

3.2.3 Polydopamine treated CNTs (PDA-CNTs)

The PDA-CNTs were prepared following the method in the literature [3]. The schematic illustration of PDA-CNTs preparation is displayed in **Figure 3.1**. Raw CNTs were ultrasonically dispersed in the mixed solution of DMF and tri (hydroxymethyl) aminomethane with pH ~8.5 till the formation of nearly homogeneous suspension. Then a predetermined amount of dopamine hydrochloride was added into the CNTs suspension, followed by continuously stirring for 6 h at room temperature. 3-4 times of repeating centrifugation and washing by deionized water were carried out to remove unreacted dopamine monomers and free polydopamine particles. The obtained PDA-CNTs were dried using a freeze dryer.

The procedure of PDA-CNTs dispersion was the same as that of raw CNTs dispersion, referred to session 3.2.1.

Figure 3.1 Synthesis procedure for the preparation of PDA-CNTs [4]

3.3 Synthesis method

3.3.1 Basic reactions of polyurethane (PU)

The polymerization of PU is based on nucleophilic addition reactions of isocyanate groups with polyols containing hydroxyl groups. The basic reaction is shown in **Figure 3.2**.

Figure 3.2 Basic reaction of isocyanate chemistry

By changing the moieties in the polyol, the physical properties of PU are able to cover the whole range from rubber to plastic, as shown in **Figure 3.3**. Consequently, PU composites can be tailored to exhibit good elasticity, excellent abrasion resistance and also controllable hardness, leading to their numerous applications, e.g., coatings, adhesives and foams.

Figure 3.3 Preparation of PU by diol and diisocyanate

The moisture in the atmosphere could react with the highly reactive isocyanate groups to produce “urea” and disturb the stoichiometry. The detailed reaction between isocyanate groups and water is given in **Figure 3.4**. Hence, reactants were dehydrated fully prior to the preparation of PU in this project.

Figure 3.4 The side reaction of isocyanate groups with water

3.3.2 Composites with Raw-CNTs

Thermoplastic PU (TPU) and thermoset PU (PU) were enhanced by raw CNTs to compare their comprehensive properties, respectively. Generally, TPU is a class of PU plastic, which is formed by the reaction of diisocyanate with diols. The final TPU consists of linear polymeric chains, which can be melted and dissolved by solvents. Therefore, TPU is popular in the literature, due to its easy handling (i.e., dissolution in solvent and solvent evaporation) and non-interference with the reaction to be studied. [5-7] By contrast, the thermoset type of PU is complicated, since at least one part is multifunctional. As a result, the obtained PU cannot be melted and reformed after curing. Considering this characteristic of thermoset PU, the polyisocyanurate and polyols are typically mixed just before preparation of composites. The stoichiometry of the reaction involved in the cross-linking is vital for determining the properties of the final composite. Thermoset PU has a broad range of industrial applications, such as coating and adhesive. According to literature, raw CNTs exhibit strong adsorption ability [8-10], which potentially disrupt the reaction between isocyanate groups and hydroxyl groups. The preparation of PU/Raw-CNTs composites is illustrated in **Figure 3.5**.

Figure 3.5 Synthesis procedure for the preparation of (a) TPU/Raw-CNTs and (b) PU/Raw-CNTs composites

Additionally, the processing of the composites is important. Therefore, the processing method of thermoset PU was also studied in this project. The detailed method is given in **Figure 3.6**. It is worth noting that the OH/Raw-CNTs composites are the same with those of PU/Raw-CNTs composites. In order to avoid confusion, the specimen was renamed as OH/Raw-CNTs composites.

Figure 3.6 The illustration of PU/Raw-CNTs composites fabrications: NCO/Raw-CNTs composites and OH/Raw-CNTs composites

3.3.3 Composites with PDA-CNTs

The incorporation of PDA on CNTs was mainly to improve the CNTs dispersion and enhance the interfacial interaction between CNTs and matrix. [11-13] Due to the presence of reactive groups containing PDA, the two-step method was used. PDA-CNTs composites were prepared through in-situ polymerization. PDA-CNTs were ultrasonically dispersed in acetone at the concentration of 0.5 mg/ml for 2 h, followed by the addition of predetermined amount of polyisocyanurate. After that, the mixture of polyisocyanurate and PDA-CNTs was continuously stirred at 80 °C for 2 h in nitrogen atmosphere. The obtained mixture was concentrated by rotary evaporation before added into three-neck flask containing the stoichiometric polyol and catalyst. Finally, the PU/PDA-CNTs films were obtained by casting the solution on glass plate and subsequently removing the solvent at 60 °C in vacuum for 24 h.

3.4 Characterization

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was a useful tool for material analysis in the laboratory. It is a simple way to identify and confirm the presence of certain functional groups in a molecule. Mid region ($5000\text{--}400\text{ cm}^{-1}$) in spectrometers is generally used for measurements. A light is generated by a source and then it will be separated into different wavelength by a monochromater. The collection of wavelengths is further selected by a slit, which shines through the sample under testing at any given time. Because of the intrinsic properties of functional groups, the lights with different wavelength would be absorbed according to their chemical properties. The radiation that passes through the sample is collected by a detector, which is reported in the form of an absorption spectrum after processing. [14]

Figure 3.6 The schematic diagram of FTIR principles

In this project, FTIR was used to confirm the modification of CNTs by PDA. The tests were carried out using a Frontier FTIR/NIR spectrometer (PerkinElmer). Before the characterization, the specimens were dried at 60 °C overnight to eliminate moisture. CNTs were uniformly mixed with KBr powder by grinding and pressed to a thin circular plate. A total of 32 scans were taken on each specimen with a resolution of 2 cm⁻¹ between 650 and 4000 cm⁻¹.

3.4.2 Scanning Electron Microscopy (SEM)

SEM can produce the images of a sample by scanning the sample surface with a focused beam of electrons. [15] Its working mechanism is dependent on the interaction of atoms in sample with the irradiated electrons. The different interactions are confirmed by various signals collected by a detector. After the signal processing, the sample surface topography and even composition will be produced in the form of the pictures. The SEM technique can easily achieve resolution of better than 1 nanometer. Due to SEM's working mechanism, the observations have to be conducted in high vacuum, resulting in the high cost and difficulty in operation. In general, high voltage is required to obtain clear pictures, thus, organic samples often suffer damage due to high voltage. Moreover, accumulation of electrostatic charge at the sample surface causes scanning faults or artifacts. Thus, the samples before SEM observation are

usually coated with a thin layer of electrically conductive materials. The most often used coatings are platinum and gold.

Figure 3.7 Schematic of a SEM

In this project, the SEM observation was employed to examine the CNTs dispersion in matrix. The fracture surfaces of composites were investigated by using a field emission-scanning electron microscope (Jeol FESEM 7600F) at 5 kV. Cryo-fracture surface and fracture surface after tensile were investigated, respectively. The cryo-surface fracture surfaces of specimens were prepared by immersing the sample in liquid nitrogen before fracture was obtained. Before the measurements, a layer of platinum coating with a thickness of 20 nm was applied on the fracture surfaces in order to obtain clear images.

3.4.3 Transmission Electron Microscopy (TEM)

TEM was employed to investigate the morphological structure of raw CNTs and PDA-CNTs. The CNTs powder was ultrasonically dispersed in ethanol for 5-10 minutes, and then the CNTs suspension was left standing for 0.5 h.

Specimens were prepared by placing one droplet of the supernatant of CNTs suspension on carbon-coated copper grid and dried at 60 °C for several minutes. The TEM images were recorded on a JEOL 2010 TEM at 200 kV in this project.

3.4.4 Raman spectroscopy

Raman spectroscopy is another useful tool for CNTs researchers, which is employed for the characterization of CNTs products widely, such as basic synthesis, purification and modification of CNTs. Raman spectroscopy is an easy and non-destructive method to characterize CNTs samples, with respect to purity, doping, functionalization, their diameter and chirality distribution, and population of specific species. [16]

CNTs are one-dimensional (1D) materials, leading to the 1D electronic and phonon confinement. These unique confinements result in the unique resonance Raman process. Because of the geometric difference between CNTs and graphite, the resonance effects of CNTs are not only enhanced by their graphite-like (π - π) structure, but highly selective due to their diameter and chirality. Therefore, Raman spectroscopy becomes a structural characterization tool for CNTs.

In this project, multi-walled CNTs was employed as fillers, thus the features of their Raman spectroscopy were investigated. Typically, there are two distinguished peaks exhibiting in Raman spectrum of CNTs. They usually appear at approximately 1350 (D band) and 1570 (G band) cm^{-1} , respectively. [17, 18] The D band is assigned to the A_{1g} breathing mode, attributed to the defects in the curved graphite sheet, amorphous carbon, sp^3 carbon atoms, or other impurities. [19] The G band is associated with the E_{2g} in-plane stretching vibration mode in the basal plane of graphite. The G bands correspond to the crystalline graphitic carbon (C=C) in CNTs. Another characteristic peak at the

higher frequency side of 2700 cm^{-1} is the second harmonic of the D band, referred to as D^* , and is independent of the defect concentration. [20] The ratio of intensity of the D and G bands (I_D/I_G) is one of the most important parameter of CNTs, which is generally used to estimate the relative extent of structural defects in CNTs after treatment. Raman spectroscopy of CNTs before and after treatments was performed at a WITec CRM200 Confocal Raman microscope (488 nm laser) in this project.

3.4.5 Direct Current (DC) Conductivity

The electrical conductivity of composite is very important for the EMI shielding performance, as discussed in chapter 2. The percolation threshold is a useful concept for this type of composites, at which the long-range conductive network forms in bulk composites. Generally, when the filler content is above on percolation threshold, the composites exhibit satisfied EMI shielding properties, because of the presence of conductive network. [21] In this thesis, the electrical conductivity of composites was investigated by resistivity meters supplied by Mitsubishi company. The model of instruments was based on their recommendations according to the electrical conductivity of composites. The recommendations of resistivity meters for the measurements of materials with various resistivity are given in **Figure 3.9**.

Figure 3.8 Recommendations of resistivity meters for the measurements of materials with various resistivities

The used resistivity meters shown in **Figure 3.10** were the models of MCP-HT450 and MCP-T370, respectively. Moreover, the calculation method of resistivity of composites is illustrated in **Figure 3.11** and **Figure 3.12**.

Figure 3.9 The digital photos of resistivity meters (a) for high resistivity (Hiresta series) and (b) for low resistivity (Loresta series)

Figure 3.10 The calculation of surface resistivity and volume resistivity for ring electrode. The RCF is the abbreviation of the term of Resistivity Correction Factor. It is given by the supplier. In this project, the used probe has RCFs 10.09 and RCF_V 0.273, respectively

Figure 3.11 The calculation of surface resistivity and volume resistivity for four-probe electrode

3.4.6 EMI shielding performances

Experimentally, shielding is measured using instrument called network analyzer. Vector network analyzer (VNA) can provide magnitude as well as phases of various signals. The incident and transmitted wave in a two port VNA can be mathematically represented by complex scattering parameters (S-parameters), i.e., S_{11} , S_{21} , S_{22} and S_{12} . These S-parameters are conveniently correlated to power efficiency, i.e., reflectance (R) and transmittance (T), which are further used to calculate the EM shielding effectiveness.

The experimental SE_{Total} , SE_A and SE_R can be achieved from experimental parameters as: [22-24]

$$SE_{Total} = -20 \log_{10}|T| \quad (1)$$

$$SE_A = -10 \log_{10}|1 - R| \quad (2)$$

$$SE_R = -10 \log_{10}|T/(1 - R)| \quad (3)$$

where the reflectance (R), absorbance (A) and transmittance (T) of the EM wave can be determined by s-parameters measurement with the VNA. [25]

Figure 3.12 Schematic of EMI shielding [26]

Moreover, the output attributes of permittivity and permeability are from the input S-parameters by Nicholson-Ross-Weir technique. [27, 28] In this study, the complex permittivity of PU/CNTs composites were measured by VNA. The conversion of permittivity from S-parameter is dependent on the measurement of reflection coefficient (Γ) and transmission coefficient (T) of the material under test.

The deduction by NRW method is shown in the following set of equations:

$$S_{11} = \frac{\Gamma(1-T^2)}{(1-T^2\Gamma^2)} \text{ and } S_{21} = \frac{T(1-\Gamma^2)}{(1-T^2\Gamma^2)} \quad (4)$$

If the S-parameters are extracted from the VNA, these values are simultaneously solved followed by Eq. 24 to give the reflection coefficient as:

$$\Gamma = X \pm \sqrt{X^2 - 1} \quad (5)$$

Of course, the correct root of this equation is found by being applied the condition that $|\Gamma| < 1$, thus the parameter X is obtained as:

$$X = \frac{S_{11}^2 - S_{21}^2 + 1}{2S_{11}} \quad (6)$$

Similarly, the transmission coefficient can be expressed as:

$$T = \frac{S_{11} + S_{21} - \Gamma}{1 - (S_{11} - S_{21})\Gamma} \quad (7)$$

The complex permeability is given by:

$$\mu = \frac{1 + \Gamma}{\Lambda(1 - \Gamma) \sqrt{\frac{1}{\lambda_0^2} - \frac{1}{\lambda_c^2}}} \quad (8)$$

where the parameters that λ_0 and λ_c are free space and cutoff wavelength, respectively, and Λ is given by the equation as: [29, 30]

$$\frac{1}{\Lambda^2} = \left(\frac{\epsilon\mu}{\lambda_0^2} - \frac{1}{\lambda_c^2} \right) = - \left[\frac{1}{2\pi L} \ln \left(\frac{1}{T} \right) \right]^2 \quad (9)$$

Therefore, the permittivity can be expressed as:

$$\epsilon = \frac{\lambda_0^2}{\mu} \left(\frac{1}{\lambda_c^2} - \left[\frac{1}{2\pi L} \ln \left(\frac{1}{T} \right) \right]^2 \right) \quad (10)$$

in which L is the sample length, and theoretically, there are infinite number of roots for Eq. (6) and (7), since the imaginary part of the term $\ln(1/T)$ is related to $i(\theta + 2\pi n)$, in which $n = 0, \pm 1, \pm 2 \dots$.

The schematic of the measurement is shown in **Figure 3.14**.

Figure 3.13 The schematic illustration of EMI shielding tester

The samples were cut into rectangular plates of $25.4 \times 12.7 \times 0.35 \text{ mm}^3$ to fit the waveguide (WR90). For each measurement, 201 data points were collected. And the experimental setup is shown in **Figure 3.15**.

Figure 3.14 The experimental setup for the EMI shielding performance of composites

3.4.7 Tensile test

Mechanical properties of the composites were evaluated by tensile test (Instron 5567). For tensile test, the specimens were punched using ASTM D638-V dog bone die (shown in **Figure 3.16**). The testing film had a gauge of length of 9.53 mm and width 3.52 mm. The crosshead speed was kept at 20 mm/min to measure the stress vs strain behavior of composites. Each composite with varied formulations was tested at least five specimens in order to obtain an average.

Figure 3.15 The sample size of composites for tensile test according to ASTM D 638-V

3.4.8 Differential Scanning Calorimetry (DSC)

DSC technique is a thermoanalytical tool for polymer materials analysis. It monitors the difference in the amount of heat required between sample and reference as a function of temperature, in which both sample and reference are maintained at the same temperature during the measurement. When the polymer occur thermal transition, the certain amount of heat (more or less) will flow to sample, which is defined as exothermic or endothermic. It is widely used in polymer field as a quality control instrument or mechanism study tool, for example, the molecular behavior, curing kinetics, sample purity and so on. [31, 32] The cartoon picture of DSC measurement is given in **Figure 3.17**.

In this study, DSC tests were performed by a TA instrument (Q10). The typical sample weight was 5 mg and studied at a heating rate of 5 °C/min under nitrogen atmosphere.

Figure 3.16 The cartoon picture of DSC measurement

3.4.9 Thermogravimetric Analysis (TGA)

TGA is a technique by monitoring the weight loss of a sample as a function of temperature in a given atmosphere (oxidizing or inert). The information provided by TGA includes that vaporization, adsorption, desorption, decomposition and sublimation. Commonly, TGA technique is used to evaluate the content of materials with different characteristics exhibiting various decomposition temperatures. In some cases, TGA is also employed to study the degradation mechanisms and reaction kinetics. [33, 34] In this project, TGA is used to determine the percentage of PDA on CNTs. A typical specimen weight was 10 mg, placed in a platinum sample pan. Specimens were studied at a heating rate of 10 °C/min under an air atmosphere (balance gas: nitrogen 60 ml/min and sample gas: air 40 ml/min). The TGA instrument is shown in **Figure 3.18**.

Figure 3.17 Instrumentation of TGA

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Chapter 4

Matrix Identification and Processing of Polyurethane Composites

In this chapter, CNTs dispersed in thermoplastic polyurethane and thermoset polyurethane matrix were compared. It was found that thermoset polyurethane exhibited better ability to disperse CNTs than the thermoplastic polyurethane, attributed to two factors, i.e., in-situ polymerization and easy wetting to CNTs surface. For thermoset polyurethane, the effect of sequences of adding CNTs into polyurethane on their dispersion was systematically studied. The relationship between the CNTs dispersion and the EMI shielding effectiveness of the composites was also investigated in this chapter.

4.1 Introduction

Compared to conventional metal-based EMI shielding materials, polymer-matrix composites containing conductive fillers are attractive for the substitution of metal-based shielding materials, arising from their easy processability, low density and corrosion resistance. [1] Attributed to the excellent versatility in selection of monomers from a huge list of polyols, diisocyanate and chain extenders, polyurethanes (PU) are one of most commonly used polymer matrices. [2-4] The properties of PU composites including good elasticity, excellent abrasion resistance and controllable hardness can be achieved by changing polyol moieties alone, which leads to their numerous applications, e.g., coatings, adhesives and foams. It is worth noting that the monomers of diisocyanate exhibit high toxicity and pose serious threat to operators' health. Herein, the polyisocyanurates from trimerization of diisocyanates are developed to replace the diisocyanates as hardener or cross-linker in thermoset coating applications. [5] An isocyanurate ring is created after trimerization, which contains three nitrogen atoms and three carbonyl groups. The introduction of isocyanurate rings is beneficial for the thermal stability and UV resistance of PU materials, [6, 7] leading to the wide spread applications of polyisocyanurate in industry. But, pure PU is insulating and thus transparent to EM waves, which could be modified by the incorporation of conductive fillers.

Carbon-based fillers exhibit promising potential because of their low density, high stability to chemical corrosion, and processing advantages, compared with other types of fillers, e.g., metals and ceramics. [8-17] It is well recognized that the electrical conductivity enhances the EMI shielding effectiveness, and polymer composites with high conductivity generally exhibited superior EMI SE. [18] The high conductivity, high aspect ratio and low cost of multi-walled carbon nanotubes (CNTs) enable composites to easily achieve high

conductivity at low CNTs loading. [19-22] Attributed to these advantages, CNTs act as an ideal option to achieve high performance EMI shielding materials. In order to fully release their potentials, some functional groups are introduced onto CNTs, which could effectively debundle the CNTs agglomerates and create the bridge between tubes and matrix. Unfortunately, the treatments always involve tedious approaches and toxic chemicals. Thus, raw CNTs are more practical for industrial applications.

As mentioned in Chapter 2, the matrix of PU consists of two types, i.e., thermoplastic PU (TPU) and thermoset (PU). In this study, we compared the effect of PU matrices (i.e., TPU and PU) on EMI SE of composites, and also investigated the effect of incorporating sequences of the raw CNTs into the PU matrix on (1) the CNTs dispersion, and (2) the EMI SE of the PU/Raw-CNTs composites. The X band was used in this thesis, which is a segment of the microwave radio frequency region of electromagnetic spectrum. It has wide applications, e.g., radar, space communications, terrestrial communications and networking. It is found that as-received CNTs exhibited obviously different dispersion states in PU matrix by changing the sequence of adding CNTs into the composite, resulting in different EMI SE of PU/Raw-CNTs composites. To the best of my knowledge, this is the first report that the EMI properties are dependent on the processing sequences of CNTs incorporation, and the mechanism for this is systematically discussed.

4.2 Materials and methods

4.2.1 Materials

Thermoplastic polyurethane (TPU, SKYTHANE R180A) was purchased from SK Chemicals, dehydrated in vacuum over at 110 °C overnight before use. Cyclohexanone (ACS reagent, Sigma-Aldrich) and acetone (analytical grade,

Fishier) was dried at least 48 h by 4A molecular sieves before use. For preparation of thermoset PU, the hardener (N3390) used in this study is polyisocyanurate supplied by Bayer Company. Polyol (Capa 3022, Perstorp) with the hydroxyl value of 521 mg KOH/g was dehydrated in vacuum oven at 110 °C overnight before use. Dibutyltin dilaurate (95%, Sigma-Aldrich) as catalyst was used without any purification. The multi-walled carbon nanotubes (CNTs, NC 7000) synthesized by chemical vapor deposition (CVD) were provided by Nanocyl S.A. To be noted that in this thesis, the abbreviation of PU corresponds to the thermoset PU and TPU stands for the thermoplastic PU.

4.2.2 Matrix identification

TPU/Raw-CNTs composites:

Dehydrated TPU pellets were dissolved in cyclohexanone at the concentration of 10 wt%. 0.5 mg/g of raw CNTs were ultrasonically dispersed in acetone for 3 h, a predetermined amount of TPU solution was added into the obtained CNTs suspension, followed by another 1 h ultrasonication. Then, the mixture was concentrated by rotary evaporator before casting. Finally, the viscous mixture was poured into a PTFE mold and left in fumehood overnight to remove the solvent, followed by placing in oven to eliminate the residual solvent at 60 °C for 24 h.

PU/Raw-CNTs composites:

The PU was synthesized by mixing polyisocyanurate and polyol in a molar ratio. The isocyanate index was fixed at 1.2:1 to account for the adverse effect from presence of moisture.

CNTs were ultrasonically dispersed in polyol in the presence of a large amount of acetone (0.5 mg/g) to get a suspension of fully wetted CNTs. Before composite preparation, the CNTs suspension was concentrated by rotary evaporator, followed by the addition of the stoichiometric amounts of the polyisocyanate. Finally, the obtained viscous mixture was poured into a PTFE mold and left in a fumehood overnight to remove the solvent, followed by placing in oven to finish the curing and eliminate the residual solvent at 60 °C for 24 h.

4.2.3 The effect of processing of PU/Raw-CNTs composites on EMI shielding properties

In previous part, the PU/Raw-CNTs composites were fabricated following the conventional procedure described by literatures that the fillers were dispersed in the part of polyol. [23] However, there is limited literature discussing the influence of processing sequence of CNTs on the properties of PU/Raw-CNTs composites. In this section, the processing of PU/Raw-CNTs composites was varied, as shown in **Figure 4.1**.

Figure 4.1 The illustration of PU/Raw-CNTs composites fabrications: (a) NCO/Raw-CNTs composites and (b) OH/Raw-CNTs composites

The procedure for PU/Raw-CNTs composites fabrication was similar to the previously reported work. [24] The CNTs were ultrasonically dispersed in either polyisocyanurate (NCO part) or polyol (OH part) in the presence of a large amount of acetone, in order to get a suspension of fully wetted CNTs. Before the composite preparation, the CNTs suspension was concentrated by rotary evaporator, followed by the addition of stoichiometric amounts of counterpart. Finally, the obtained viscous mixture was poured into a PTFE mold and left in fumehood overnight to remove the residual solvent, followed by placing in oven to finish the curing and eliminate the residue of solvent at 60 °C for 24 h. According to the addition sequences of the two parts of PU, the specimens were designated as NCO/Raw-CNTs X and OH/Raw-CNTs X, in which X stands for the weight percentage of CNTs. It is worth noting that the OH/Raw-CNTs composites are the same with those in **section 4.2.2**. In order to avoid the confusion, the specimen is named as OH/Raw-CNTs composites.

4.2.4 Characterization

CNTs dispersions in matrix were investigated by field emission scanning electron microscope (FESEM) at 5 KV. Thermal behaviors of the composites were examined by differential scanning calorimetry (DSC, Q10, TA Instruments). The DC electrical conductivities of composites with high resistivity and low resistivity were collected with MCP-HT450 and MCP-T370 (Mitsubishi company), respectively. The EMI shielding measurements and complex permittivity of composites were carried out in the frequency range of 8.2-12.8 GHz using a PNA-L Network Analyzer (Agilent N5230A) measurement system. The samples were cut into rectangle plates of 25.4 * 12.7 * 0.35 mm³ to fit the waveguide (WR90). For each measurement, 201 data points were collected. The setup is shown in **Figure 4.2**. Tensile test was conducted to determine the mechanical properties of composites by Instron 5567 with the crosshead speed of 20 mm·min⁻¹. The specimens for tensile tests

were punched using ASTM D638-V dog bone die. Five specimens for each composite were tested in order to obtain an average.

Figure 4.2 ASTM 4935 D99 measurement setup and specimen

4.3 Results and discussion

4.3.1 Matrix identification

The surface morphologies of PU/Raw-CNTs and TPU/Raw-CNTs composites are investigated by SEM (**Figure 4.3**). It is obvious that “island-structures” formed in TPU/Raw-CNTs composites, which was attributed to CNTs aggregation. By contrast, CNTs were uniformly dispersed in PU/Raw-CNTs composites since only the interaction of polymer (TPU chains) wrapping existed in the TPU system. However, in PU system, a two-step dispersion method was employed. Firstly, CNTs were well-wetted by small molecules monomers (i.e., polyol), which could more easily diffuse into CNTs bundles compared with TPU molecules. With the incorporation of polyisocyanurate, the polymer network gradually formed by reaction between NCO groups and OH groups. Thus, the dispersion of CNTs was uniform in PU/Raw-CNTs composites than those in TPU/Raw-CNTs composites.

Figure 4.3 Cryo-fracture surfaces of (a) TPU/Raw-CNTs 5, (b) TPU/Raw-CNTs 10, (c) PU/Raw-CNTs 5 and (d) PU/Raw-CNTs 10

As a consequence, the apparent differences in EMI SE of the composites obtained from the two types of matrices were observed, shown in **Figure 4.4**. It was found that the EMI SE of PU/Raw-CNTs composites were much higher than those of TPU/Raw-CNTs composites. It was attributed to the better dispersion of CNTs in PU/Raw-CNTs composites, shown in **Figure 4.3**. Based on the results obtained so far, it seems that the thermoset type PU has a better processibility for CNT based EMI shielding composites. My studies therefore focused on thermoset polyurethane in the subsequent chapters

Figure 4.4 EMI shielding properties of TPU/Raw-CNTs and PU/Raw-CNTs composites

4.3.2 Microstructure and DC conductivity of PU/Raw-CNTs composites

The comprehensive comparison between TPU/Raw-CNTs composites and PU/Raw-CNTs composites indicated the PU/Raw-CNTs composites with higher EMI SE as a better candidate for the fabrication of EMI shielding material.

By changing the CNTs incorporation sequences, two types of PU/Raw-CNTs composites were prepared (**Figure 4.1**). The CNTs dispersion was observed by SEM. The cryo-fracture surfaces of PU/Raw-CNTs composites are shown in **Figure 4.5**. **Figure 4.5 (a)** and **Figure 4.5 (b)** to illustrate the CNTs dispersions in NCO/Raw-CNTs composites. As seen in **Figure 4.5(a)**, CNTs were dispersed uniformly in matrix at the content of 5 wt%. Uniform dispersion was also observed upon increasing CNTs to 10 wt%. While CNTs aggregates formed obviously in OH/Raw-CNTs composites at the CNTs loading of only 5 wt%, shown in **Figure 4.5(c)** and **Figure 4.5(d)**. Moreover, it was found that compared with OH/Raw-CNTs composites, the CNTs were found to preferentially immerse in PU matrix for NCO/Raw-CNTs composites, indicating that the interaction between CNTs and matrix in NCO/Raw-CNTs composites were stronger than that in OH/Raw-CNTs composites. The observed different dispersions of CNTs in two types of composites were attributed to the different abilities of the two parts of PU towards CNTs wetting, leading to the various dispersion states of CNTs after curing. In the study, CNTs were isolated in organic solvent, following by the addition of one part of PU, i.e., polyisocyanurate or polyols. After that, the mixture of CNTs and monomers was concentrated by rotary evaporator to obtain a viscous mixture, prior to reacting with the other component of the PU (**Figure 4.1**). During the process of concentration, the strong interaction between polyisocyanurate and CNTs promoted the interpenetration of polyisocyanurate into CNTs agglomerates, which formed a homogeneous mixture for composites with well-dispersed CNTs, i.e., NCO/Raw-CNTs composites. On the contrary, CNTs were poorly dispersed in OH/Raw-CNTs composites, which may result from the weak interaction between polyol and CNTs.

Figure 4.5 Surface morphologies of (a) NCO/Raw-CNTs 5, (b) NCO/Raw-CNTs 10, (c) OH/Raw-CNTs 5 and (d) OH/Raw-CNTs 10 composites

The formation of electrical conductive network was influenced by the CNTs dispersion, leading to varied DC conductivity (σ_{DC}) of PU/Raw-CNTs composites. The σ_{DC} of NCO/Raw-CNTs and OH/Raw-CNTs composites as a function of CNTs weight percentages are given in **Figure 4.6**. It was found that the σ_{DC} of OH/Raw-CNTs composites were in the same magnitude of $10^{-6} \text{ S} \cdot \text{m}^{-1}$ below 3 wt% of CNTs loading, while the conductivity of OH/Raw-CNTs 5 displayed a dramatic increase of 7 orders of magnitude (up to $10 \text{ S} \cdot \text{m}^{-1}$), indicating the formation of an interconnected conductive network at 5 wt% of CNTs. The highest conductivity at the magnitude of $10^2 \text{ S} \cdot \text{m}^{-1}$ was obtained by further increasing CNTs loading to 10 wt%. Interestingly, the conductivity of NCO/Raw-CNTs composites increased linearly with the increasing CNTs weight percentages below 10 wt % of CNTs, which could be the increasing connective CNTs network formed by the uniform dispersion. Compared with OH/Raw-CNTs composites, the σ_{DC} of NCO/Raw-CNTs composites were

much lower when at the same CNTs loading. For example, the σ_{DC} of NCO/Raw-CNTs 5 was at the order of $10^{-5} \text{ S}\cdot\text{m}^{-1}$, indicating the absence of conductive network. Literature reports always concluded that better dispersion led to percolation at a lower filler content. The percolation path in NCO/Raw-CNT sample was delayed to a higher CNT content is therefore unique. One possible explanation is the wrapping effect of CNTs by insulating polymer. Continuously increasing CNTs to 10 wt%, the σ_{DC} of $15 \text{ S}\cdot\text{m}^{-1}$ in NCO/Raw-CNTs composites was observed, implying the formation of a conductive network. However, it was still 1 order of magnitude lower than that of OH/Raw-CNTs 10 composites. This means that in NCO/Raw-CNTs composites, the CNTs were wrapped by polymer matrix, which added to extra-resistance for electrons tunnelling. The composites will only become conductive when the CNTs concentration is high enough, and the spacing between CNTs is narrow enough to allow electron movements.

Figure 4.6 The DC conductivity of PU/Raw-CNTs composites

4.3.3 EMI shielding effectiveness of PU/Raw-CNT composites

On the basis of basic plane wave theory and transmission-line theory [25], the total SE of a sample is expressed in decibels (dB), as shown in Eq. (1):

$$SE_{Total} = 10 \log(P_{in}/P_{out}) = SE_A + SE_R + SE_M \quad (1)$$

where P_{in} and P_{out} are the power incident on and transmitted through a shielding material. SE_A , SE_R and SE_M are the absorption loss, reflection loss and multi-reflection loss, respectively.

By definition total SE is:

$$\begin{aligned} SE_{Total} &= 20 \log_{10} \left| \frac{(1 - qe^{-2\gamma t})e^{\gamma t}}{p} \right| \\ &= 20 \log_{10}|e^{\gamma t}| - 20 \log_{10}|p| + 20 \log_{10}|1 - qe^{-2\gamma t}| \\ &= SE_A + SE_R + SE_M \end{aligned} \quad (2)$$

then, the reflection loss, absorption loss and multi-reflection loss are: [26]

$$SE_R = -20 \log_{10}|p| = 20 \log_{10} \frac{|n+1|^2}{4|n|} \quad (3)$$

$$SE_A = 20 \log_{10}|e^{\gamma t}| = 8.686\alpha t \quad (4)$$

$$SE_M = 20 \log_{10} \left| 1 - \frac{(n-1)^2}{(n+1)^2} e^{-2\gamma t} \right| \quad (5)$$

where α , β and γ are defined as following equations, t is the thickness of the shielding material.

$$\alpha = \omega \sqrt{\frac{\epsilon\mu\sqrt{1+\tan^2 \delta \mp 1}}{2}} \quad (6)$$

$$n = \sqrt{\frac{\mu\epsilon\sqrt{1+\tan^2 \delta \pm 1}}{2}} + i \sqrt{\frac{\mu\epsilon\sqrt{1+\tan^2 \delta \mp 1}}{2}} \quad (7)$$

$$\gamma = \omega \sqrt{\frac{\mu\epsilon\sqrt{1+\tan^2 \delta \mp 1}}{2}} + i\omega \sqrt{\frac{\mu\epsilon\sqrt{1+\tan^2 \delta \pm 1}}{2}} \quad (8)$$

The experimental SE_{Total} , SE_A and SE_R can be achieved from experimental parameters as: [10, 27, 28]

$$SE_{Total} = -20 \log_{10}|T| \quad (9)$$

$$SE_A = -10 \log_{10}|1 - R| \quad (10)$$

$$SE_R = -10 \log_{10}|T/(1 - R)| \quad (11)$$

where the reflectance (R), absorbance (A) and transmittance (T) of the EM wave can be determined by s-parameters measurement with the VNA. [14]

In this study, the EMI SE was examined by varying the sequences of CNTs incorporation into composites with two concentrations, i.e., 5 wt% and 10 wt%, respectively. It is very interesting that a distinct EMI SE was observed in **Figure 4.7a**. The OH/Raw-CNTs composites showed higher EMI SE compared with NCO/Raw-CNTs composites at the same CNTs content. For example, the EMI SE of OH/Raw-CNTs 5 and 10 were higher by 4 dB and 7 dB, respectively. The contribution of adsorption and reflection for EMI SE of PU/Raw-CNTs composites is illustrated in **Figure 4.7b**. It was found that both two systems exhibited absorption dominating mechanism to EM wave, which is in agreement with the investigation of shielding mechanism of CNTs based polymeric composites. [27] The SE_R of the two types of composites at the same CNTs loading was similar, and the differences of EMI SE between these two types of composites were mainly caused by SE_A .

Figure 4.7 (a) Total SE and (b) the contribution of absorption and reflection shielding mechanism of PU/Raw-CNTs composites

The EMI SE is closely related to the imaginary part of the complex permittivity (ϵ' and ϵ'') of the shielding materials, given in **Figure 4.8a** and **b**. In general, the ϵ'' of a material can be converted to the AC conductivity (σ_{AC}) by the Eq. (12). It is obvious that OH/Raw-CNTs composites showed higher σ_{AC} than those of NCO/Raw-CNTs composites (**Figure 4.8c**). For example, the σ_{AC} of NCO/Raw-CNTs 5 and 10 were nearly half of those of OH/Raw-CNTs 5 and 10, respectively. Furthermore, based on Eq. (12), the contribution of σ_{AC} for EMI SE is the sum of two parts, i.e., DC conductivity (σ_{DC}) and the conductivity from dielectric polarization (ϵ''_{DP}): [\[18, 29, 30\]](#)

$$\sigma_{AC} = 2\pi f \epsilon_o \epsilon''_i = \sigma_{DC} + 2\pi f \epsilon_o \epsilon''_{(DP)} \quad (12)$$

It is worth noting that the σ_{AC} of NCO/Raw-CNTs 5 was in 10 order of magnitude, significantly higher than its σ_{DC} ($\sim 10^{-5} \text{ S}\cdot\text{m}^{-1}$), indicating that ϵ''_{DP} contribution in NCO/Raw-CNTs composites was dominant. The highest ϵ''_{DP} contribution (i.e., 100 %) was achieved at 5 wt% of CNTs, shown in **Figure 4.8d**. While in the case of OH/Raw-CNTs 5, the contribution of ϵ''_{DP} was obviously lower than those of NCO/Raw-CNTs 5 ($\sim 90\%$). Because the presence of electrically conductive network in OH/Raw-CNTs 5 facilitated the transportation of free electrons when subject to EM wave, resulting in the energy conversion from EM energy to heat energy. Further increased CNTs to 10 wt%, the DP contribution of OH/Raw-CNTs 10 significantly decreased by 60%. The drastic decrease was contributed to increased possibility of CNTs contacting with the increasing CNTs content. By contrast, DP contribution of NCO/Raw-CNTs 10 slightly decreased by 20%, attributed to the presence of insulating polymer matrix between nanotubes. It is suggested that the well-dispersed situation of CNTs was adverse for their contacting, resulting in the dominating loss from dielectric polarization on interfaces between CNTs and matrix.

Figure 4.8 The (a) real part (ϵ') and (b) imaginary part (ϵ'') of complex permittivity of composites, and the contribution of (c) AC conductivity and (d) dielectric polarization to EMI SE

4.3.4 Mechanism

In order to further understand the relationship of CNTs dispersion with EMI SE of PU/Raw-CNTs composites, the average interparticle distance (IPD) theory is introduced here. The composite is divided into cubic elements, in which one conductive unit is in the center. [20, 31] Depending on the dispersion state, the conductive unit could be either single CNT or a bundle of CNTs. Two extreme cases are considered, i.e., all CNTs are perfectly dispersed in matrix and all CNTs exist in the form of aggregates. There is also an intermediate state of CNTs within the polymer matrix that a mixture of individual nanotube and CNTs agglomerates, as shown in **Figure 4.9**.

If CNTs were all in the forms of agglomerates, large amount of CNTs would be required to build up a conductive network. Furthermore, if the CNTs were all perfectly dispersed in PU matrix, the individual CNT would be fully wrapped by insulating polymer, resulting in the barrier of electron tunneling between neighbor tubes. According to the tunneling effect, [32] electron hopping occurs only when IPD is equal to or less than 10 nm, which results in a sharp increase of electrical conductivity of the composites. In this study, the IPD (d) is the distance between each conductive unit. By combining the SEM images and electrical conductivities of PU/Raw-CNTs composites, the NCO/Raw-CNTs composites were classified into the nearly perfectly dispersed state, while CNTs dispersed in OH/Raw-CNTs composites were in the form of individual CNTs and agglomerates.

Figure 4.9 Cartoons of CNTs reinforced polymer composites containing various dispersed CNTs

Moreover, CNTs within matrix associated with the surrounding insulating polymer could be described as equivalent circuits of capacitors and resistors by Maxwell-Wagner model, shown in **Figure 4.9**. [33-35] If the IPD is larger than 10 nm, the capacitors could be viewed as “open circuits”, leading to non-

conductive property under direct electrical field (e.g., NCO/Raw-CNTs 5). However, when the alternative electrical field with high frequency is applied, the capacitors become “short circuits”, resulting in a conductive property. Therefore, NCO/Raw-CNTs 5 with well-dispersed CNTs exhibited electrical insulating property under direct electrical field, while became conductive under alternative EM field. Continuously increasing CNTs to 10 wt%, the σ_{DC} of NCO/Raw-CNTs 10 jumped to $15 \text{ S} \cdot \text{m}^{-1}$, but still lower than that of OH/Raw-CNTs 10 because of the presence of insulating polymer in the transportation paths of electrons, shown in **Figure 4.9**. Meanwhile, the presence of CNTs agglomerates imparted the extremely high conductivity in localized scale in OH/Raw-CNTs composites, acting as EM wave absorbing units to enhance the EMI SE, as shown in EMI SE_A results (**Figure 4.7b**). However, poor dispersion of CNTs was adverse for the composites fabrication, resulting in cracks during the process of curing. When the CNTs aggregation occurred, solvent evaporation followed a tortuous path. The mechanism of crack formation in composites with poorly dispersed CNTs is proposed in **Figure 4.10**.

Figure 4.10 The proposed mechanism of crack formation

4.3.5 Thermal behaviors and mechanical properties of PU/Raw-CNTs composites

The changes in dispersion states of CNTs in composites could also be evaluated by their varied thermal behaviors. The DSC curves are given in **Figure 4.11**. **Table 4.1** summarizes the DSC results of two types of PU/Raw-CNTs composites with different CNTs loadings. It was clearly seen that all composites showed decreased glass transition temperatures (T_g) with the CNTs incorporation, compared with neat PU. This result could be contributed to the disruption of reaction between NCO groups and OH groups by CNTs incorporation and the absence of chemical bonding between CNTs and matrix. Generally, T_g of polymer composites are mainly ascribed to the free volume and the confinement of polymer chains. [36] In PU systems, two T_g should be taken into account because of phase separations, i.e., T_g from soft segments and T_g from hard segments. As discussed before, CNTs were poorly dispersed in OH/Raw-CNTs composites. This may be due to the unfavorable interactions between hydrophilic OH part and hydrophobic CNTs, resulting in the increased free volume for soft segments. Thus the T_g of soft segments in OH/Raw-CNTs were much lower than those in NCO/Raw-CNTs composites. On the contrary, in NCO/Raw-CNTs composites, CNTs preferentially interacted with polyisocyanurate, leading to the stronger interaction with hard segments and less disruption to soft segments caused by CNTs incorporation. Therefore, the T_g of soft and hard segments in NCO/Raw-CNTs composites were higher than those in OH/Raw-CNTs composites, respectively.

Figure 4. 11 The DSC curves of of PU/Raw-CNTs composites

Table 4.1 The thermal behaviors of PU/Raw-CNTs composites

Samples	Filler content / wt%	T_g / °C	
		T_g (soft)	T_g (hard)
Neat PU	0	9	87
NCO/Raw-CNTs 5	5	-7	69
OH/Raw-CNTs 5	5	-20	46
NCO/Raw-CNTs 10	10	0	82
OH/Raw-CNTs 10	10	-7	53

In general, the modulus of composites would be enhanced by the introduction of CNTs attributed to their high modulus. [37] This case is more complex as, in addition to the mechanical reinforcement effect, the CNT may have indirectly affected the crosslinking chemistry by affecting stoichiometry ratio of reactive functional groups. The polyisocyanurate in PU matrix acted as hardener, which was responsible for the modulus enhancement. Hence, the contribution of the strong interaction of CNTs with polyisocyanurate deteriorated the mechanical property of composites due to the absence of chemical bonding, although it could facilitate the CNTs dispersion. The mechanical properties of the two

types of PU/Raw-CNTs composites were investigated by tensile tests. The detailed Young's moduli are displayed in **Figure 4.12**. It was found that the disruption to stoichiometry of PU reaction acts as dominating factor at high CNTs loading, while CNTs dispersion determined the mechanical property of composites at low CNTs loading.

Figure 4.12 Young's moduli of PU/Raw-CNTs composites

4.4 Conclusions

In summary, the effect of the sequences of CNT incorporation into two-part PU was systematically studied. It was found that the CNTs dispersion states were varied by simply changing the processing sequences. The formation of DC conductive network was delayed obviously in the NCO/Raw-CNTs composites with well-dispersed CNTs, indicating that polyisocyanurate exhibited stronger interaction with as-received CNTs. As a consequence, EMI SE of the NCO/Raw-CNTs composites was decreased compared with OH/Raw-CNTs composites with poorly dispersed CNTs. The contribution for EMI SE of NCO/Raw-CNTs composites was mainly from dielectric polarization, and that of conductive network was negligible; on the contrary, electrical conductive network performed a remarkable effect for OH/Raw-CNTs composites,

resulting in the higher EMI SE. Therefore, it is suggested that DC conductive network is not the only scientific criterion for EMI SE, which is also dependent on the intrinsic conductivity of CNTs themselves. Furthermore, it is suggested by this study that well-dispersed CNTs has high electrical resistance, associated with good EMI SE, is possible to be obtained by simply changing the processing sequences.

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Chapter 5

The Study of CNTs Dispersion by Electromagnetic Signals

This is the first time understanding on oscillation of the permittivity curves of composites. In this study, three theoretical models were employed to explain the complex permittivity of composites and the resonance phenomenon of conductive fillers in polymer matrix. The oscillation of the dielectric permittivity curves resulting from the aggregation of fillers was used to evaluate fillers dispersion state. This developed method was verified by several cases, e.g., composites prepared by different processing methods, composites contained fillers dispersed by various surfactants and composites filled by various dimensional fillers, i.e., 1D, 2D and 0D. It was found that this method could be employed to not only distinguish the efficiency of surfactants, but measured the maximum loading of filler in the same dispersion state.

5.1 Introduction

After CNTs were first discovered by Iijima [1], an enormous amount of research into CNTs applications has been done, arising from their extremely high modulus [2, 3], ballistic electrical transport [4-6] and thermal transport [7, 8]. These exceptional intrinsic characteristics make them an ideal candidate to enhance the properties of host matrices and further exploit their special properties. Despite their great potential, progress in balancing between dispersion and comprehensive properties has proved difficult, since the most challenging issue is to fully isolate individual nanotubes in the matrices [9]. The increasing demand for fabrication of composites with well-dispersed CNTs has triggered the development of CNTs dispersion techniques [10-12].

Unfortunately, the observation of CNTs dispersion in matrices till now is still very much limited to macroscopic investigation which mainly relies on the SEM and TEM. [13-22] Additionally, the specimen preparation of SEM and TEM is destructive, complicated and non-representative. Another drawback of using SEM and TEM is the difficulty of evaluating dispersion at high filler loading, as the filler cannot be distinguished as being individually dispersed or aggregated by observation. All of those restrict the industrial applications of SEM and TEM.

As discussed in pervious chapters, it was found that CNTs are good candidates for EMI shielding applications. The shielding mechanism is dependent on the conductivity of CNTs themselves as well as the conductive network of CNTs formed in the bulk material. It is also found that it is not easy to compare CNTs dispersion in composites for EMI shielding application at high CNTs loading. Considering such this situation, the evaluation of CNTs dispersion would be seriously influenced by scanning spot, magnification, and cross section, sometimes resulting in non-representative conclusions.

It is reasonable to assume that composites with different dispersion states endow various electrical properties and EMI shielding performances, which was proved in chapter 4. Moreover, the complex permittivity of composites was determined by the CNTs dispersion, which further influenced the oscillation of ϵ' (or ϵ'') curves, shown in **Figure 4.8a** and **b**.

For a long time, there has been an interest in “noise” investigation, and noise measurement or diagnostics have already been proven as an useful method for various applications, e.g., electrochemical application for evaluation of corrosion behavior for organic coatings [23], study of disordered materials [24], diagnostics of PN junctions [25, 26] and optocouplers with phototransistors [27]. These successful applications offer the possibility to monitor and evaluate the CNTs dispersion by using EM field.

Herein is reported a new method based on several classical models (i.e. Lorentz-Drude, Pendry and Maxwell-Wagner) for the evaluation of CNTs dispersion on a macroscopic scale, which is non-destructive and easy to use. The principle is based on the sensitivity of electrical resonance to external EM field, which is attributed to the hyperconjugation phenomenon of CNTs. One of the most attractive parameters is the dielectric permittivity (the real part of complex permittivity).

Briefly, the complex permittivity is described by Lorentz-Drude model [28-30],

$$\epsilon = 1 + \sum_{j=0}^k \frac{f_j \omega_p^2}{\omega_{oj}^2 - \omega^2 - j\gamma_j \omega}, \text{ where } \omega_p \text{ is the plasma frequency } (\omega_p^2 = \frac{Ne^2}{\epsilon_0 m_e}),$$

ω_{oj} is the resonance frequency, k is the number of oscillators with resonant frequency ω_{oj} , and strength f_j . According to the Lorentz-Drude model, it is found that complex permittivity is frequency-dependent, and determined by the plasma frequency of fillers. It must be noted that plasma frequency is an intrinsic property of materials, but it is affected by the dispersion state of fillers since the effective mass and concentration of electrons is determined by the 3D

network of filler described by Pendry's model [31, 32]. Dilution of the CNTs would result in reduced density and increased effective mass of active electrons in CNTs, leading to the ω_p shifted to a lower frequency range [33]. Moreover, CNTs in polymer could be described by Maxwell-Wagner model of two layer capacitor and its equivalent circuit (**Figure 5.1**), which is widely used in CNTs/polymer composites [34-36]. Different CNTs aggregates lead to different plasma frequencies of CNTs, corresponding to specific signals (resonance frequency) when subject to EM field. The more fluctuated permittivity curves, the more divergent dispersion status in CNTs system.

All these theories are used as theoretical basis to discuss the CNTs dispersion in this chapter. And the detailed introduction on these theories will be given later. As far as can be determined, this is the first attempt time to be made to quantify the oscillation of dielectric permittivity curves of composites to discuss the CNTs dispersion. In this study, the specimens were measured in X-band range (8.2-12.4 GHz) of EM waves. 201 data points were collected from Vector Network Analyzer, in which every point was viewed as a response of CNTs inside composites to EM field in the range of testing frequency.

Figure 5.1 (a) Theoretical model of Maxwell-Wagner two layer capacitor and its equivalent circuit, and the equivalent circuits of composites at (b) uniform CNTs dispersion and (c) poor CNTs dispersion. R is the resistivity of single nanotube and C_p is capacitance of insulating polymer outside CNT, respectively. R_i ($i=1, 2, 3, 4, 5, \dots$) correspond to the resistivity of CNTs agglomerates with various amount of nanotubes

5.2 Materials and methods

5.2.1 Materials

The multi-walled carbon nanotubes (CNTs, Nanocyl™ NC 7000, containing 10 wt% of metal oxide residue as catalyst), polyvinyl pyrrolidone (PVP, Mw ~630 000, TCI), dibutyltin dilaurate (Sigma-Aldrich), dimethylformamide (DMF, anhydrous, Aesar), span® 80 (Sigma-Aldrich), triton X-100 (Sigma-Aldrich) and polyisocyanurate (N3390, Bayer Company) were used as received. Thermoplastic polyurethane (TPU) pellets (SK R180A) and polyol (Capa 3022, Perstorp) were dried in a vacuum oven at 110 °C overnight before use.

Cyclohexanone (ACS reagent, Sigma-Aldrich) and analytical grade acetone (Fisher) was dried for at least 48 h by 4A molecular sieves before use.

5.2.2 Preparation of PU/Raw-CNTs composites

The preparation procedure followed the method described in Chapter 4.2.3. The procedure of PU/Raw-CNTs composites fabrication was similar with the reported work. [37] The CNTs were ultrasonically dispersed in either polyisocyanurate (NCO part) or polyol (OH part) at the presence of large amount of acetone, in order to get a suspension of fully wetted CNTs. Before the composite preparation, the CNTs suspension was concentrated by rotary evaporator, followed by the addition of stoichiometric amounts of counterpart. Finally, the obtained viscous mixture was poured into a PTFE mold and left in fumehood overnight to remove the residual solvent, followed by placing in oven to finish the curing and eliminate the residue of solvent at 60 °C for 24 h. According to the addition sequences of the two parts of PU, the specimens were designated as NCO/Raw-CNTs X and OH/Raw-CNTs X, in which X stands for the weight percentage of CNTs.

5.2.3 Preparation of thermoplastic polyurethane (TPU)/surfactant-CNTs composites (i.e., PVP, Span® 80 and Triton X-100)

In this part, TPU was used to avoid the interferences of chemical stoichiometry in matrix caused by the incorporation of surfactants. CNTs were added into acetone and ultrasonically dispersed for 1 h. Then, certain amount of surfactant (weight ratio of CNTs and surfactant was controlled at 1:1 in this study) was incorporated into CNTs suspension followed by the addition of 10% TPU in cyclohexanone solution. The TPU/surfactant-CNTs solution was further ultrasonically mixed in ultrasonic bath at room temperature. Before the film preparation, the TPU/surfactant-CNTs solution was concentrated by rotary

evaporation in order to get a viscous solution. The viscous solution was poured into a PTFE mold and dried at 80 °C in an oven to eliminate solvent completely.

5.2.4 The verification of the new method by 0D and 2D fillers

PU/Carbon black composites

The carbon blacks were ultrasonically dispersed in polyol at the presence of large amount of acetone. Before the composite preparation, the carbon black suspension was concentrated using a rotary evaporator, followed by the addition of stoichiometric amounts of polyisocyanurate. Finally, the obtained viscous mixture was poured into a PTFE mold and left in fumehood overnight to remove the residual solvent, followed by placing in oven to finish the curing and eliminate the residue of solvent at 60 °C for 24 h. The content of carbon black was controlled by loading different amounts of carbon black.

PU/reduced graphene oxide (rGO) composites

Preparation of GO and rGO

Modified Hummer's method [38] and [39] was used to prepare GO in this study. Natural flake graphite (2.5 g) with sodium nitrate were mixed in an ice bath at the presence of 120 ml concentrated H₂SO₄. Then 15 g KMnO₄ was added into the above slurry five times, in which each time 3 g KMnO₄ was added. After that, the mixture was continuously stirred for 6 hours at 35 °C, followed by careful addition of 150 ml deionized (DI) water. The diluted suspension was maintained for 15 min at 90 °C, and then was poured into a beaker containing 700 ml DI water. 60 ml H₂O₂ was further added to purify the obtained GO, followed by the complete washing by diluted hydrochloric, and DI water till the

pH value of supernatant was close to 7. The purified GO was dried by freeze dryer for 48 h.

Chemical reduction method was employed to prepare rGO. The detailed procedure was briefly introduced as follow. [40] 100 mg GO was dispersed in DI water, and exfoliated by 1 h ultrasonication. The suspension was mixed with 80 ml hydrazine solutions used as reducing agents. Then the pH of the suspension was tuned by ammonia solution. After that, the mixture was stirred for several minutes to get a homogeneous suspension, followed by further stirring at 95 °C for 2 h. The chemically rGO was collected by repeat filtration and washing for 3-4 times. Finally, the obtained rGO was dried for 48 h by freeze dryer.

PU/rGO composites preparation

The rGO were ultrasonically dispersed in polyol at the presence of large amount of acetone. Before the composite preparation, the rGO suspension was concentrated by rotary evaporator, followed by the addition of stoichiometric amounts of polyisocyanurate. Finally, the obtained viscous mixture was poured into a PTFE mold and left in fumehood overnight to remove the residual solvent, followed by placing in oven to finish the curing and eliminate the residual solvent at 60 °C for 24 h. The content of rGO was controlled by loading different amount of rGO.

5.2.5 Characterization

The visualization of CNTs dispersion in PU was realized by field emission scanning electron microscope (FESEM) at 5 KV. Before the observation, the cryo-fracture surfaces were coated a layer of Pt with a thickness of 20 nm.

The dielectric properties were measured in the frequency range of 8-12 GHz using a PNA-L Network Analyzer (Agilent N5230A) measurement system. The samples were cut into rectangular plates of 25.4 * 12.7 * 0.35 mm to fit the waveguide sample holder. For each sample, 201 data points were taken. It should be noted that all 201 data points were analyzed in this study. The setup is shown in **Figure 5.2**.

Figure 5.2 ASTM 4935 D99 measurement setup and specimen

5.3 Theoretical background

5.3.1 Lorentz-Drude Model

Complex permittivity

Lorentz model is useful for the explanation of dielectric properties of materials. Typically, the electrons bounded or lattice will interact with EM field, resulting in the oscillation around their equilibrium position, as shown in **Figure 5.3**. From quantum mechanical point of view, these changes of energy could be expressed as the system transiting from one energy state to another one.

Figure 5.3 The cartoon illustration of the harmonic oscillator

The oscillation is approximated by a damped oscillator. As shown in **Figure 5.4**. Generally, the damping force exists in various situations of collisions, such as electron-electron interaction, electron lattice interaction, etc. Thus, three forces to be considered in an oscillator, i.e., driving force, spring force and damping force.

In simple case that the spring oscillator is undriven and undamped, Hooke's Law and Newton's 2nd Law are the only forces controlling the motion of masses. But, the damping force is negligible in real case as mentioned. In order to simply the deduction, we assume that the type of damping is linearly proportional to the velocity of the mass. Then, the total expression is:

$$m \frac{d^2 y}{dt^2} = F_{driving} + F_{damping} + F_{spring} = F_{driving} - m\gamma \frac{dy}{dt} - m\omega_0^2 y \quad (1)$$

The driving force will be rewritten as:

$$F_{driving} = m \frac{d^2 y}{dt^2} + m\gamma \frac{dy}{dt} + m\omega_0^2 y \quad (2)$$

where the ω_0 is the natural frequency and γ is the damping factor.

If the solid harmonics placed in electric field (varied in time with angular frequency), the displacement in y direction will be expressed as:

$$y(t) = Ae^{-i\omega t} \quad (3)$$

Moreover, the driving force will be:

$$F_{driving} = -eE_0 e^{-i\omega t} \quad (4)$$

When substituting Eq. (3) and (4) to (2) to solve A, one gets

$$A = -\frac{eE_0}{m} \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (5)$$

and

$$y(t) = \frac{eE_0}{m} \frac{e^{-i\omega t}}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (6)$$

By the definition of polarization of an oscillator in electrical field, the total polarization per unit is written as:

$$P = N_0 e y(t) = \frac{N_0 e^2 E_0}{m} \frac{e^{-i\omega t}}{\omega_0^2 - \omega^2 - i\gamma\omega} = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \epsilon_0 E \quad (7)$$

in which is introduced a new term (plasma frequency), which will be discussed later in detail,

$$\omega_p^2 = \frac{N_0 e^2}{m \epsilon_0} \quad (8)$$

Figure 5.4 Lorentz oscillator model

Then the concept of polarization of an oscillator is transferred to the case of dipole, the polarization can be expressed as:

$$P = \chi \varepsilon_0 E \quad (9)$$

in which the χ is

$$\chi = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (10)$$

The complex permittivity is

$$\varepsilon = 1 + \chi = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} = \varepsilon_r + i\varepsilon_i \quad (11)$$

By splitting the two parts of complex permittivity, i.e., real part and imaginary part, one gets:

$$\varepsilon_r = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (12)$$

$$\varepsilon_i = \frac{\omega_p^2\gamma\omega}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2} \quad (13)$$

in which the ω_0 is the resonance frequency of the harmonic oscillator. In the quantum mechanics, the resonance frequency is described as the energy difference between the final and the ground states.

For metal, the free electrons are not bonded to ions, meaning that no spring forces exist, thus the resonance frequency equals to zero, the complex permittivity becomes

$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \quad (14)$$

$$\varepsilon_i = \frac{\omega_p^2\gamma}{\omega(\omega^2 + \gamma^2)} \quad (15)$$

So far, only one simply harmonic oscillator is discussed. If multiple resonances are involved at a macroscopic level, the complex permittivity can be expressed as:

$$\epsilon = 1 + \sum_{j=0}^k \frac{f_j \omega_p^2}{\omega_{oj}^2 - \omega^2 - j\gamma_j \omega} \quad (16)$$

where ω_p is the plasma frequency ($\omega_p^2 = \frac{Ne^2}{\epsilon_0 m_e}$), ω_{oj} is the resonance frequency, k is the number of oscillators with resonant frequency ω_{oj} , and strength f_j .

Plasma frequency

In plasma physics, plasma frequency is the time-scale fundamental concept. For any material, there is a different plasma frequency. As stated, plasma is ionized, electrically conducting gas of charged particles. Many of plasma effects take place collectively, such as cool effects (polar light). One of the effects of plasma is plasma oscillation.

Ideally, the electric fields of the electrons and nuclei exhibit the neutralized state in equilibrium; however, the equilibrium is difficultly maintained.

Instead of dealing with the individual motion of electrons and nuclei, the center of mass of the nuclei and the center of mass of the electrons are considered because of their chaotic states. They tend to shift and move chaotically, but a Coulomb force between them tries to restore their position, which initiates an oscillatory behavior. The frequency at which these oscillations resonate is defined as the plasma frequency.

According to the Eq. (8), it is found that the plasma frequency is proportional to the electron density. And it can be calculated for any materials if the density is given. It is worth noting that the plasma frequency for “non-plasma” material

stands for the natural collective oscillation frequency of a “sea” of electrons (i.e., electron cloud) in material, rather than that of individual dipoles.

The plasma frequency of metallic thin wires was discussed by Pendry, [31, 32] in which the electromagnetic response of thin wires was based on the 3D network of thin wires shown in **Figure 5.5**. Three independent investigations including analytic theory, computer simulation and experiments on the proposed model structure were employed to discuss the properties of structures from 3D continuous thin wires.

Figure 5.5 A periodic structure of thin wires infinitely arranged in cubic lattice. The value of a and r might be a few millimeters and micrometers, respectively

Constraining electrons to transport along the thin wires results in two consequences, i.e., reduced average electron density and increased effective mass of electrons. [31] These two changes result in the decreased plasma frequency, according to Eq. (8). In addition, based on Pendry’s calculation, the plasma frequency can also be rewritten as:

$$\omega_p^2 = \frac{N_{eff}e^2}{m_{eff}\epsilon_0} = \frac{2\pi c_0^2}{a^2 \ln(a/r)} \quad (17)$$

where c_0 is the velocity of light in free space.

It can be concluded that more diluted thin wires, less plasma frequency exhibited in system.

5.3.2 Maxwell-Wagner model

A well-known prototype for a simple analysis of the interfacial polarization is Maxwell-Wagner model. This model is established to investigate inhomogeneous materials, e.g., suspensions, colloids, phase separated polymers, or crystalline polymers. [41] The double-layers structure is shown in **Figure 5.6**.

Figure 5.6 Maxwell-Wagner two-layer structure and its equivalent circuit

Each layer of material with thickness (d) has its electric permittivity (ϵ) and conductivity (σ). The permittivity of composite material containing these two layers of materials is obtained from literature. [35, 42-44]

The complex permittivity is written,

$$\epsilon = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + j\omega\tau} - j \frac{\sigma}{\omega} \quad (18)$$

in which

$$\epsilon_{\infty} = \frac{(d_1 + d_2)\epsilon_1\epsilon_2}{(d_1\epsilon_2 + d_2\epsilon_1)\epsilon_0} \quad (19)$$

$$\epsilon_s = \frac{d_1 + d_2}{\epsilon_0} * \frac{(\epsilon_1 d_1 \sigma_2^2 + \epsilon_2 d_2 \sigma_1^2)}{(\sigma_1 d_2 + \sigma_2 d_1)^2} \quad (20)$$

$$\sigma = \frac{(d_1 + d_2)\sigma_1\sigma_2}{(d_1\sigma_2 + d_2\sigma_1)} \quad (21)$$

$$\tau = \frac{\varepsilon_1 d_2 + \varepsilon_2 d_1}{\sigma_1 d_2 + \sigma_2 d_1} \quad (22)$$

Additionally, the relative properties of two layers have the relationship as:

$$\frac{R_2}{R_1} = \frac{\sigma_1 d_2}{\sigma_2 d_1} \quad \frac{C_2}{C_1} = \frac{\varepsilon_2 d_1}{\varepsilon_1 d_2} \quad (23)$$

In our study, the interfaces are created by the insulating polymer and the CNTs. Through comparing with their relative properties, i.e., resistivity and capacitance, the equivalent circuit is simplified as **Figure 5.1a**. In other words, the CNTs can act as a resistor. Furthermore, the CNTs also perform as thin wire, due to their high aspect ratio (>100) satisfying the requirement of thin wire. [31, 45] In summary, it is reasonable that evaluating CNTs dispersion by discussing the oscillation of dielectric permittivity of composites in the range of testing frequency. As shown in **Figure 5.7**, every correlation was strongly supported by related theory. It could be clearly seen that the complex permittivity values of the CNTs composites were closely related to their dispersion in matrix.

Figure 5.7 The flow chart of the development of this method

5.3.3 Nicholson-Ross-Weir (NRW) technique

Experimentally, shielding is measured using instrument called network analyzer. Vector network analyzer (VNA) can provide magnitude as well as phases of various signals. The incident and transmitted wave in a two port VNA can be mathematically represented by complex scattering parameters (S-parameters), i.e., S_{11} , S_{21} , S_{22} and S_{12} . These S-parameters are conveniently correlated to power efficiency, i.e., reflectance (R) and transmittance (T), which are further used to calculate the EM shielding effectiveness.

Moreover, the output attributes of permittivity and permeability are from the input S-parameters by Nicholson-Ross-Weir technique. [46, 47] In this study, the complex permittivity of PU/CNTs composites was measured by VNA. The conversion of permittivity from S-parameter is dependent on the measurement of reflection coefficient (Γ) and transmission coefficient (T) of the material under test.

The deduction by NRW method is shown in the following set of equations:

$$S_{11} = \frac{\Gamma(1-T^2)}{(1-T^2\Gamma^2)} \text{ and } S_{21} = \frac{T(1-\Gamma^2)}{(1-T^2\Gamma^2)} \quad (24)$$

If the S-parameters are extracted from the VNA, these values are simultaneously solved followed by Eq. (24) to give the reflection coefficient as:

$$\Gamma = X \pm \sqrt{X^2 - 1} \quad (25)$$

Of course, the correct root of this equation is found by applying the condition that $|\Gamma| < 1$, thus the parameter X is obtained as:

$$X = \frac{S_{11}^2 - S_{21}^2 + 1}{2S_{11}} \quad (26)$$

Similarly, the transmission coefficient can be expressed as:

$$T = \frac{S_{11} + S_{21} - \Gamma}{1 - (S_{11} - S_{21})\Gamma} \quad (27)$$

The complex permeability is given by:

$$\mu = \frac{1 + \Gamma}{\Lambda(1 - \Gamma) \sqrt{\frac{1}{\lambda_0^2} - \frac{1}{\lambda_c^2}}} \quad (28)$$

where the parameters that λ_0 and λ_c are free space and cutoff wavelength, respectively, and Λ is given by the equation as: [48, 49]

$$\frac{1}{\Lambda^2} = \left(\frac{\epsilon\mu}{\lambda_0^2} - \frac{1}{\lambda_c^2} \right) = - \left[\frac{1}{2\pi L} \ln \left(\frac{1}{T} \right) \right]^2 \quad (29)$$

Therefore, the permittivity can be expressed as:

$$\epsilon = \frac{\lambda_0^2}{\mu} \left(\frac{1}{\lambda_c^2} - \left[\frac{1}{2\pi L} \ln \left(\frac{1}{T} \right) \right]^2 \right) \quad (30)$$

in which L is the sample length, and theoretically, there are infinite number of roots for Eq. (6) and (7), since the imaginary part of the term $\ln(1/T)$ is related to $i(\theta + 2\pi n)$, in which $n = 0, \pm 1, \pm 2 \dots$.

5.4 Results and discussion

5.4.1 Changing the sequence of adding CNTs into matrix

It has been proven that simple alternating sequences of CNTs incorporation into PU matrix resulted in differently dispersed CNTs in matrix. In order to verify this new method, oscillation of real part of the permittivity curves of two composite systems with different CNT contents (i.e., 5 and 10 wt %) were examined. It was found that polyisocyanurate exhibited higher efficiency to disperse CNTs than polyol, resulting in the better dispersed CNTs in NCO/Raw-CNTs composites. **Figure 5.8a** shows the dielectric permittivity at the whole range of frequency. Real permittivity of NCO/Raw-CNTs composites was higher compared with that of OH/Raw-CNTs, accounting for the formation of more interfaces in NCO/Raw-CNTs composites. The real part of permittivity

of PU/CNTs composites depends on the configuration [50], which is proportional to the amount of charges stored on the surface. The more interface created, the higher real permittivity. Hence, there were more interfaces being created in NCO/Raw-CNTs composites. This conclusion is consistent with SEM pictures in chapter 4.

Moreover, it was found that the curves of NCO/Raw-CNTs were much smoother than those of OH/Raw-CNTs. The quantitative illustration is shown in **Figure 5.8b**. The oscillation of complex permittivity could be quantified by calculating the standard deviation of permittivity at the range of frequency, in which 201 data points were employed. It was found that the standard deviations of dielectric permittivity for the two types of composites tested were obviously different, and the composites with better dispersed CNTs showed smaller standard deviation.

Figure 5.8 Real permittivity of NCO/Raw-CNTs composites and OH/Raw-CNTs composites

5.4.2 The effect of surfactants incorporation on CNTs dispersion

To further examine the accuracy and sensitivity of this method, several commonly used surfactants which could facilitate CNTs dispersion were employed. In this part, thermoplastic PU (TPU) was chosen as matrix. The calculated real permittivity followed the same method was reported in **Figure 5.9**, exhibiting the dispersion efficiencies of PVP, Span 80 and Triton X-100, respectively. It is expected that the utilization of surfactants would enhance the CNTs dispersion, the dispersion mechanism has been comprehensively discussed in literatures [10, 11, 51]. The decreased standard deviation of real permittivity obtained by using surfactants was consistent with expectation, which strongly supported the hypothesis made that evaluation of CNTs dispersion can be performed by this method.

Figure 5.9 Real permittivity of TPU/surfactant-CNTs composites

As supported by SEM observations, the CNTs were dispersed more uniformly with the aid of surfactants, given in **Figure 5.10**. With the incorporation of surfactants, the CNTs aggregates found in TPU/Raw-CNTs composites size decreased following the sequences of Triton-100, PVP and Span 80,

respectively. This trend of the effectiveness of surfactants on CNTs dispersion was consistent with that of standard deviations of the real part of the permittivity of TPU/CNTs composites (**Figure 5.9**).

Figure 5.10 Cryo-fracture surfaces of (a) TPU/Raw-CNTs 5, (b) TPU/PVP-CNTs 5, (c) TPU/Span 80-CNTs 5 and (d) TPU/Triton 100-CNTs 5 composites

5.4.3 The maximum loading of CNTs

Based on the previous hypothesis, under the same dispersion state, ϵ' of composites would increase gradually with increasing CNTs loading while the standard deviation of ϵ' should be the same. However, it was impossible to obtain a series of composites with the same CNTs dispersion state when the CNTs concentration is increased. The practical situation should be that the CNTs gradually aggregate with the increased CNTs loading. Thus the standard deviation of ϵ' should increase following a specific function of CNTs contents.

In this study, it is assumed that if the standard deviation is not in the fitting function, which means that the dispersion state of CNTs becomes serious and CNTs cannot be dispersed well by the particular dispersion method used.

With the above assumption, a series of NCO/Raw-CNTs were prepared. The respective standard deviations of ϵ' in composites increased gradually with increasing CNTs contents. The fitted function is given in **Figure 5.11**. The first two points (i.e., neat PU and NCO/Raw-CNTs 0.5) were excluded from the fitting, since they were nearly the same. It was attributed to the contribution of polyisocyanurate to CNTs dispersion, resulting in the perfect dispersion of CNTs at the loading of 0.5 wt%. Moreover, the value of NCO/Raw-CNTs 10 was also not included in the curve of the function vs CNTs contents, because the rule of fitting was to plot a curve to include as many points as possible. By employing the fitted equation, the theoretical standard deviation of NCO/Raw-CNTs 10 was calculated around 11.61, much lower than the experimental value (i.e., 16.2), indicating the 10 wt% of CNTs was already beyond the ability of polyisocyanurate to CNTs dispersion. Thus, it can be concluded that this method can also be employed to explore the maximum loading of CNTs.

Figure 5.11 (a) Real permittivity and (b) standard deviation of NCO/Raw-CNTs composites. The red star is the theoretical standard deviation of NCO/Raw-CNTs 10, while the orange heart are the experimental standard deviations of OH/Raw-CNTs 5 and OH/Raw-CNTs 10, respectively

5.4.4 The dispersion of conductive fillers with different dimensions

The discussion made so far was focused on 1D filler, i.e., CNTs, the differently dimensional fillers, e.g., 0D carbon black and 2D graphene, were employed to further verify the method proposed. Following the same procedure, the real part of permittivity and its standard deviation are given in **Figure 5.12**.

As stated in **Figure 5.12**, both fittings on standard deviations of PU/Carbon black composites and PU/rGO composites followed linear functions *vs* filler contents. And it was found that the standard deviations increased with the increasing filler concentrations, indicating the developed method in this study was not only restricted to the measurement and evaluation of the dispersion of 1D conductive fillers and also suitable for 0D and 2D conductive fillers.

Figure 5.12 Real permittivity and standard deviation of (a) PU/Carbon black composites and (b) PU/rGO composites

5.5 Conclusions

In this study, three theoretical models were employed to explain the complex permittivity of composites and the resonance phenomenon of conductive fillers in polymer matrix. The oscillation of the real part permittivity was used to evaluate the fillers dispersion state, resulting from the aggregation of fillers. This developed method was verified by several cases, e.g., composites by changing processing method, composites with the aid of various surfactant and statistical analysis. It was found that this method could be employed to not only distinguish the efficiency of surfactants, but measured the maximum filler loading. Furthermore, it is not only restricted to 1D fillers; and it can be served as a tool for evaluation of 0D and 2D fillers dispersion by measuring their permittivity as well. This method is in principle valid for all conductive fillers dispersed in a dielectric matrix.

This non-destructive, easy to use and time-saving method shows great potentials to be used in industrial field. One of the potential applications is the evaluation of uniformity of fillers within the composites. It is possible to conduct automated sequential measurements, aided by translational movements of composite or tester probe. By analyzing the standard deviations from numbers of measurement, the uniformity of fillers within the composites can be evaluated. Moreover, further study is needed to investigate if and how comparison can be made in among more complex systems, e.g., changing matrix or filler type, in order to broaden the application of this method.

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Chapter 6

The Mussel-Inspired Strategy towards the High Performance Polyurethane (PU)/Carbon Nanotubes (CNTs) Composites for EMI Shielding Application

The CNTs were modified by polydopamine (PDA) through self-oxidation polymerization of dopamine (DA) and successfully incorporated into PU matrix. The PDA modification to CNTs by retained the intrinsic structure of CNTs. The presence of PDA coating had a potential to facilitate the secondary modification of CNTs by magnetic particles according to the literature. Thus, it is vital to investigate the influences of CNTs modification on PU/PDA-CNTs composites. In this chapter, PU/PDA-CNTs composites were systematically compared with PU/Raw-CNTs composites, including the EMI properties, mechanical property and CNTs dispersion.

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6.1 Introduction

Electromagnetic radiation from electronic devices tends to interfere with other electronics, particularly at high frequency (e.g., radio waves and satellites), leading to the increasing demands for the developments of shielding materials. It is well recognized that the EMI shielding effectiveness could be enhanced by electrical conductivity and that shielding materials with high conductivity exhibit superior EMI SE. [1-3] CNTs reinforced polymer composites have attracted much attention for EMI shielding applications, since CNTs could impart high electrical conductivity and excellent mechanical properties to the obtained composites at relatively low CNTs loadings compared with metallic fillers. [4-6]

However, in order to obtain sufficient EMI SE, a high volume fraction of CNTs is required, resulting in poor processability and decreased mechanical properties of a shielding material because of the strong interaction between nanotubes and poor bonding between fillers and matrix. [7] To overcome these issues, many approaches have been developed, in which chemical functionalization of CNTs by partially oxidizing CNTs sidewalls is much more effective. It could effectively improve the CNTs dispersion in matrix and create the chemical bonding between CNTs and matrix. But, the unique structure of CNTs would be destroyed, associated with structural defects and fragmentation of CNTs, leading to the deteriorated electrical properties of CNTs. [8-10] Also, it is suggested by some research groups that the electrical conductivity of CNT itself is essential for EMI SE, and the conductive network of CNTs in composite only improve the EMI SE. [7, 11-13] Therefore, the inevitable destroy to CNTs by chemical treatment is undesirable for EMI shielding applications, even the improved mechanical properties are obtained.

Polymer encapsulation (with the polymer generated in situ) or wrapping is another method to modify CNTs and introduce functional groups comprising the polymer to CNTs. [14] Motivated by mussel adhesive proteins [15], dopamine was found to form PDA layer on various types of materials including polymers, ceramic and metals through self-polymerization dopamine in aqueous solution. [16, 17] PDA coatings have been widely used in numerous materials for biomedical applications due to their physicochemical properties and strong surface adhesion abilities to various surfaces. [18-20] PDA is also employed as a functionalization modifier, e.g., anti-fouling coatings [21], nanofiltration for antibiotics removal [22], CO₂-philic for gas separation [23] and superhydrophobicity for oily water treatment [24]. Besides these direct PDA applications, secondary treatments can be easily achieved based on their intrinsic capacity, including inorganic Au [25], Ag [26] nanoparticles and CNTs-PDA/Co₃O₄ for Li-air batteries [27]. Moreover, PDA coating of CNTs was reported to improve the dispersion of CNTs in various solvents or polymer matrices, recently. [25, 28, 29] However, current PDA studies are mainly focused on surface modification for improved biocompatibility and fabrication of hybrid materials for energy or catalytic applications. Recently, an eco-friendly method was reported to modify CNTs through self-oxidation polymerization of dopamine (DA). [30] The monomers of dopamine were firstly absorbed on CNTs through π - π interactions. This weak interaction would possibly retain the intact structure of CNTs. [16, 28] Moreover, after polymerization, the large amount of functional groups (e.g., -OH and -NH-) created on PDA coatings, which are beneficial for the creation of chemical bonding with polymer matrix. It has been proved that CNTs modified by polydopamine (PDA) not only improve the CNTs dispersion, but enhance the mechanical properties of CNTs composites.

In this study, PDA modified CNTs (PDA-CNTs) were prepared and incorporated into a PU matrix. The effect of PDA modification on CNTs

structure was studied and the EMI properties of PU/PDA-CNTs composites were measured in the frequency of 8.4-12.8 GHz, and comparisons were made with those of PU composites with raw CNTs.

6.2 Materials and methods

6.2.1 Materials

The CNTs with an average diameter of 9.5 nm and length of 1.5 μm , respectively, were synthesized by chemical vapor deposition by Nanocyl S.A. Desmodur N 3390 as hardener and Capa 3022 as polyol were chosen to prepare the PU matrix. Anhydrous N, N-dimethylformamide (Alfa Aesar) and acetone (analytical grade from Scientific Fishier) were used as received without any purification. Cyclohexanone (ACS reagent) was dried at least 48 h by 4A molecular sieves before use. Dopamine hydrochloride (99%) and tris (hydroxymethyl) aminomethane hydrochloride were purchased from Sigma-Aldrich.

6.2.2 The fabrication of PU/CNTs composites

The preparation of PDA-CNTs

The PDA-CNTs were prepared followed by the description in the literature [30]. Raw CNTs were ultrasonically dispersed in the mixed solution of DMF and tri (hydroxymethyl) aminomethane with pH ~ 8.5 till the formation of nearly homogeneous suspension. Then the certain amount of dopamine hydrochloride was added into the CNTs suspension, followed by continuously stirring for 6 h at room temperature. 3-4 times of repeating centrifugation and washing by deionized water were carried out to remove unreacted dopamine monomers and

free polydopamine particles, and then the obtained PDA-CNTs were dried using a freeze dryer.

Fabrication of PU/CNTs composites

PU/PDA-CNTs composites were prepared through the two-step reaction in order to facilitate the complete reaction, since the presence of PDA coatings containing hydroxyl and amine groups. The detailed procedure was described as follows. Briefly, PDA-CNTs were ultrasonically dispersed in acetone at the concentration of 0.5 mg/ml for 2 h. The polyisocyanurate was further incorporated followed by continuous ultrasonication for 2 h. Prior the incorporation of poyol, the mixture of polyisocyanurate and PDA-CNTs was concentrated by rotary evaporator to obtain a viscous mixture. The well-mixed casting solution was obtained by mild stirring for several minutes, which was poured into a cleaned PTFE mold and left in fumehood to remove the solvent residue and finish curing. The PU/Raw-CNTs (NCO/Raw-CNTs) composites were prepared following the same procedure.

6.2.3 Characterization

Raman spectroscopy was employed to investigate the structural changes of CNTs before and after treatments by a WITec CRM200 Confocal Raman microscope (488 nm laser). Cryo-surface morphologies of specimens were obtained by using a Jeol FESEM 7600F. The DC electrical conductivities of PU/CNTs composites were collected with MCP-T370 (Four probes, Mitsubishi Company). The EMI SE was measured in the frequency range 8.2-12.8 GHz using a PNA-L Network Analyzer (N5230A, VNA) measurement system. The samples were fabricated to rectangle plates with the size of $25.4 \times 12.7 \times 0.3$ mm³ to fit the waveguide sample holder. The tensile tests were carried out using an Instron Tester (Model 5567) according to ASTM Standard D638.

6.3 Results and discussion

6.3.1 Modification of CNTs by PDA coating

In this study, the as-received CNTs were used without any purification, in order to retain their intrinsic structure. The PDA-CNTs were prepared by self-oxidative polymerization of dopamine in DMF solution (as exhibited in **Figure 6.1**).

The successful PDA coating onto the surface of raw CNTs was confirmed by comparing FTIR spectra of raw CNTs and PDA-CNTs, as shown in **Figure 6.2a**. It was seen that raw CNTs exhibited strong peaks at 3430 and 1400-1640 cm^{-1} due to the -OH groups and benzene rings [31], respectively. The presence of -OH group was assumed to be the slight oxidation of CNTs when manufactured or moisture effect [32]. Compared with raw CNTs, some new peaks appeared after being coated by PDA layers. The broad absorption band at 3424 cm^{-1} was assigned to the overlap of -OH groups and -NH stretching vibrations [32]. In addition, the peaks at 2970, 2900 and 2857 cm^{-1} were attributed to aliphatic C-H vibration stretching modes, and the characteristic peak at 1739 cm^{-1} was assigned to carbonyl groups. Moreover, another two new peaks clearly appeared at 1540 and 1378 cm^{-1} that are assigned to -C=N and -C-N-C, respectively [33]. The presence of these new peaks confirmed that PDA was successfully coated onto CNTs through the simple oxidative-polymerization method.

Figure 6.1 Schematic illustration for the preparations of PDA-CNTs

To quantify the amount of PDA coated on the CNTs, TGA tests of raw CNTs and PDA-CNTs were performed. As shown in **Figure 6.2b**, the weight loss of PDA-CNTs was more obvious than that of raw CNTs, which arose from the degradation of PDA. From the TGA curve of raw CNTs, the onset degradation temperature of CNTs was found about 493 °C. Meanwhile, the weight residue of PDA-CNTs was 85.1% at 493 °C. Accordingly, the approximation of weight percentage of PDA covered over CNTs was calculated to be ~15%.

Figure 6.2 (a) FTIR spectra and (b) TGA curves of raw CNTs, PDA-CNTs and pure PDA

Figure 6.3 TEM images of (a) raw CNTs and (b) PDA-CNTs. Arrows show the PDA coating wrapped on the nanotubes. The high magnified images with a scale bar at 10 nm were given for better clarity

The thickness and morphology of the CNTs before and after modification were examined by TEM. It can be seen from **Figure 6.3a**, the diameter of raw CNTs with a smooth surface is between 10-20 nm. After modification, the CNTs were covered by a layer of PDA with the thickness of ~1-2 nm, as seen in **Figure 6.3b**. The low magnified TEM picture indicates that the PDA layers uniformly covered the CNTs.

Figure 6.4 Raman spectra of raw CNTs and PDA-CNTs

It was proved that CNTs were successfully coated by PDA through self-oxidative polymerization of dopamine. The ~15 wt% of PDA was coated on CNTs by controlling the dopamine loading as stated in experimental section. The conductivity of CNT itself is highly dependent on its intrinsic properties, thus it is necessary to investigate the structural changes of CNTs after PDA modification by Raman. As shown in **Figure 6.4**, there were three distinct peaks in all Raman spectra, which are denoted as D (1340 cm^{-1}), G (1570 cm^{-1}) and D' (2688 cm^{-1}) bands, respectively. Generally, the D band is attributed to the defects in the curved graphite sheet, sp^3 hybridized carbon and amorphous carbon. [34] The G band is associated with the vibration of crystalline graphitic carbon in CNTs. [35] Another characteristic peak at 2688 cm^{-1} is the second harmonic of the D band, which is independent of the defect concentration. The ratio of intensities of the D and G bands was typically employed to evaluate the extent of structural defects by surface treatment. [32] In the raw CNTs, the ratio was around 1.01. This value was still 1.01 after being coated by PDA, indicating the PDA modification did not cause the formation of defects on the CNTs crystalline structure. Moreover, no peak shifting was observed in the

spectra of raw CNTs and PDA-CNTs, illustrating the PDA adsorbed onto CNTs through non-covalent interaction.

6.3.2 EMI shielding properties of PU/CNTs composites

In this study, the EMI SE of the two types of PU/CNTs composites was investigated over the frequency range of 8.4-12.8 GHz (X-band). EMI SE is the logarithm function of the power balance data, which could be obtained from the measurement with the VNA. [36] The mathematical interpretations of the definitions are given in Eq. (1) - (3). [1, 11]

$$SE_{Total} = SE_R + SE_A = 10 \log \frac{1}{1-R} + 10 \log \frac{1-R}{T} = 10 \log \frac{1}{T} \quad (1)$$

$$SE_R = 10 \log \frac{1}{1-R} \quad (2)$$

$$SE_A = 10 \log \frac{1-R}{T} \quad (3)$$

where SE_A and SE_R are the absorption and reflection mechanisms, respectively.

The EMI shielding properties of PU/CNTs composites are given in **Figure 6.5**. It is found that the EMI SE_{Total} of both PU/Raw-CNTs and PU/PDA-CNTs composites were increased with the increasing of CNTs loadings and the PU/PDA-CNTs composites exhibit decreased SE_{Total} compared with PU/Raw-CNTs composites, shown in **Figure 6.5a**. Similarly, the SE_A 's and SE_R 's of PU/Raw-CNTs are higher than those of PU/PDA-CNTs composites (**Figure 6.5b**).

Figure 6.5 EMI SE of the as-fabricated PU/CNTs composites

It is suggested that EMI SE of PU/CNTs composites is closely related to the imaginary part of complex permittivity. [3, 37] **Figure 6.6a** shows the imaginary part of complex permittivity as a function of CNTs concentrations, in which the reported values were the average values in the X-band frequency range. It was found that the value of ϵ'' in PU/PDA-CNTs composites gradually increased with the increasing CNTs contents; on the contrary, those in PU/CNTs composites increased rapidly with the increasing CNTs contents. In

general, ε'' is the sum of losses from dielectric polarization $\varepsilon_i''(DP)$ and a loss from electrical conductivity $\varepsilon_i''(\sigma)$, expressed in Eq. (4): [38, 39]

$$\varepsilon_i'' = \varepsilon_i''(DP) + \varepsilon_i''(\sigma) \quad (4)$$

where $\varepsilon_i''(\sigma)$ could be related to DC conductivity σ_{DC} in Eq. (5):

$$\varepsilon_i''(\sigma) = \sigma_{DC} / (2\pi f \varepsilon_0) \quad (5)$$

The ε_i'' of a shielding material can be converted to the alternative conductivity (σ_{AC}) followed by the Eq. (6):

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon_i'' = \sigma_{DC} + 2\pi f \varepsilon_i''(DP) \quad (6)$$

where the f and ε_0 are frequency and dielectric constant in free, respectively.

The σ_{AC} of PU/CNTs composites is illustrated in **Figure 6.6b**. The obvious differences between two types of PU/CNTs composites were observed, indicating the conductivity of PU composites was prone to PDA modification. From the Raman results, it could be found that PDA treatment was non-destructive method, which maintained the intact structure of CNTs. Thus, the contribution to the electrical conductivity of composites was attributed to the electrical conductive network. To get a deep understanding upon the conductivity mechanism, the DC conductivity of PU/PDA-CNTs composites with 10 wt% CNTs was investigated, i.e., 0.22 S m^{-1} , which is the 2 orders of magnitude lower than that of PU/Raw-CNTs 10 (15.8 S m^{-1}). It indicates that the presence of PDA coatings delayed the tunneling conduction between individual tubes. For 10 wt% of CNTs, the contribution to conductivity of PU/PDA-CNTs composite was totally from dielectric polarization (given in **Figure 6.6c**, exhibiting that contribution of conductivity of CNTs themselves to EMI SE was dominant. While in the case of PU/Raw-CNTs composite, the 20% of contribution was attributed to the electrical conductive network. These results are strongly consistent with that proposed by literatures, which suggested that intrinsic conductivity of the CNTs is predominant for the EMI

shielding and the conductive network can only improve the EMI SE. [7, 12, 13, 40]

Figure 6.6 The (a) imaginary part (ϵ'') of complex permittivity of composites, and (b) AC conductivity and (c) the contribution of dielectric polarization to EMI SE

6.3.3 CNTs dispersion states of PU/CNTs composites

The dispersion of CNTs in PU matrix before and after treatment was investigated by SEM. Before the observation, the cryo-fracture surfaces were coated a layer of Pt coating with the thickness of around 20 nm. The SEM pictures showing the CNTs dispersion is given in **Figure 6.7**. There was no obvious difference being observed. One of the possible reasons is the good

dispersion of CNTs in both of these two types of composites. As mentioned in chapter 4, raw CNTs could be dispersed well by polyisocyanurate. And the PDA-CNTs exhibited great potential to disperse well in the matrix. [30] Another reason is that the SEM technique is sometimes not representative, since only localized situations can be observed. Thus, the dispersions of raw CNTs and PDA-CNTs in matrix could not be distinguished by SEM in this case.

Figure 6.7 SEM pictures of the cryo-fracture surfaces of (a) PU/Raw-CNTs 10 composite and (b) PU/PDA-CNTs 10 composite

In the previous chapter, it was proved that the oscillation of e' curves could determine the CNTs dispersion state in PU/CNTs composites. Therefore, the oscillations of e' curves of two types of composites were quantified over the

whole range of frequency, shown in **Figure 6.8**. For both composites, the ϵ' increased with the increasing CNTs contents, attributed to the increased ability of energy storage contributed by CNTs.

Figure 6.8 (a) The real permittivity and (b) its standard deviation of PU/Raw-CNTs and PU/PDA-CNTs composites

It was found that the increasing rate of the standard deviation of PU/PDA-CNTs composites was much lower than that of the PU/Raw-CNTs composites. And the point of the ϵ' standard deviation of PU/Raw-CNTs 10 was excluded from the fitting curve due to the abrupt increase. As discussed, the phenomenon was

observed that the CNTs dispersion became much worse at this concentration. However, the abrupt increase in standard deviation was not observed in PU/PDA-CNTs composites, indicating the presence of PDA coating prevented the CNTs aggregation. In other words, the PDA-CNTs could be well dispersed in matrix, illustrating the improved dispersibility by PDA surface treatment. The presence of PDA coating formed outside nanotubes destroyed the π - π interaction between nanotubes, resulting in the uniform dispersion of CNTs. The schematic illustration for network formation of PU/PDA-CNTs composites is illustrated in **Figure 6.9**.

Figure 6.9 Schematic illustration for network formation of PU/PDA-CNTs composites

6.3.4 Mechanical property of PU/CNTs composites

PDA-CNTs were incorporated into PU matrix via in-situ polymerization to study the influences of PDA-CNTs on PU composites. The PDA-CNTs were firstly added into polyisocyanurate and followed by reacting with polyol, in order to avoid the adverse interference of competing reactions between polyol and PDA-CNTs with polyisocyanurate.

In this study, the stress-strain curves and Young's modulus of PU/Raw-CNTs composites and PU/PDA-CNTs composite are given in **Figure 6.10**. In chapter 4, it was found that at the condition of same isocyanate index (i.e., the ratio of NCO groups to OH groups), better CNTs dispersion, and lower Young's modulus was resulted from the interfered stoichiometry. It was slightly different with the previous trend that the Young's modulus was increased to 244 MPa from 225 MPa (around 10%). The enhanced modulus was attributed to the interfacial bonding between the PDA-CNTs and the matrix, as reported. [29, 30] However, the modulus of PU/PDA-CNTs 10 was still lower than OH/Raw-CNTs 10. It means that the enhanced modulus has not reached their expected value. But compared with the challenges of CNTs dispersion, the decreased Young's modulus is not a serious issue for the fabrication of CNTs composites, which could be enhanced by the increased isocyanate index or incorporation of other filler.

Figure 6.10 (a) Representative stress-strain curves and (b) Young's modulus of PU/CNTs composites

6.4 Conclusions

The PDA-CNTs were prepared by a facile, eco-friendly method and successfully incorporated into PU matrix. The modification of PDA maintained the CNTs intrinsic structure and provided good dispersion of CNTs in PU

matrix. It was found that the presence of PDA coating enhanced the mechanical property of PU/PDA-CNTs composites, attributed to the enhanced interfacial interaction between PDA-CNTs and PU matrix, which can effectively transfer load from polymer matrix to CNTs. But the presence of insulating PDA coating decreased the electrical conductivity of PU/PDA-CNTs composite. As a consequence, the EMI SE was decreased and the contribution for EMI SE of composite was mainly from the conductivity of CNTs themselves. The PDA is a promising candidate for further modification of CNTs to prepare PU composites with high EMI performances through the incorporation of magnetic particles.

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Chapter 7

Conclusions and Future Work

This chapter summarizes the outcomes and conclusions of this project and proposes the future work based on the conclusions. The effects of the type of PU and processing sequence on EMI shielding properties were discussed. More importantly, a new method for the evaluation of CNTs dispersion was developed through observing the dielectric permittivity to compliment the SEM technique. The surface treatment of CNTs does not only further enhance the CNTs dispersion, but exhibit great potentials for secondary modification to allow incorporation of magnetic particle to further improve the EMI shielding properties. Further study should be focused on (1) the incorporation of magnetic particle; (2) enhancing the mechanical properties of composites; (3) decreasing the amount of solvents used during the processing.

7.1 Outcomes of this project

The project was motivated by the increasing demands for high performance EMI shielding materials and the lacking of understanding on the relationship of CNTs dispersion and EMI shielding properties. Although a great number of publications have shown that good CNTs dispersion could be achieved by surface treatment and processing approaches, but the relationship of CNTs dispersion and EMI shielding properties was not clearly understood yet, i.e., (1) how does one define a good dispersion and (2) does a good dispersion correspond to high EMI shielding properties?

This study aimed to correlate the CNTs dispersion to EMI shielding properties, further guiding the design of shielding materials. The problem stated in the previous chapter that SEM is not capable of evaluating the CNTs dispersion at high loading was also addressed in this study. In the third part, an effective approach to CNTs modification was studied, which will be beneficial for further improving the EMI shielding performance of materials.

7.1.1 Polymer matrix identification and processing of composites

The type of PU matrix was identified between thermoplastic and thermoset PU. The CNTs concentrations were fixed at 5 wt% and 10 wt% in two types of PU/CNTs composites, in order to compare the EMI properties of composites. The electrical conductivity plays an important role in EMI properties, thus, these two CNTs concentration were used, which is commonly above the percolation threshold based on the literatures. [1] In this part, the thermoset PU was synthesized following the procedure commonly reported by literature, in which CNTs was blended with the polyols moiety considering the high reactivity of polyisocyanurate.

It is obvious that “island-structure” (CNTs aggregates) formed in TPU/Raw-CNTs composites since the only form of interaction assisting in the dispersion in the TPU system is TPU chains wrapping. On the contrary, the CNTs were uniformly dispersed in PU/Raw-CNTs composites by the two-step method. CNTs were first wetted by small molecules monomers (i.e., polyol), which were easily diffused into CNTs bundles compared to the TPU molecules. With the incorporation of polyisocyanurate, the polymer network gradually formed by reaction between NCO groups and OH groups. Thus, the CNTs dispersion was more uniform in PU/Raw-CNTs composites than that in TPU/Raw-CNTs composites. As result, the apparent differences of EMI SE of the composites from the two distinct types of matrices were observed. It was found that the EMI SE of PU/Raw-CNTs composites were much higher than those of TPU/Raw-CNTs composites, which was attributed to the distinct CNTs dispersion state. In a conclusion, the thermoset PU was more suitable for the fabrication of high performance EMI shielding materials.

Since the synthesis of thermoset PU requires two parts, i.e., polyisocyanurate and polyol, the effect of the sequences of incorporating the as-received CNTs into PU on CNTs dispersion and EMI SE of the PU/CNTs composites was also investigated in this study. It was found that the CNTs dispersion states could be varied by simply changing the processing sequences. The formation of electrically conductive network was delayed obviously in NCO/Raw-CNTs composites, indicating that polyisocyanurate exhibited stronger interaction with the as-received CNTs. As a consequence, EMI SE of the NCO/Raw-CNTs composites was decreased compared with OH/Raw-CNTs composites due to the insufficient electrical network obtained from the poorly dispersed CNTs. The contribution for EMI SE of NCO/Raw-CNTs composites was mainly contributed by the dielectric polarization of CNTs themselves, and that of conductive network was negligible. On the contrary, the electrically conductive network achieved performed a remarkable effect in OH/Raw-CNTs composites,

resulting in the improved EMI SE. Therefore, it is suggested that DC conductive network is not the only scientific criterion to obtain superior EMI SE, which is also dependent on the intrinsic conductivity of CNTs themselves.

7.1.2 The study of CNTs dispersion by electromagnetic signals

In this study, a new method was developed based on several classical models (i.e. Lorentz-Drude, Pendry and Maxwell-Wagner) for the evaluation of CNTs dispersion on a macroscopic scale, which is non-destructive and easy to operate. The principle is based on the sensitivity of electrical resonance to external EM field, which is attributed to the hyperconjugation phenomenon of CNTs. One of the most attractive parameters is the dielectric permittivity (the real part of complex permittivity). The complex permittivity is described by Lorentz-Drude model [2-4], $\varepsilon = 1 + \sum_{j=0}^k \frac{f_j \omega_p^2}{\omega_{oj}^2 - \omega^2 - j\gamma_j \omega}$, where ω_p is the plasma frequency ($\omega_p = \frac{Ne^2}{\varepsilon_0 m_e}$), ω_{oj} is the resonance frequency, k is the number of oscillators with resonant frequency ω_{oj} , and strength f_j . According to the Lorentz-Drude model, it is found that complex permittivity is frequency-dependent, and determined by plasma frequency of fillers.

It is worth noting that plasma frequency is intrinsic property of materials, but it is affected by the dispersion state since the effective mass of electrons is determined by 3D network of nanofiller described by Pendry's model [5, 6]. Dilution of the CNTs would result in reduced density and increased effective mass of active electrons in CNTs, leading to the ω_p shifted to a lower frequency range [7]. Moreover, CNTs in polymer could be described by Maxwell-Wagner model of two-layer capacitor and its equivalent circuit, which is widely used in CNTs/polymer composites [8-10]. Different CNTs aggregates lead to different plasma frequencies of CNTs, corresponding to specific signals (resonance

frequency) when subject to EM field. The more fluctuated permittivity curves, the more divergent dispersion status in CNTs system.

By employing the surfactant and proper processing method, this assumption of the proposed method was proved accurate. Moreover, it was found that this method could be employed to not only distinguish the efficiency of surfactants, but estimated the maximum filler loading. Furthermore, it is not only restricted to 1D fillers; and it can be served as a tool for evaluation of 0D and 2D fillers dispersion by measuring their permittivity as well. This method is in principle valid for all conductive fillers dispersed in a dielectric matrix.

This non-destructive, easy to use and time-saving method shows great potentials to be used in industrial field. One of the potential applications is the evaluation of uniformity of fillers within the composites. It is possible to conduct automated sequential measurements, aided by translational movements of composite or tester probe. By analyzing the standard deviations from numbers of measurement, the uniformity of fillers within the composites can be evaluated. Moreover, further study is needed to investigate if and how comparison can be made in among more complex systems, e.g., changing matrix or filler type, in order to broaden the application of this method.

7.1.3 CNTs treated by Polydopamine (PDA-CNTs)

Polymer encapsulation was employed to modify CNTs and introduce functional groups to CNTs. [11] It was achieved through self-oxidation polymerization of dopamine (DA). [12] The monomers of DA were firstly absorbed on CNTs through π - π interactions. This weak interaction would leave the structure of CNTs intact, which was proved by Raman spectrum. [13, 14] Moreover, after polymerization, the large amount of functional groups (e.g., -OH and -NH-)

created on PDA coatings will be beneficial for the creation of chemical bonding with polymer matrix.

It was found that the incorporation of PDA-CNTs enhanced the mechanical property of PU/PDA-CNTs composites. The PDA layer provided good dispersion of PDA-CNTs in PU matrix and the high interfacial interaction between PDA-CNTs and PU matrix could effectively transfer load from polymer matrix to CNTs. But the presence of PDA coating decreased the electrical conductivity of PU/PDA-CNTs composites compared with PU/Raw-CNTs composites. As a consequence, the EMI SE was decreased since the contribution for EMI SE of composite was mainly from the conductivity of CNTs themselves. Nevertheless, the layer of PDA coating is a promising candidate for further modification of CNTs to prepare PU composites with high EMI performances through the incorporation of magnetic particles. [15]

7.2 Future work

In this project, the issue of CNTs dispersion was improved through mixing with polyisocyanurate and modified by PDA. However, it was found that the chemical stoichiometry was easily affected by the presence of raw CNTs and PDA-CNTs, resulting in the deteriorated mechanical properties. Moreover, the good dispersion of CNTs was attributed to the wrapping of insulating polymer, which decreased the conductivity of composites. Therefore, the EMI shielding properties were lower than those of composites with poorly dispersed CNTs. According to the EMI theory, both the permittivity and permeability of composites determine the EMI shielding performances. The incorporation of as-received CNTs could only improve the permittivity of composites. Thus, the incorporation of magnetic particles to further improve the EMI SE is of significant importance. Furthermore, in order to obtain a better EMI SE, a high CNTs concentration will be required in the EMI shielding materials.

Consequently, large amount of solvent will be used. By realizing these issues, further study should be conducted to overcome these drawbacks.

7.2.1 Incorporation of magnetic particles

Magnetic particle could improve the permeability for shielding material, resulting in enhanced EMI SE. Kim et al. compared the composites made from purified CNTs and unpurified CNTs (containing Fe catalyst). It was found that the EMI SE of composites contacting unpurified CNTs was much higher than that of composites containing purified CNTs, attributed to the contribution of permeability. [16] Wang et al. prepared a hybrid material consisting of Fe_3O_4 grown on CNTs for microwave absorption application. It was also reported that the hybrid materials exhibited higher EM absorbing ability than physical mixture of Fe_3O_4 and CNTs. [17]

In this study, the successful modification of CNTs by PDA promises the possibility of secondary modification of PDA-CNTs by magnetic decoration. [18, 19] The PDA has a structure as shown in **Figure 7.1** The rich amount of -OH and -NH makes PDA an excellent candidate as binding agent for metal oxide precursors, which could be further converted to metal oxide particles. PDA as intermediate layer for binding metal oxide particles has been proved as effective method to get uniform distribution of particles on CNTs. [20] The typical scheme for the preparation of CNTs-PDA- Fe_3O_4 particles is shown in **Figure 7.2**.

Figure 7.1 The proposed PDA structure

Figure 7.2 Schematic of the preparation of CNTs-PDA-Fe₃O₄ [18]

7.2.2 Improvement of mechanical properties

As discussed before, the decreased mechanical properties were mainly caused by the interference of chemical stoichiometry between polyisocyanurate and polyol. Thus, the improvement of mechanical properties could be enhanced by increasing the molar ratio of isocyanate groups. The effect of isocyanate index on mechanical properties of PU composites was discussed in literatures. [21, 22] Huang et al. systematically discussed the influence of the ratio of NCO and OH groups on mechanical properties of castor oil-based PU. They found that with an increase of NCO/OH ratio, the tensile strength, glass transition temperature, and stiffness of PU increased, as a consequence, the elongation at break decreased.

Moreover, it is found that the mechanical properties of composites could also be enhanced by increasing the interfacial interaction between fillers and matrix, i.e., PDA-CNTs. Therefore, the functional fillers or multi-functional polymers could also be used for the improvement of mechanical properties, such as silica, hyperbranched polymer. [23] The illustrated dendrimer and hyperbranched polymer are shown in **Figure 7.3**.

Figure 7.3 Schematic structures of (a) dendrimers, and (b) hyperbranched polymers. D: dendritic units; T: terminal units; L: linear units

Figure 7.4 The scheme of the preparation of composite enhanced by different mechanisms: (a) conventional composites-phase separated, (b) intercalated composites and (c) exfoliated composites [24]

7.2.3 Decreasing the amount of solvents

Solvent was used to decrease the viscosity of the highly viscous casting solution, caused by the incorporation of high CNTs loading. The strong π - π interaction among the nanotubes resulted in CNTs aggregation, thus destroying this

interaction will achieve a casting solution with low viscosity. Furthermore, substituting the solvent by reactive small molecules, such as oxazolidine and aldimine (shown in **Figure 7.5**), which can not only acts as solvent, but performs as part of matrix when suffers moisture.

Figure 7.5 Schematic illustration showing the reaction of oxazolidine with moisture

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