DIELECTRIC BEHAVIORS OF A NOVEL POLYMER NANOCOMPOSITE

Siripetch Kaewwata

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science

The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with

The University of Michigan, The University of Oklahoma,
Case Western Reserve University and Institut Français du Pétrole

2006

ISBN 974-9990-03-x

Thesis Title:

Dielectric Behaviors of a Novel Polymer Nanocomposite

By:

Siripetch Kaewwata

Program:

Polymer Science

Thesis Advisors:

Dr. Hathaikarn Manuspiya

Prof. Hatsuo Ishida

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

Nantaya Yanumet . College Director

(Assoc. Prof. Nantaya Yanumet)

Thesis Committee:

Hathaileam Momspiya

(Dr. Hathaikarn Manuspiya)

(Prof. Hatsuo Ishida)

Nartaya Januar . (Assoc. Prof. Nantaya Yanumet)

R. Magnings

(Assoc. Prof. Rathanawan Magaraphan)

ABSTRACT

4772025063: Polymer Science Program

Siripetch Kaewwata: Dielectric behaviors of a novel polymer

nanocomposite

Thesis Advisors: Dr. Hathaikarn Manuspiya, Prof. Hatsuo Ishida 78

pp. ISBN 974-9990-03-x

Keywords: Benzoxazine / Barium strontium titanate / Nanocomposite / Sol-gel

This research attempted to develop a novel nanocomposite polymer by using polybenzoxazine as a polymer matrix and barium strontium titanate (BST) as a filler for potential uses in electrical application at microwave frequency range. Barium strontium titanate was prepared by sol-gel process and the temperatures of the synthetic process were studied. The electrical properties of both pure materials and composites were investigated.. XRD patterns showed that after the proportion of strontium was increased, the temperature required for thermal decomposition in the sol-gel process was also increased. All nano-BST compounds were measured the dielectric properties by the independence analyzer. TEM was used in order to study particle size and dispersion of nano-BST. The compression molding technique was employed to form the composite. The ratio of BST (filler) to polybenzoxazine (matrix) was 1% and 5% by weight. The nanocomposites were measured for their dielectric constants and thermal properties.

บทคัดย่อ

นางสาวศิริเพชร แก้ววาตะ : พฤติกรรมทางไดอิเลกทริกของพอลิเมอร์นาโนคอมพอ สิตชนิดใหม่ (Dielectric behaviors of a novel polymer nanocomposite) อ. ที่ปรึกษา : คร.หทัยกานต์ มนัสปียะ และ ศ.คร.ฮัทซีโอะ อิชิคะ 78 หน้า ISBN 974-9990-03-x

ในการวิจัยนี้ทำการพัฒนาพอลิเมอร์นาโนคอมพอสิต โดยใช้พอลิเบนซอกชาซินเป็น ส่วนของเมทริกซ์และแบเรียมสตรอนเทียมไททาแนตเป็นสารเติมแต่ง (filler) เพื่อที่จะนำไปใช้ต่อ ในงานด้านไฟฟ้าที่ใช้งานในช่วงของคลื่นความถี่ไมโครเวฟ โดยทำการเตรียมแบเรียม สตรอนเทียมไททาแนตโดยวิธีโซลเจลและทำการศึกษาอุณหภูมิที่ใช้ในกระบวนการสังเคราะห์ และ สมบัติทางไฟฟ้า ในการวิเคราะห์ทางเอกซ์เรย์ดิฟเฟรกชัน พบว่าหลังจากทำการเพิ่มปริมาณ ของสตรอนเทียมใน สตรอนเทียมแบเรียมไททาเนต แล้ว อุณหภูมิที่ใช้ในการสังเคราะห์ก็เพิ่มขึ้น ตามไปด้วย กล้องจุลทรรศน์อิเลกตรอนแบบส่องผ่านถูกนำมาใช้ในการศึกษาขนาดของอนุภาค และการกระจายตัวของแบเรียมสตรอนเทียมไททาเนต เทคนิคการขึ้นรูปแบบกดอัตถูกนำมาใช้ใน การขึ้นรูปของวัสคุดอมพอสิตโดยสัดส่วนของสารเติมแต่ง (แบเรียมสตรอนเทียมไททาเนต) และ เมทริกซ์ (พอลิเบนซอกซาซิน) เท่ากับ 1 และ 5 เปอร์เซ็นต์โดยน้ำหนัก วัสคุนาโนคอมพอสิตถูก นำมาศึกษาค่าคงที่ไดอิเลกทริกและสมบัติทางความร้อนต่อไป

ACKNOWLEDGEMENTS

This work would not have been possible without the assistance of the following individuals.

First of all, the author would like to gratefully give special thanks to her advisors, Dr. Hathaikarn Manuspiya for her intensive suggestions, valuable guidance, encouragement and vital help throughout this research work and Professor Hatsuo Ishida for his constructive suggestions and valuable guidance. Gratitude is also extended to all other committee members, Assoc. Prof. Nantaya Yanumet and Assoc. Prof. Rathanawan Magaraphan for taking time to serve on the committee and their valuable comments on her thesis.

Special thanks is directed to Dr. Pitak Laoratanakul and MTEC staffs for their kindness and help. Additional thanks go to all of the Petroleum and Petrochemical College's faculties who have tendered invaluable knowledge and to the college staff who willingly gave her support and encouragement.

The author gratefully acknowledges the partial scholarship and partial funding of the thesis work provided by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

Finally, the author would like to take this opportunity to thank PPC Ph.D. students and all her PPC friends for their friendly assistance, cheerfulness, creative suggestions, and encouragement. Also, sincerely thanks to her parents Wallop and Manit, sister Siriwan, and Myq who have always supported, helped, loved, and encouraged throughout her life.

TABLE OF CONTENTS

		PAGE
Titl	e	i
Ab	stract (in English)	iii
Abs	stract (in Thai)	iv
Acl	cnowledgements	v
Tab	le of Contents	vi
List	of Tables	ix
List	of Figures	x
List	of Schematic	xiv
СНАРТЕ	CR	
I	INTRODUCTION	1
	1.1 Benzoxazine	4
	1.2 Piezoelectric Ceramic	7
	1.3 Piezoelectric Polymer Composite	10
п	LITERARURE REVIEW	11
	2.1 Benzoxazine	11
	2.2 Piezoelectric Ceramic	13
	2.3 Piezoelectric Polymer Composite	16
Ш	EXPERIMENT	18
	3.1 Materials	18
	3.2 Equipment	18
	3.2.1 Fourier Transform Infared Spectrometer (FTIR)	18
	3.2.2 Gel-permeable Chromatography (GPC)	18
	3.2.3 Thermogravimetric Analysis (TGA)	18

CHAPTER	PAGE
3.2.4 Differential Scanning Calorimeter (DSC7)	19
3.2.5 X-ray Diffraction (XRD)	19
3.2.6 Scanning Electron Microscope (SEM)	. 19
3.2.7 Compression Molding Machine	19
3.2.8 Transmission Electron Microscope (TEM)	. 19
3.2.9 Impedance/gain-phase Analyzer	19
3.3 Methodology	20
3.3.1 Monomer Preparation	20
3.3.2 Barium Strontium Titante Preparation	22
3.3.2.1 Sol-Gel Process of Barium Strontium	Titanate 22
3.3.2.2 Ceramic Pellet Preparation	25
3.3.3 Composite Preparation	26
3.3.4 Morphology Crystal Structure and Particle Siz	ze
Determination	27
3.3.5 Sample Preparation for Dielectric Measurement	nts 27
IV RESULTS AND DISCUSSION	28
4.1 Benzoxazine Monomer Characterization	28
4.2 Barium Titanate/Barium Strontium Titanate Characte	erization 31
4.3 Thermal Characterization	45
4.4 Electrical Measurement	49
V CONCLUSIONS AND SUGGESTED WORK	57
REFERENCES	59

CHAPT	ER	PAGE
	APPENDICES	63
	Appendix A	63
	Appendix B	65
	Appendix C	67
	Appendix D	75
		(a)
	CURRICULUM VITAE	78

LIST OF TABLES

ΓAΒΙ	Æ	PAGE
1.1	Comparative properties of various high performance	
	polymers	6
3.1	Weight of each chemicals in preparing barium	
	titanate/barium strontium titanate.	24
3.2	Temperature program for compression molding process	26

LIST OF FIGURES

FIGU	JRE	PAGE
1.1	Structure of phenolic resins and polybenzoxazines.	2
1.2	Structure of Barium Strontium Titanate, Ba _{1-x} Sr _x TiO ₃ (BST).	3
1.3	Structures of benzoxazine monomers.	4
1.4	Perovskite structure of Barium Titanate.	7
1.5	Structure of Barium Strontium Titanate, Ba _{1-x} Sr _x TiO ₃ (BST).	8
1.6	Overview of sol-gel process.	9
2.1	XRD pattern showing (200) peaks of BaTiO ₃ (BTO),	
	SrTiO ₃ (STO), and the graded BST(BTO/STO)film with 20	
	in 44-48°.	14
3.1	Temperature program for the 2-step thermal decomposition	
	method.	24
3.2	Temperature program for the sintering process of ceramic	
	pellet.	25
4.1	FTIR spectra of the diamine-based benzoxazine monomer	
	pellet.	28
4.2	TGA thermogram of the diamine-based benzoxazine	
	monomer.	30
4.3	DSC thermogram of the diamine-based benzoxazine	50
	monomer.	30
4.4	(a) XRD patterns of barium titanate powders at room	30
	temperature (reference, Cho, S.D. et al, 2004) and (b) XRD	
	spectrum from experiment of barium titanate after sol-gel	
	and sintering process.	32
4.5	SEM images of BaTiO ₃ (a) reference sol-gel BT powder, (b)	32
	after the sol-gel process, (c) and (d) after sintering at 1200°C	22
	at 1200°C	33

FIG	URE	PAGE
4.6	XRD spectrum of (Ba _{0.95} Sr _{0.05})TiO ₃ after sol-gel and	
	sintering process.	34
4.7	SEM images of (Ba _{0.95} Sr _{0.05})TiO ₃ (a) reference sol-gel BST	
	powder (Hu, T., et al, 2004), (b) after sol-gel process, (c)	
	after sintering at 1200°C, and (d) after sintering at 1330°C.	35
4.8	XRD spectrum of (Ba _{0.7} Sr _{0.3})TiO ₃ after sol-gel process	36
4.9	XRD spectrum of (Ba _{0.5} Sr _{0.5})TiO ₃ after sol-gel process.	36
4.10	XRD spectrum of BaTiO ₃ after sintering process at 1200°C	
	and 1330°C	37
4.11	SEM images of BaTiO ₃ (a) and (b) after sintering at 1330°C	38
4.12	XRD spectrums of Barium strontium titanate after sol-gel	
	process at 800°C and 1000°C (a) (Ba _{0.7} Sr _{0.3})TiO ₃ (b)	
	$(Ba_{0.5}Sr_{0.5})TiO_3.$	39
4.13	XRD spectrum of (Ba _{0.7} Sr _{0.3})TiO ₃ after sol-gel and sintering	
	process	40
4.14	XRD spectrum of (Ba _{0.5} Sr _{0.5})TiO ₃ after sol-gel and sintering	
	process	41
4.15	SEM images of (Ba _{0.7} Sr _{0.3})TiO ₃ (a) and (b) after the sol-gel	
	process at 800°C, (c) and (d) after sol-gel process at 1000°C,	
	(e) fracture picture after sintering at 1330°C, and (f) planar	
	picture after sintering at 1330°C	42
4.16	SEM images of (Ba _{0.5} Sr _{0.5})TiO ₃ (a) and (b) after the sol-gel	
	process at 800°C, (c) and (d) after sol-gel process, (e) planar	
	picture after sintering at 1330°C and (f) fracture picture after	
	sintering at 1330°C.	43
4.17	TEM images of (Ba _{0.7} Sr _{0.3})TiO ₃ after sol-gel process at	
	1000°C.	44

FIGU	RE	PAGE
4.18	DSC thermogram of (a) Polybenzoxazine (PBZ), (b) 1% Barium titanate polybenzoxazine composite (1% BT-PBZ), (c) 5% Barium titanate polybenzoxazine composite (5% BT-	
	PBZ), (d) 1% (Ba _{0.7} Sr _{0.3})TiO ₃ polybenzoxazine composite (1% BST0.7-PBZ), (e) 5% (Ba _{0.7} Sr _{0.3})TiO ₃ polybenzoxazine composite (5% BST0.7-PBZ), (f) 1% (Ba _{0.5} Sr _{0.5})TiO ₃ polybenzoxazine composite (1% BST0.5-PBZ), and (g) 5% (Ba _{0.5} Sr _{0.5})TiO ₃ polybenzoxazine composite (5% BST0.5-	
4.10	PBZ).	46
4.19	TGA thermogram of (a) Polybenzoxazine (PBZ), (b) Barium titanate (BT), (c) 1% Barium titanate polybenzoxazine composite (1% BT-PBZ), (d) 5% Barium titanate polybenzoxazine composite (5% BT-PBZ), (e) 1%	2
	(Ba _{0.7} Sr _{0.3})TiO ₃ polybenzoxazine composite (1% BST0.7-PBZ), (f) 5% (Ba _{0.7} Sr _{0.3})TiO ₃ polybenzoxazine composite	
	(5% BST0.7-PBZ), (g) 1% (Ba _{0.5} Sr _{0.5})TiO ₃ polybenzoxazine composite (1% BST0.5-PBZ), and (h) 5% (Ba _{0.5} Sr _{0.5})TiO ₃	40
4.20	polybenzoxazine composite (5% BST0.5-PBZ). Dielectric constant as a function of frequency from 1 kHz to	48
	1 MHz at room temperature of (a) polybenzoxazine (PBZ), (b) (Ba _{0.7} Sr _{0.3})TiO ₃ (BST _{0.7}), and (c) (Ba _{0.5} Sr _{0.5})TiO ₃	
4.21	(BST0.5). Dielectric constant as a function of frequency from 1 kHz to	50
	1 MHz at room temperature of barium titanate benzoxazine composite.	51

FIGURE		PAGE
4.22	Dielectric constant as a function of frequency from 1 kHz to	
	1 MHz at room temperature of barium strontium titanate	
	(Ba _{0.7} S _{7.3})TiO ₃ benzoxazine composite.	51
4.23	Dielectric constant as a function of temperature from 30°C to	
	110°C of (a) polybenzoxazine (PBZ), (b) 5% barium titanate	
	polybenzoxazine composite (5% BT-PBZ). (c)	
	(Ba _{0.7} Sr _{0.3})TiO ₃ (BST0.7), (d) 5% (Ba _{0.7} Sr _{0.3})TiO ₃	
	polybenzoxazine composite (5% BST0.7-PBZ), (e)	
	$(Ba_{0.5}Sr_{0.5})TiO_3$ (BST0.5), and (f) 5% $(Ba_{0.5}Sr_{0.5})TiO_3$	
	polybenzoxazine composite (5% BST0.5-PBZ).	52
4.24	Loss tangent as a function of temperature from 30°C to	
	110°C of (a) polybenzoxazine (PBZ), (b) (Ba _{0.7} Sr _{0.3})TiO ₃	
	(BST0.7), (c) (Ba _{0.5} Sr _{0.5})TiO ₃ (BST0.5), (d) 5%	
	(Ba _{0.7} Sr _{0.3})TiO ₃ polybenzoxazine composite (5% BST0.7-	
	PBZ), and (e) 5% (Ba _{0.5} Sr _{0.5})TiO ₃ polybenzoxazine	
	composite (5% BST0.5-PBZ).	55

LIST OF SCHEMATICS

SCHEMATIC		PAGE	
3.1	Monomer Preparation	21	
3.2	Barium Strontium Titanate Preparation.	23	