



**Scholars'
Press**

Mohammad Arjmand
Uttandaraman Sundararaj

Electrical Properties of Carbon Nanotube/Polymer Composites

**Mohammad Arjmand
Uttandaraman Sundararaj**

Electrical Properties of Carbon Nanotube/Polymer Composites



Scholar's Press

Impressum / Imprint

Bibliografische Information der Deutschen Nationalbibliothek: Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <http://dnb.d-nb.de> abrufbar.

Alle in diesem Buch genannten Marken und Produktnamen unterliegen warenzeichen-, marken- oder patentrechtlichem Schutz bzw. sind Warenzeichen oder eingetragene Warenzeichen der jeweiligen Inhaber. Die Wiedergabe von Marken, Produktnamen, Gebrauchsnamen, Handelsnamen, Warenbezeichnungen u.s.w. in diesem Werk berechtigt auch ohne besondere Kennzeichnung nicht zu der Annahme, dass solche Namen im Sinne der Warenzeichen- und Markenschutzgesetzgebung als frei zu betrachten wären und daher von jedermann benutzt werden dürften.

Bibliographic information published by the Deutsche Nationalbibliothek: The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

Any brand names and product names mentioned in this book are subject to trademark, brand or patent protection and are trademarks or registered trademarks of their respective holders. The use of brand names, product names, common names, trade names, product descriptions etc. even without a particular marking in this works is in no way to be construed to mean that such names may be regarded as unrestricted in respect of trademark and brand protection legislation and could thus be used by anyone.

Coverbild / Cover image: www.ingimage.com

Verlag / Publisher:

Scholar's Press

ist ein Imprint der / is a trademark of

OmniScriptum GmbH & Co. KG

Heinrich-Böcking-Str. 6-8, 66121 Saarbrücken, Deutschland / Germany

Email: info@scholars-press.com

Herstellung: siehe letzte Seite /

Printed at: see last page

ISBN: 978-3-639-71252-0

Zugl. / Approved by: Calgary, University of Calgary, Diss., 2014

Copyright © 2014 OmniScriptum GmbH & Co. KG

Alle Rechte vorbehalten. / All rights reserved. Saarbrücken 2014

**Mohammad Arjmand
Uttandaraman Sundararaj**

Electrical Properties of Carbon Nanotube/Polymer Composites

To:

My Parents, Spouse and Siblings

for their heartfelt supports

Acknowledgment

Back in September 2009, my great supervisor, Dr. Uttandaraman Sundararaj, and I were new to the University of Calgary. At that time, Dr. Sundararaj had just moved to the University of Calgary as the Head of the Department of Chemical and Petroleum Engineering and his postdoctoral fellows were still at University of Alberta, who moved to Calgary a few months later. Being my supervisor's first graduate student at University of Calgary along with the difficulties of occupying and organizing new laboratories depicted a challenging PhD career towards me. Nonetheless, my supervisor was a tremendous source of management, unconditional support and encouragement. I am truly indebted to his support during the last four years, not only as a prominent supervisor, but also as an elder friend who guided me with academic and real lives.

I would like to convey my wholehearted gratitude to the members of Polymer Processing Group, particularly, Dr. Genaro Gelves and Mr. Ali Sarvi, who assisted me with my graduate life in Calgary. I express my warmest appreciation to Dr. Simon Park and Dr. Mehdi Mahmoodi for their collaboration in manufacturing the mold and injection molding of the composites (chapters 4 and 6). Special thanks go to Dr. Michal Okoniewski and Mr. Thomas Apperley for their contributions to the analysis of electrical properties data (chapter 5). A sincere appreciation goes to Dr. Rosario Bretas and Dr. Aline Silva for their cooperation with producing the copper nanowire composites and their characterization (chapter 8).

The financial supports from the Natural Science and Engineering Research Council (NSERC) of Canada and Alberta Innovates Technology Futures (AITF) are highly appreciated. I also owe a great deal of appreciation to Dr. Tieqi Li and Ms. Jeri-Lynn Bellamy in Nova

Chemicals[®], Calgary, AB, Canada for the polymer extrusion/blending. I would like to thank Dr. Samaneh Abbasi of Ecole Polytechnique (Montreal, Canada) for assistance with Raman spectroscopy. My appreciation and thanks to Dr. Michael Schoel and Dr. Tobias Furstenhaupt who contributed me with microscopy imaging. I am also very grateful to Americas Styrenics LLC, who generously provided me with the neat polystyrene.

The deepest gratitude goes to my parents, spouse and siblings who though have been geographically far away from me during my PhD career, but have always been in my heart.

Preface

Driven by the ever-growing demand for versatile electronics with increased functionality, high performance, light weight, low cost and improved design options, conductive filler/polymer composites (CPCs) have emerged as a distinctive solution. Manipulating the conductive network formation in CPCs allows them to be employed in a wide range of applications, such as charge storage, electrostatic discharge dissipation and electromagnetic interference (EMI) shielding.

In this dissertation, controlling the conductive network formation was the key aspect in designing the morphology of CPCs for electrical applications. Multi-walled carbon nanotube (MWCNT) was chosen as conductive filler due to its surprising electronic structure and growing industrial usage. We employed two distinct techniques to improve or deteriorate conductive network formation to improve the electrical properties in MWCNT/polymer composites, i.e. electrical conductivity, EMI shielding and dielectric properties. These techniques comprise (1) aligning MWCNTs using an injection molding machine, and (2) replacing MWCNTs with copper nanowires (CuNWs).

Prior to exploring the influence of the above-mentioned techniques on the electrical properties of CPCs, a series of studies were implemented on MWCNT/polymer composites to obtain a general understanding from the electrical behaviors of CPCs as a function of MWCNT content. The results over the X-band (8.2 – 12.4 GHz) showed that the electrical conductivity, EMI shielding and dielectric properties rose with MWCNT content. The increase in electrical conductivity with MWCNT loading was attributed to the formation of conductive paths across the composite. Increase in EMI shielding with MWCNT content was related to a greater number of

interacting nomadic charges and also higher real permittivity (polarization loss) and imaginary permittivity (Ohmic loss). Moreover, the broadband dielectric spectroscopy ($10^{-1} - 10^{+6}$ Hz) showed that both real permittivity and imaginary permittivity increased drastically as the MWCNT concentration approached the percolation threshold. Increase in real permittivity was related to the formation of a large number of nanocapacitor structures, MWCNTs as electrodes and polymer matrix as dielectric material, and increase in imaginary permittivity was ascribed to greater number of dissipating charges, enhanced conductive network formation and boosted polarization loss arising from interfacial polarization.

MWCNT alignment, induced by an injection molding machine, was observed to deteriorate the conductive network formation. As inferior conductive network formation reduces imaginary permittivity, this technique was introduced as an innovative technique to improve the dielectric properties of MWCNT/polymer composites. Nonetheless, MWCNT alignment indicated an adverse influence on the percolation threshold, electrical conductivity and EMI shielding due to its negative influence on conductive network formation. In brief, unavoidable flow-induced alignment of MWCNTs in injection molding process was presented as an opportunity to improve the dielectric properties for charge storage or as a challenge to be avoided for producing conductive CPCs.

CuNWs were creatively displayed to be competent substitutions for MWCNTs for charge storage applications. Unavoidable oxide layer formation on the surface of CuNWs, which has always been a disadvantage for electronics applications, was employed as a benefit to decay the conductive network formation and reduce the imaginary permittivity.

Moreover, higher conductivity of fresh core of CuNWs relative to MWCNTs provided the composites with more free charges contributing to real permittivity. In conclusion, high conductivity of fresh core of CuNWs combined with the presence of the oxide layer on CuNW surfaces depict a promising future for CuNW/polymer composites as charge storage materials.

Mohammad Arjmand
University of Calgary

List of Symbols and Abbreviations

Abbreviations

AC	Alternating current
ASTM	American society for testing and material
CISPR	Comité International Spécial des Perturbations Radioélectriques
CNT	Carbon nanotube
CPC	Conductive filler/polymer composites
CuNW	Copper nanowire
CVD	Chemical vapor deposition
DC	Direct current
DMF	N,N-Dimethylformamide
EMI	Electromagnetic interference
ESD	Electrostatic discharge
hr	Hour
LED	Light-emitting diode
LFD	Low-frequency dispersion
LM	Light microscopy
MeOH	Methanol
min	Minute
MUT	Material under test
MWCNT	Multi-walled carbon nanotube
MWS	Maxwell-Wagner-Sillars
NIR	Near-infrared
PAO	Porous aluminum oxide
PC	Polycarbonate

PCB	Printed circuit board
PNA	Programmable network analyzer
PPG	Polymer Processing Group
PVDF	Poly(vinylidene fluoride)
PS	Polystyrene
RC	Resistance/capacitance
SiP	System-in-package
SE	Shielding effectiveness
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotube
TEM	Transmission electron microscopy
VGCNF	Vapor grown carbon nanofiber
VNA	Vector network analyzer
WAXD	Wide angle x-ray diffraction
3-D	Three dimensional

Symbols

A	Area of sample
\hat{a}_z	Electric or magnetic field strength unit vector
C_0	Capacitance of free space
C_1	Mold temperature
C_2	Melt temperature
C_3	Injection/holding pressure
C_4	Injection velocity
d	Thickness of sample
dB	Decibel (unit of shielding effectiveness)
e	Charge of an electron

E	Electric field
E_I	Incident electric field
E_T	Transmitted electric field
f	Electromagnetic wave frequency
H	Magnetic field
H_I	Incident magnetic field
H_T	Transmitted magnetic field
I	Electric current
I_R	Resistive current
I_C	Capacitive current
J	Current density
M	Ratio of conducting aggregate to average gap width
N_e	Number of electrons
P	Power density
P_I	Incident power
P_T	Transmitted power
Q	Stored charge
q	Charge of particle
R	Resistance
r_1	Contact resistance
r_2	Resistance of cable
R_x	Resistance of sample
S	Siemens (unit of electrical conductivity)
SE_{OA}	Overall shielding effectiveness
SE_R	Shielding by reflection
SE_A	Shielding by absorption
SE_{MR}	Shielding by multiple-reflection

S_{11}	Ratio of reflected power to incident power in port 1
S_{12}	Ratio of transmitted power from port 1 to port 2 to incident power in port 1
S_{21}	Ratio of transmitted power from port 2 to port 1 to incident power in port 1
S_{22}	Ratio of reflected power to incident power in port 2
t	Critical exponent of percolation threshold
T	Torque
$\tan\delta$	Dissipation factor
V	Voltage
W	Watt (Unit of power)
V_C	Percolation threshold
Z'	Real impedance
Z''	Imaginary impedance

Greek Letters

α	Attenuation constant
β	Phase constant
γ	Propagation constant
δ	Skin depth
ϵ'	Dielectric (real) permittivity
ϵ''	Dielectric loss (Imaginary permittivity)
ϵ_0	Dielectric permittivity of free space
ϵ_r	Relative dielectric permittivity

η	Intrinsic Impedance of shielding materials
η_0	Intrinsic impedance EM wave in free space
μ	Magnetic permeability
μ_0	Magnetic permeability of free space
μ_r	Relative magnetic permeability
ρ_0	Volume resistivity of conductive filler
ρ_s	Surface resistivity
ρ_v	Volume resistivity
σ	Electrical conductivity
σ_0	Electrical conductivity of copper
σ_r	Relative electrical conductivity
τ	Time constant
Ω	Ohm (unit of resistance)
ω	Angular frequency

Table of Contents

Chapter 1 – Introduction	1
1.1. General Background	1
1.2. State-of-the-Art	2
1.3. References	5
Chapter 2 – Literature Review	7
2.1. Conductive Filler/Polymer Composites (CPCs): Structure, Applications and Market	7
2.2. Electrical Conductivity	11
2.3. Electrostatic Discharge (ESD)	13
2.4. Electromagnetic Interference (EMI) Shielding	17
2.4.1. General Background	17
2.4.2. Magic of Shielding	19
2.4.3. Shielding Effectiveness	21
2.4.4. Reflection, Absorption and Multiple-reflection for Conductive Monolithic Materials	23
2.4.4.1. Shielding by Reflection	24
2.4.4.2. Shielding by Absorption	26
2.4.5. Effect of Real Permittivity on Shielding of Conductive Monolithic Materials	29
2.5. Dielectric Theory	30
2.5.1. Dielectric Material	30
2.5.2. Permittivity	31
2.5.3. Dielectric Mechanisms	34
2.5.4. The Electrical Current of Dielectrics under a Step DC Voltage	38
2.6. Electrical Properties of Conductive Filler/Polymer Composites	41