LIBRARY Michigan State University

PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due. MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE
NOT 0 9 2004		
JUN 1 20	10 2	
110512		

6/01 c:/CIRC/DateDue.p65-p.15

STRUCTURE/PROPERTY RELATIONSHIPS OF POLYMERS CONTAINING HYBRID NANO-FILLER---POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS)

Вy

Haiping Geng

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering & Materials Science

2002

517 (n ina ph) and disp ach Wer poly Poly part inve DS រាចា Elec rheo

•

ABSTRACT

STRUCTURE/PROPERTY RELATIONSHIPS OF POLYMERS CONTAINING HYBRID NANO-FILLER ---POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (POSS)

Вy

Haiping Geng

Polyhedral Oligomeric Silsesquioxane (POSS) is a three-dimensional structurally well-defined cage-like molecule represented by formula $(RSiO_{1.5})_n$ (n = 6, 8, 10 or higher, R is an organic group). POSS macromers have an inorganic silica-like core, which is surrounded by organic groups, and the physical size of the POSS cage is about 1.5 nm. Because of their hybrid nature and nanometer-scale feature, as shown in this study, POSS macromers were dispersed in a molecular level into polymeric systems by blending, in effect achieved POSS/Polymer nano-blends. The POSS macromers used in this work were cubic-caged POSS macromers bearing different organic corner groups. polystyrene (PS) and polydimethyl siloxane (PDMS) were used as model polymers.

The investigations involved in this work include two parts. In the first part, the microstructures and thermal properties of the POSS macromers were investigated by using X-ray diffractometer, Differential Scanning Calorimetry (DSC), and Thermogravimetric Analysis (TGA). In the second part, the morphologies of POSS/Polymer blends were examined using Transmission Electronic Microscopy (TEM), and X-ray diffractometer. Their thermal and rheological properties were studied with DSC, TGA, and Rheometer.

Th cage aff macrome macrome POSS m undergo T that dep structure morphol homoger TI under el result of polymer turn sho gel relat under lar The results of this work showed that different corner groups on the POSS cage affected the morphological structures and properties of the POSS macromers. The higher the degree of the symmetry and regularity of the POSS macromers and the smaller the size of the corner groups, the more ordered the POSS macromers. The POSS macromers with functionalities, which may undergo chemical cross-linking reactions, possessed high thermal stabilities.

The morphology studies of POSS/PS and POSS/PDMS blends showed that depending on the attached organic groups on the POSS cages, the structures of the polymer matrix and the composition of the blends, the morphologies of the POSS/polymer blends ranged from complete separation to homogeneous dispersion in the nanoscopic scale.

The rheological investigations of the POSS/PDMS blends revealed that under elevated temperatures, gelation occurred in the POSS/PDMS blends as a result of intermolecular association between POSS nano-fillers and PDMS polymer chains. The formation of gel exhibited a solid-like behavior, which in turn showed a significantly improved creep resistance. Since the formation of gel relates with only physical interaction, the POSS/PDMS gel can be destroyed under large stain/stress and re-formed under elevated temperatures.

WHC

DEDICATION

То

MY FAMILY AND MY FRIENDS

WHO LOVED ME AND SUPPORTED ME DURING THE PAST YEARS!

guidu
also
comr
Greg
who
who
of !
like
sup
Pro
die
3

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Andre Y. Lee, for his guidance, support and encouragement throughout this entire research. I also would like to express my gratefulness to the members of my committee, Dr. Dahsin Liu, Dr. Krishnamurthy Jayaraman, and Dr. Gregory L. Baker for their input and guidance.

In addition, great appreciation must be given to Mr. Ben Simkin, who assisted me in TEM and X-ray operation, and Mr. Robert Pcionek, who helped me in my dissertation writing.

Special thanks go to the Air Force Research and Laboratory, state of Michigan-Research Excellent Funds for the financial support. I also like to thank General Electric Silicone and Hybrid Plastics, Inc. who supplied some materials used in this work.

Last, I'd like to express my thankfulness to Graduate School for providing me the Graduate Office Fellowship, so I could complete my dissertation in the spring of 2002.

v

List of

List of

Chapt

Cha

F

TABLE OF CONTENTS

List of Tablesxi
List of Figures xii
Chapter 1: Introduction1
1.1 Statement of Problems1
1.2 Introduction of this Research Work4
1.2.1 Objective4
1.2.2 Research Approach4
1.2.3 Contributions to the POSS Nano-Technology7
Chapter 2: Literature Review9
2.1 Chemistry of Silsesquioxanes9
2.1.1 Abbreviations for Silsesquioxanes
2.1.2 Brief History of Silsesquioxanes10
2.1.3 Structure and Classification of Silsesquioxanes11
2.1.4 Synthesis of Silsesquioxanes12
2.2 Polymeric Materials Containing POSS
2.2.1 Organic-Inorganic Hybrid Polymers Containing POSS21
2.2.2 POSS/Polymer Nanoscopic Materials27

PART I	I: Investigatio	s of POSS	Macromers		29
--------	-----------------	-----------	-----------	--	----

Chapter 3
3.1
3.2
3.3
3 1
+ .c
3.5
PART II
Preface .
Chanta
Bland
sicuds .
4.
4.:

Chapter 3: Structure-Property Studies of POSS Macromers30
3.1 Introduction30
3.2 Experimental31
3.2.1 Materials 31
3.2.2 Sample Preparations 31
3.2.3 Characterization Techniques 35
3.3 X-Ray Crystallographic Analysis of POSS Macromers36
4.3.1 Effects of POSS Corner Groups36
4.3.2 Summary45
3.4 Thermal Stability Study of POSS Macromers47
3.4.1 Effects of POSS Corner Groups51
3.4.2 Summary 63
3.5 Transition Temperatures of POSS Macromers 64
3.5.1 Effects of POSS Corner Groups64
3.5.1 Summary73
PART II: Investigations on POSS/Polymer Blends 74
Preface 75
Chapter 4: Morphology and Interaction Studies of POSS/Polystyrene (PS)
Blends78
4.1 Introduction78
4.2 Experimental79

	4.2.1 Materials 79
	4.2.2 Sample Preparations80
	4.2.3 Characterization Techniques 80
4.3 Elec	Morphological Studies of POSS/PS Blends by Transmission tronic Microscope (TEM)82
	4.3.1. Effects of POSS Macromers with Different Corner Groups on the Morphologies of POSS/PS2M Blends (50wt% POSS Loading) 82
	4.3.2. Effects of POSS Loading on the Morphologies of POSS/PS2M Blends 89
	4.3.3 Effects of PS Molecular Weight on the Morphologies of POSS/PS Blends 93
	4.3.4 Discussion 94
	4.3.5 Summary 96
4.4	X-Ray Crystallographic Analysis of POSS/PS Blends 96
	4.4.1 Effects of POSS Chemistry and POSS Loading97
	4.4.2 Effects of PS Molecular Weight108
	4.4.3 Summary109
4.5	Glass Transitions of POSS/PS Blends110
	4.5.1 Effects of POSS Chemistry and POSS Loading110
	4.5.2 Discussion121
	4.5.3 Summary122
4.6	Thermal Stability Studies of POSS/PS Blends123
	4.6.1 Effects of POSS Chemistry and POSS Loading123
	4.6.2 Summary 129

.

Chapter 5 (PDMS) F
5.1
5.2
5.3
5.4 Th
3.2

Chapter 5: Morphology and Properties of POSS/ Polydimethyl Siloxane (PDMS) Blends
5.1 Introduction 130
5.2 Experimental132
5.2.1 Materials132
5.2.2 Sample Preparations132
5.2.3 Characterization Techniques133
5.3 Morphological Structures of POSS/PDMS Blends135
5.4 Thermal Stability Studies of POSS/PDMS Blends By Thermogravimetric Analysis (TGA)141
5.5 Rheological Properties of POSS/PDMS Blends148
5.5.1 Effects of POSS Macromers on the Rheological Behaviors of PDMS148
5.5.2 Gelation Process of POSS/PDMS Blends150
5.5.2.1 Background of Gelation150
5.5.2.2 Gelation Process of POSS/PDMS Blends154
5.5.3 Rhological Properties of Gelled POSS/PDMS Blends159
5.5.4 Physical Nature of POSS/PDMS Gelation164
5.5.4.1 DSC Result of POSS/PDMS Blend164
5.5.4.2 Destruction of Gelled POSS/PDMS Blends and Re- Gelation165
5.5.4.3 Physical Nature of POSS/PDMS Gelation173
5.5.5 Effects of Compositions and Experimental Conditions on the Gelation Processes of POSS/PDMS Blends174
5.5.5.1 Rate of Storage Modulus Change (R _G)— Characterization of the Gelation Rates of the POSS/PDMS Blends174

Chapter

.

6.1

6.

Referenc

	5.5.5.2 Effects of the POSS Chemistry on the Gelation Processes of the POSS /PDMS Blends175
	5.5.5.3 Gelation Behaviors of POSS/PDMS Blends with Different POSS Concentrations 179
	5.5.5.4 Influence of PDMS Molecular Weight on the Gelation Rates of the POSS/PDMS Blends 180
	5.5.5.5 Effects of the Annealing Temperatures on the Gelation Rate of the POSS/PDMS Blends182
5.5.6	Discussion 183
	5.5.6.1 Gelation Mechanism of the POSS/PDMS Blends183
	5.5.6.2 Gelation Process of the POSS/PDMS Blends187
5.5.7	Summaries188
Chapter 6: Concl	usions and Recommendations190
6.1 Conclus	ions190

6.2 Recommendations	<u>1</u> 96

References19	98
--------------	----

•

Table 3. Macrome Table 3.1 parenthes . curves) – Table 3.3 Table 3.4 Inorganic Table 3.5: Table 4.1: Table 4.2: X-ray Diff Table 4.3: X-ray Diff Table 4.4: Blends (fr Table 4.5: X-ray Diff Table 4.6: X-ray Diff Táble 4.7 Blends (fr Table 4.8 (from X-r. Table 4.9 Biends (f: Table 4.1 Table 5.1

LIST OF TABLES

Table 3.1: Abbreviations, Chemical formulae, and Molecular Weight of POSSMacromers32
Table 3.2: Peak Positions (unit: $^{\circ}2 \theta$) and their corresponding d-spacing (as shown in parentheses, unit Å) of POSS Macromers (Summarized from their X-ray diffraction curves)43
Table 3.3: Thermal Stabilities of POSS Macromers with different Corner Groups 58
Table 3.4: Molecular Weight of POSS Macromers, and the Weight Percentage of theirInorganic Si-O Portion and Organic C-H Portion59
Table 3.5: Transition Temperatures of POSS Macromers (DSC Results) 72
Table 4.1: Phase Characteristics of POSS/PS2M Blends (50 wt% POSS) 83
Table 4.2: Comparison of Peak Positions of Cp8POSS and Cp8POSS/PS2M Blends (from X-ray Diffraction Curves in Figure 4.16)98
Table 4.3: Comparison of Peak Positions of Cy8POSS and Cy8POSS/PS2M Blends (from X-ray Diffraction Curves in Figure 4.17)99
Table 4.4: Comparison of Peak Positions of Styrenyl ₈ POSS and Styrenyl ₈ POSS/PS2MBlends (from X-ray Diffraction Curves in Figure 4.18)101
Table 4.5: Comparison of Peak Positions of Ph8POSS and Ph8POSS/PS2M Blends (from X-ray Diffraction Curves in Figure 4.19)102
Table 4.6: Comparison of Peak Positions of V8POSS and V8POSS/PS2M Blends (from X-ray Diffraction Curves in Figure 4.20)103
Table 4.7: Comparison of Peak Positions of ST1Cp7POSS and ST1Cp7POSS /PS2MBlends (from X-ray Diffraction Curves in Figure 4.21)
Table 4.8: Comparison of Peak Positions of V1Cp7POSS and V1Cp7POSS /PS2M Blends(from X-ray Diffraction Curves in Figure 4.22)106
Table 4.9: Comparison of Peak Positions of CyHe1Cp7POSS and CyHe1Cp7POSS /PS2MBlends (from X-ray Diffraction Curves in Figure 4.23)107
Table 4.10 Glass Transition Behaviors of POSS/PS1M Blends111
Table 5.1: Characteristics of Polydimethyl Siloxane (PDMS) 132

Figure 1.1 Cubic Shar
Figure 1.2 with a Per-
Figure 2.1
Figure 2.2
Figure 2.3
Figure 2.4
Figure 2.5
Figure 2 : Condensa:
Figure 2.7
Figure 2.8
Figure 2.4
Figure 2.1
Figure 2.1
Figure 2.1
ngure 3.1 Figure 3.1
Figure 3.2
Figure 2
Figure 2 a
Figure 2.
Figure 3 -

LIST OF FIGURES

Figure 1.1: Schematic Diagram of Polyhedral Oligomeric Silsesquioxane (POSS) with a Cubic Shape $(R_7Y_1Si_8O_{12})$ 3
Figure 1.2: POSS Macromer with Monofunctional Group Converted to Hybrid Polymer with a Pendent Architecture 3
Figure 2.1 Schematic Diagram of Silsesquioxanes with a Cubic Shape $(X_8Si_8O_{12})$ 12
Figure 2.2: Complex Products of RSiCl ₃ Hydrolytic Polycondensation Reaction 16
Figure 2.3: Examples of Fully Condensed POSS Systems 17
Figure 2.4: Examples of Incompletely Condensed POSS Systems 18
Figure 2.5: Corner Capping of $R_7T_4D_3(OH)_3$ 19
Figure 2.6: Incompletely Condensed Silsesquioxane Prepared by the Hydrolytic Condensation of $(c-C_6H_{11})SiCl_3$ 20
Figure 2.7: Base-mediated Cleavage of Fully Condensed [C ₆ H ₁₁) ₈ Si ₈ O ₁₂] 20
Figure 2.8: Architecture of Linear POSS-based Polymers 23
Figure 2.9: Polymerization of Methacrylates-POSS Homopolymer and Copolymer24
Figure 2.10: Free Radical Polymerization of Styryl-POSS based Copolymer25
Figure 2.11: POSS-Siloxane Copolymer 25
Figure 2.12: Schematic of the Curing Cycle of the POSS-Epoxy System 26
Figure 3.1: POSS Macromers With Different Corner Groups 33
Figure 3.2: X-ray Diffraction Profile of Cp ₈ POSS Macromer 37
Figure 3.3: X-ray Diffraction Profile of Cy ₈ POSS Macromer 37
Figure 3.4: X-ray Diffraction Profile of Styrenyl ₈ POSS Macromer 38
Figure 3.5: X-ray Diffraction Profile of Ph ₈ POSS Macromer 38
Figure 3.6: X-ray Diffraction Profile of V ₈ POSS Macromer 39
Figure 3.7: X-ray Diffraction Profile of Isobu ₈ POSS Macromer 39

Figure 3. Figure3.1 Figure 3.1 Figure 3. Figure (Styreny), Figure 3.1 and V_1C_7 Figure 3 Isobu_sPC

Figure 3.8: X-ray Diffraction Profile of ST ₁ Cp ₇ POSS Macromer 40
Figure 3.9: X-ray Diffraction Profile of Styrenyl ₁ Cp ₇ POSS Macromer 40
Figure 3.10: X-ray Diffraction Profile of CyHe ₁ Cp ₇ POSS Macromer 41
Figure 3.11: X-ray Diffraction Profile of V ₁ Cp ₇ POSS Macromer 41
Figure 3.12: X-ray Diffraction Profile of ST ₁ Isobu ₇ POSS Macromer 42
Figure 3.13: X-ray Diffraction Profile of Styrenyl ₁ Isobu ₇ POSS Macromer 42
Figure 3.14: TGA curve of Cp ₈ POSS Macromer49
Figure 3.15: TGA curve of Cy ₈ POSS Macromer 49
Figure 3.16: TGA Curve of Styrenyl ₈ POSS Macromer 50
Figure 3. 17: TGA Curve of Ph ₈ POSS Macromer 50
Figure 3. 18: TGA Curve of Isobu ₈ POSS Macromer 51
Figure 3. 19: TGA Curve of V ₈ POSS Macromer 51
Figure 3. 20: TGA Curve of ST ₁ Cp ₇ OSS Macromer 52
Figure 3. 21: TGA Curve of Styrenyl ₁ Cp ₇ POSS Macromer 52
Figure 3. 22: TGA Curve of CyHe ₁ Cp ₇ POSS Macromer 53
Figure 3. 23: TGA Curve of V ₁ Cp ₇ POSS Macromer 53
Figure 3. 24: TGA Curve of ST ₁ Isobu ₇ POSS Macromer 54
Figure 3. 25: TGA Curve of Styrenyl ₁ Isobu ₇ POSS Macromer 54
Figure 3.26: TGA Curves of the R ₈ POSS Macromers: Cp ₈ POSS, Cy ₈ POSS, Styrenyl ₈ POSS, Ph ₈ POSS, Isobu ₈ POSS, and V ₈ POSS 55
Figure 3.27: TGA Comparisons of ST_1Cp_7POSS , $Styrenyl_1Cp_7POSS$, $CyHe_1Cp_7POSS$, and V_1Cp_7POSS with Cp_8POSS 56
Figure 3.28: TGA Comparisons of Styrenyl ₁ Isobu ₇ POSS, and ST ₁ Isobu ₇ POSS with Isobu ₈ POSS57

Figure 3. Figure 4. Figure 4. Figure 4. Figure 4. Figure 4. Figure 4. Figure 4 Figure 4 Figure 4. Figure 4 Figure 4

Figure 3.29: DSC Curve of Cp ₈ POSS Macromer	- 66
Figure 3.30: DSC Curve of Cy ₈ POSS Macromer	- 66
Figure 3.31: DSC Curve of Styrenyl ₈ POSS Macromer	67
Figure 3.32: DSC Curve of Ph ₈ POSS Macromer	67
Figure 3.33: DSC Curve of V ₈ POSS Macromer	68
Figure 3.34: DSC Curve of Isobu ₈ POSS Macromer	- 68
Figure 3.35: DSC Curve of ST ₁ Cp ₇ POSS Macromer	69
Figure 3.36: DSC Curve of Styrenyl ₁ Cp ₇ POSS Macromer	- 69
Figure 3.37: DSC Curve of CyHe ₁ Cp ₇ POSS Macromer	- 70
Figure 3.38: DSC Curve of V ₁ Cp ₇ POSS Macromer	- 70
Figure 3.39: DSC Curve of ST ₁ Isobu ₇ POSS Macromer	71
Figure 3.40: DSC Curve of Styrenyl ₁ Isobu ₇ POSS Macromer	- 71
Figure 4. 1: TEM Image of Cp ₈ POSS/PS2M Blend (50 wt% POSS)	84
Figure 4. 2: TEM Image of ST ₁ Cp ₇ POSS/PS2M Blend (50 wt% POSS)	84
Figure 4. 3: TEM Image of Styrenyl ₈ POSS/PS2M Blend (50 wt% POSS)	85
Figure 4. 4: TEM Image of Ph ₈ POSS/PS2M Blend (50 wt% POSS)	86
Figure 4. 5: TEM Image of Cy8POSS/PS2M Blend (50 wt% POSS)	87
Figure 4. 6: TEM Image of V ₈ POSS/PS2M Blend (50 wt% POSS)	87
Figure 4. 7: TEM Image of CyHe ₁ Cp ₇ POSS/PS2M Blend (50 wt% POSS)	88
Figure 4. 8: TEM Image of V ₁ Cp ₇ POSS/PS2M Blend (50 wt% POSS)	88
Figure 4. 9: TEM Image of Cp ₈ POSS/PS2M Blend (20 wt%)	90
Figure 4. 10: TEM Image of Cy ₈ POSS/PS2M Blend (20 wt%)	- 90
Figure 4. 11: TEM Image of Styrenyl ₈ POSS/PS2M (20 wt%)	91

.

Figure 4. 12:TEM Image of Ph ₈ POSS/PS2M Blend (20 wt%)91
Figure 4. 13: TEM Image of V ₈ POSS/PS2M Blend (20 wt%)92
Figure 4. 14: TEM Image of ST ₁ Cp ₇ POSS/PS2M Blend (20 wt%)92
Figure 4. 15: TEM Image of Ph ₈ POSS/PS216K Blend (20 wt%)93
Figure 4. 16: X-Ray Diffraction Profile of Cp ₈ POSS/PS2M Blends97
Figure 4.17: X-Ray Diffraction Profile of Cy ₈ POSS/PS2M Blends99
Figure 4.18: X-Ray Diffraction Profile of Styrenyl ₈ POSS/PS2M Blends100
Figure 4. 19: X-Ray Diffraction Profile of Ph ₈ POSS/PS2M Blends101
Figure 4. 20: X-Ray Diffraction Profile of V ₈ POSS/PS2M Blends103
Figure 4.21: X-Ray Diffraction Profile of ST ₁ Cp ₇ POSS/PS2M Blends104
Figure 4.22: X-Ray Diffraction Profile of V ₁ Cp ₇ POSS/PS2M Blends105
Figure 4.23: X-Ray Diffraction Profile of CyHe ₁ Cp ₇ POSS/PS2M Blends106
Figure 4.24: X-ray Diffraction Profiles of Cp ₈ POSS/PS (20wt%) Blends with Different M.W. PS108
Figure 4.25: X-ray Diffraction Profiles of ST ₁ Cp ₇ POSS/PS (20wt%) Blends with Different M.W. PS109
Figure 4.26: DSC Curve of PS1M112
Figure 4.27: DSC Curve of PS1M/Cp ₈ POSS (20wt% POSS Loading)112
Figure 4.28: DSC Curve of PS1M/Cp ₈ POSS (50wt% POSS Loading)113
Figure 4.29: DSC Curve of PS1M/Cp ₈ POSS (80wt% POSS Loading)113
Figure 4.30: DSC Curve of PS1M/Styrenyl ₈ POSS (20wt% POSS Loading) 114
Figure 4.31: DSC Curve of PS1M/Styrenyl ₈ POSS (50wt% POSS Loading)114
Figure 4.32: DSC Curve of PS1M/Styrenyl ₈ POSS (80wt% POSS Loading)115
Figure 4.33: DSC Curve of PS1M/Ph ₈ POSS (20wt% POSS Loading)115

Figure 4. Figure 4. Figure 4 Figure 4. Figure 4.-Figure 4. Figure 4.4 Figure 4. Figure 4.4 Figure 4.4 Figure 5.1 Figure 5.2 Figure 5.3 Figure 5.4 Figure 5.5 Figure 5.1 Figure 5.

Figure 4.34: DSC Curve of PS1M/Ph ₈ POSS (50wt% POSS Loading)116
Figure 4.35: DSC Curve of PS1M/Ph ₈ POSS (80wt% POSS Loading)116
Figure 4.36: DSC Curve of PS1M/Isobu8POSS (20wt% POSS Loading)117
Figure 4.37: DSC Curve of PS1M/Isobu8POSS (50wt% POSS Loading)117
Figure 4.38: DSC Curve of PS1M/Isobu8POSS (80wt% POSS Loading)118
Figure 4.39: DSC Curve of PS1M/ST ₁ Cp ₇ POSS (20wt% POSS Loading)118
Figure 4.40: DSC Curve of PS1M/ ST ₁ Cp ₇ POSS (50wt% POSS Loading) 119
Figure 4.41: DSC Curve of PS1M/ST ₁ Cp ₇ POSS (80wt% POSS Loading) 119
Figure 4. 42: TGA Curves of PS2M/Cp ₈ POSS Blends 124
Figure 4.43: TGA Curves of PS2M/Cy8POSS Blends124
Figure 4.44: TGA Curves of PS2M/V ₈ POSS Blends 125
Figure 4. 45: TGA Curves of PS2M/ST ₁ Cp ₇ POSS Blends125
Figure 4.46: TGA Curves of PS2M/V ₁ Cp ₇ POSS Blends126
Figure 4. 47: TGA Curves of PS2M/CyHe ₁ Cp ₇ POSS Blends126
Figure 4.48: TGA Curves of PS2M/Styrenyl ₈ POSS Blends 127
Figure 4.49: TGA Curves of PS2M/Ph ₈ POSS Blends 127
Figure 5.1: Chemical Structure of Polydimethyl Siloxane (PDMS) 130
Figure 5.2: X-ray Profile of SE72/Cp ₈ POSS Blend (20 wt% POSS loading) 136
Figure 5.3: X-ray Profile of SE72/V ₈ POSS Blend (20 wt% POSS loading) 136
Figure 5.4 X-ray Profile of SE72/Isobu ₈ POSS Blend (20 wt% POSS loading) 137
Figure 5.5: X-ray Profile of SE72/ST ₁ Cp ₇ POSS Blend (20 wt% POSS loading) 137
Figure 5.6: X-ray Profile of SE72/Styrenyl ₁ Cp ₇ POSS Blend (20 wt% POSS loading)-138
Figure 5.7: X-ray Profile of SE72/CyHe ₁ Cp ₇ POSS Blend (20 wt% POSS loading)138

		Figure 1
		Figure 1
		Figure :
		Figure
		Figure 1
		Figure 1
		Figure 1
		Figure
		Figure
		Figure :
		Figure
		Figure 5
		Figure 5
		Figure 5 of frequ (open sy
		Figure 4 /SE72 B
		Figure struction
		Figure 5 gelied ar
		Figure Isobu, Pr at 30 C

Figure 5.20: Storage Modulus, as a function of frequency, of POSS/SE72 Blends at 30°C-

Figure 5.21: Comparison of Modulus (G' and G"), and Loss Tangent (tan δ), as a function of frequency, of Isobu₈POSS/SE72 Blend (10wt% POSS Loading) before annealing (open symbols) and after annealed for 60 hours at 200°C (filled symbols)-------155

Figure 5.22: Rheological Properties Changes of the 10 weight % Loading Isobu₈POSS /SE72 Blend with Annealing Time at 200°C ------ 156

Figure 5.23: Comparison of the Storage Modulus (G') and Loss Modulus (G"), as a function of frequency, of PDMS (SE72) at different annealing time at 200°C------158

Figure 5.24: Comparison of Rheological Properties, as a function of frequency, of ungelled and gelled Isobu₈POSS/Visc100M (10wt%) Blend at 30°C ------ 160

Figure 5.25: Storage Modulus, as a function of strain, for un-gelled and gelled Isobu₈POSS/Visc100M Blends of 10wt% POSS loading. The experiment was performed at 30°C and with angular frequency of 62.9 1/s------162

Figure 2 POSS) I Figure 200°C I Figure 1 Blends Figure 1 during 0 Figure POSS Io Figure f POSS lo Figure Isobu_sP(Figure 5 Figure 5 Blend (1) Figure 5. different Figure 5... (Visc100) Figure 5.3 PDMS Bly Figure 5.3 PDMS (V Figure 5 COwt? P Figure 5. 120wt% P

Figure 5.1

Figure 5.26: Creep Behavior of the un-gelled and gelled Isobu₈POSS/Visc30M (20wt% POSS) Blends. The experiment was conducted at 30°C, and shear stress of 500Pa ---- 163

Figure 5.27: DSC Result of Isobu₈POSS/SE72 (20wt% POSS Loading) Blend under 200°C Isothermal Condition for 6hr ------ 165

Figure 5.28: Creep Compliances of gelled Isobu₈POSS/Visc30M (10 wt% POSS loading) Blends under shear stresses of 5 and 10 KPa at 30°C ------166

Figure 5.29: Shear Rate of Gelled Isobu₈POSS/Visc30M Blends (10wt% POSS loading) during creep test (under shear stresses of 5 and 10 KPa at 30°C)-----167

Figure 5.30: Viscosity, versus time, of Gelled Isobu₈POSS/Visc30M Blends (10wt% POSS loading) during creep test (under shear stresses of 5 and 10 KPa at 30°C)------167

Figure 5.31: Modulus Comparison of the Gelled Isobu₈POSS/Visc30M Blend (10 wt% POSS loading) before and after the 5 KPa creep test ------168

Figure 5.32: Comparison of Modulus, as a function of frequency, of Gelled Isobu₈POSS/Visc30M Blends (10wt% POSS) before and after the 10 KPa creep test--169

Figure 5.33: Re-Gelation of Isobu₈POSS/Visc30M Blend (10wt%POSS) at 200°C ----170

Figure 5.34: Modulus, as a function of frequency, of Re-gelled Isobu₈POSS/Visc30M Blend (10wt% POSS) 30°C-----171

Figure 5.35: Gelation Rates of Blends of PDMS (SE72) with POSS Macromers bearing different Corner Groups (20wt% POSS Loading) at 200°C------176

Figure 5.37: Effects of PDMS Molecular Weights on the Gelation Rates of Isobu₈POSS/ PDMS Blends (20wt% Loading) ------181

Figure 5.38: Effects of Annealing Temperatures on the Gelation Rates of Isobu₈POSS/ PDMS (Visc30M) Blends (10wt% POSS Loading)------ 182

Figure 5.39: X-ray Diffraction Profiles of Styryl₁Isobu₇POSS/PDMS (SE72) Blends (20wt% POSS Loading) Before and After Gelation ------ 184

Figure 5.40: X-ray Diffraction Profiles of Styrenyl₁Isobu₇POSS/ PDMS (SE72) Blends (20wt% POSS Loading) Before and After Gelation ------ 184

Figure 5.41: Schematic Diagram of the Formation of the POSS-PDMS Network -----186

Figure 5.-Mixture----

.
1.1 Stat		
Si		
played a		
this incr		
usage te		
Ir		
fillers i		
has exh		
two ch		
(process		
(therma		
nanome		
with siz		
scientis		
which J		
(
the inc		
traditic		
structu		
(RSiO		

CHAPTER 1

INTRODUCTION

1.1 Statement of the Problems

Since their discovery almost 150 years ago, synthetic polymers have played an increasingly important role in daily life. However, along with this increased use have come more demanding requirements such as higher usage temperature and greater resistance to oxidation, etc.

In recent years, the use of small amounts of nanoscopic inorganic fillers in commodity polymers such as nylon, polypropylene, epoxy, etc. has exhibited significant performance enhancement. This approach has two characteristics. First, it combines the properties of polymers (processability and toughness) with the properties of inorganic compounds (thermal and oxidative stability). Second, it has an inorganic phase with a nanometer size. Nano-phase materials belong to a new family of materials with size intermediate to those usually studied by chemists and material scientists. They often exhibit enhanced physical and chemical properties, which are sometimes dramatically different from their neat counterparts.

Our approach to organic-inorganic nanoscopic materials involves the incorporation of Polyhedral Oligomeric Silsesquioxanes (POSS) into traditional polymeric systems. POSS macromer is a three-dimensional structurally well-defined cage-like molecule represented by formula $(RSiO_{1.5})_{\rm R}$ (n= 6, 8, 10..., R is organic corner groups). POSS technology

has two POSS m. by organ. of POSS organic J POSS m compatib these or Second. nearly eq Be macrome material polymer reactive variety monofur to produ organic compat: reinforc polyme

has two unique features. First, the chemical composition is a hybrid: POSS macromers have an inorganic silica-like core, which is surrounded by organic groups. One example, as shown in Figure 1.1, is the structure of POSS macromer with a cubic shape $(R_7Y_1Si_8O_{12})$. The nature of the organic corner groups on the POSS cages determines the properties of the POSS macromers, such as: crystallinity, solubility, reactivity and their compatibility with polymers. Furthermore, it is also possible to modify these organic corner groups to produce the desired functionalities. Second, the physical size of POSS macromers is about 1.5 nm ^[1], which is nearly equivalent in size to most polymer segments and coils.

Because of its hybrid nature and nanometer scale feature, POSS macromer is a promising material for preparing nano-reinforced polymeric materials. There are two methods to incorporate POSS macromers into polymeric systems. First, POSS macromers, which contain functional reactive sites, can be incorporated with organic species to produce a variety of organic-inorganic hybrid polymers. An example of a monofunctional POSS macromer co-polymerized with an organic monomer to produce a linear hybrid polymer is shown in Figure 1.2.^[2] Second, the organic groups surrounding the POSS framework can be made to be compatible with polymer matrix to form blends with nano-filler reinforcement. These two approaches combine the best features of polymers with the best features of ceramics. In comparison to











convent		
exhibit		
В		
develop		
modifie		
and ela		
concent		
effort t		
address		
12110-m		
matrix.		
materia		
1.2 Intr		
1.2.1 0		
Т		
and pro		
POSS/P		
lead to		
1.2.2 p		
This u		
Part 1.		

conventional filled-polymers, these POSS-containing polymers may exhibit a significant number of enhanced properties.

Because blending is the most effective engineering approach to develop materials with improved properties, (for example: organic modified clay, carbon black, and fumed silica have been used in plastics and elastomers to form nanoscopic-materials by blending), this work is concentrated on the blending of POSS macromers with polymers in an effort to prepare POSS/polymer nanoscopic materials. We attempt to address fundamental issues involving in the formation of POSS/polymer nano-materials ----- how POSS is "molecularly" dispersed in polymeric matrix, and what are the structure/property relationships of these nanomaterials.

1.2 Introduction to this Research Work

1.2.1 Objective:

The objective of this research work was to study the morphologies and properties (such as: thermal and rheological properties) of the POSS/Polymer blends, and to develop structure-property relationships that lead to optimum performance of the POSS/Polymer nano-materials.

1.2.2 Research Approach:

This work is composed of two parts:

Part I: Investigations of POSS Macromers

Stru Chapter 3 the corne properties the POSS using Dif Analysis examined higher th and the s macrome undergo stabilitie Part II: I St (PS) and Chapter Tł between dispersio effects c different Structure/Property Studies of POSS macromers were reported in Chapter 3. In particular, we were interested in understanding the impacts of the corner groups on the morphologies (ordered or amorphous) and properties (such as transition temperature, decomposition temperature) of the POSS macromers. Thermal property and stability were investigated using Differential Scanning Calorimeter (DSC), and Thermogravimetric Analysis (TGA), while crystalline structures of POSS macromers were examined using wide angle X-ray diffraction. The results showed that the higher the degree of the symmetry and regularity of the POSS macromers and the smaller the size of the corner groups, the more ordered the POSS macromers. And the POSS macromers with functionalities, which may undergo chemical cross-linking reactions, possessed high therma! stabilities.

Part II: Investigations of POSS/Polymer Blends

Studies of the morphologies and properties of the POSS/Polystyrene (PS) and POSS/Polydimethyl Siloxane (PDMS) mixtures are described in Chapter 4 and Chapter 5, respectively.

The morphologies of the POSS/polymer blends and the interface between the two components are the key points in developing molecular dispersion of POSS nano-cluster in polymers with desired properties. The effects of the POSS macromers with varying corner groups, polymers with different molecular weights, and amounts of POSS macromers used on the

morpholog Microscop the interac The depending chemical POSS/pol in the nat T٢ was exa gelation In order of the followi macron polyme experi was po under blends PDMS behav. morphologies of the blends were examined using a Transmission Electron Microscope (TEM), and X-ray diffractometer. DSC was used to investigate the interactions between POSS macromers and PS.

The morphologies of the POSS/PS and POSS/PDMS showed that depending on the attached chemical groups on the POSS cages and the chemical features of the polymer matrix, the morphologies of the POSS/polymer ranged from complete separation to homogeneous dispersion in the nanoscopic scale.

The interaction between POSS with varying organic groups in PDMS was examined using rheological techniques. We found that physical gelation occurred in PDMS with molecularly dispersed POSS incorporation. In order to examine the nature of the POSS/PDMS gelation, the properties of the gelled POSS/PDMS systems were studied, and the impacts of the following factors on the POSS/PDMS associations were investigated: POSS macromers with different chemical structures, molecular weight of polymer, annealing temperature, and POSS concentration. Based on the experimental results, the gelation mechanism of the POSS/PDMS blends was postulated.

The rheological results of the POSS/PDMS blends revealed that under elevated temperatures, the gelation occurred in the POSS/PDMS blends was a result of intermolecular association between POSS filler and PDMS polymer chains. The formation of gel exhibited a solid-like behavior. Gelled POSS/PDMS blends exhibited high modulus and

significa nonlinea physical stain/str POSS c revealed macrom macrom gelation tempera molecul Ir groups also in v 1.2.3 C S first tin the know () (such a Property the corn significantly improved creep resistance, and they also displayed stronger nonlinear rheological behaviors than the un-gelled blends. Because of its physical nature, the POSS/PDMS gel could be destroyed under large stain/stress and re-formed under elevated temperatures. The studies of the POSS chemistry's effects on the gelation of the POSS/PDMS blends revealed that associations tended to occur in systems where POSS macromers were well dispersed in polymer matrix, i.e. where POSS macromers had good compatibility with polymer. It was also found that the gelation rates of POSS/PDMS blends increased with raising the annealing temperatures and the POSS concentrations, and with lowering the PDMS molecular weights.

In addition, the effects of POSS macromers with different corner groups on the thermal properties of POSS/PS and POSS/PDMS blends were also investigated with TGA.

1.2.3 Contributions to the POSS Nano-Technology:

Systematic studies on the POSS/polymer nano-materials were, for the first time, conducted in this research work. Contributions of this work to the knowledge of POSS Nano-Technology are:

(1) POSS macromers with desired microstructures and properties (such as: crystallinity, reactivity, solubility, surface property, thermal property, compatibility with other materials) can be obtained by modifying the corner groups on the POSS cage.

(2)	
miscibilit	
miscible,	
blends ra	
nanosco	
(
chemica	
massive	
exceller	
(
POSS/I	
maduli	
UCCUT There	
malfix	
_	
nanosc	
intera	
and ir	
intera	
disper	
requir	
funci	

(2) Through appropriate functionalization of the POSS cages, the miscibility between POSS macromer and polymer varies from immiscible to miscible, and correspondingly, the morphology of the POSS/polymer blends ranges from complete separation to homogeneous dispersion in the nanoscopic scale.

(3) POSS macromers with proper reactive corner groups induce chemical reactions between POSS and polymer. The attachment of POSS massive cages to polymer chains renders POSS/polymer blends with excellent heat resistance.

(4) The physical gelation between POSS and PDMS endows the POSS/PDMS blends with a solid-like behavior. Gelled blends exhibit high modulus and significantly improved creep resistance. Associations tend to occur in blends where POSS macromers are well dispersed in polymer matrix, i.e. where POSS macromers have good compatibility with polymer.

In summary, the crucial factors in developing POSS/polymer nanoscopic materials with desired properties are the compatibility and interactions between the two components, which determine the morphology and interface of the POSS/polymer blends. Good compatibility and strong interactions between POSS macromer and polymers result in a nanodispersed POSS/polymer blend with excellent performance, and these two requirements may be achieved by selecting POSS macromers with desired functional corner groups.

Το
high perf
studying
One clas
polyhedr
generic
equal to
silsesqu
homoger
additive
modifie
polyme
2.1 Ch
2
with or
^{bond} e
strong;
Theref
chemis

CHAPTER 2

LITERATURE REVIEW

To meet the challenges for a new generation of lightweight, and high performance polymeric materials, materials scientists have been studying the possibility of nanoscale reinforcements for nearly a decade. One class of compounds potentially suited for such development is polyhedral oligomeric silsesquioxanes (POSS). POSS are compounds with generic formula ($RSiO_{1.5}$)_n, where R are various hydrocarbons and n is equal to 6, 8, 10 or higher. Chemically and structurally well-defined silsesquioxanes can be used as models for silica, as ligands in homogeneous models for aluminosilicates, silica-supported catalyst, as additives (such as crosslinking agents, flame retardants, thermal modifiers, and nano-reinforcing fillers) and as building blocks for polymers.

2.1 Chemistry of Silsesquioxanes

Second only to carbon, silicon forms the largest number of bonds with other elements. However, unlike carbon, where C-C, C-O, and C-H bond energies are approximately equal, the Si-O bond is considerably stronger than the Si-H bond and much stronger than the Si-Si bond. Therefore, chains of Si-O-Si-O-Si make up the skeletons of silicate chemistry.

S the form silicate dimens therefo silicate higher; are also is conn 2.1.1 A H to int silsesq commo atoms. atoms. for (HS 2.1.2 B S 1800s. hydroly

Silicates can occur as rings, connected in chains and layers, or in the form of cages. Among these four types of silicates, the cage structured silicates compounds represent a rather versatile class of potential threedimensional building block units for the synthesis of new materials, and therefore they are of considerable theoretical and practical interest. Cage silicates, with a general formula of $(XSiO_{1.5})_n$, (where n = 6, 8, 10 or higher; and X can be hydrogen atoms, organic groups or siloxy groups), are also referred as Sil-ses-quioxanes, which denote that each silicon atom is connected to three oxygen atoms.

2.1.1 Abbreviations for Silsesquioxanes:

Before discussing the chemistry of silsesquioxanes, it is necessary to introduce the notations used to shorten the formulae of the silsesquioxanes. In silicates chemistry, M, D, T and Q letters are commonly used to abbreviate a silicon atom bearing 1, 2, 3, or 4 oxygen atoms, respectively. Subscripts are used to indicate the number of silicon atoms, and superscripts to designate the function borne. Examples are T_n^H for $(HSiO_{1.5})_n$, R_nT_n for $(RSiO_{1.5})_n$, and Q_n for $(RR'R"SiOSiO_{1.5})_n$.

2.1.2 Brief History of Silsesquioxanes:

Silsesquioxanes were first synthesized by Ladenburg^[3] in the late 1800s. In the early 1900s, Meads and Kipping ^[4] investigated the hydrolysis and condensation reactions of trifunctional silanes and arrived

at the c leads to conclusi underde Vogt^{15.6}

thermal

phenyl

silsesqu

early s

function

T

only du

discove

access

silsesqu

increas

develor

manipu

silsesq

as octa

availab

at the conclusion that polycondensation of "siliconic acids" invariably leads to extremely complex mixtures with little synthetic value. This conclusion caused the chemistry of silsesquioxanes to remain underdeveloped for a long time. It wasn't until 1965 that Brown and Vogt^[5,6] found that phenyl oligosilsesquioxanes exhibit remarkable thermal stability and can be prepared in high yields from readily available phenyl trichlorosilane. Since then, many stoichiometrically well-defined silsesquioxane frameworks have been reported ^[7-9]. However, during the early studies, the majority of known silsesquioxanes lacked sufficient functionality for most chemical applications.

The pool of known silsesquioxane frameworks expanded rapidly only during the past several years. Some of this expansion is due to the discovery of new spontaneous self-assembly reactions that provide ready access to multi-gram quantities of several synthetically versatile silsesquioxane frameworks ^[10, 11]. Another important reason for the rapid increase in the number of known silsesquioxane frameworks is the development of general and highly efficient methodology for synthetically manipulating both the Si/O core and organic pendant groups on silsesquioxane frameworks. Highly functionalized silsesquioxanes, such as octaepoxidePOSS, and octapropyIPOSS, can be prepared with readily available octavinyIPOSS and the methodology is quite general ^[12-14].

2.1.3 Stru

Thd

formula (

silicon at

vertices t

the one c

cubic sha

the cente

.

Figure

^{on} the

^{\$0-c}a]]

comma

2.1.3 Structure and Classification of Silsesquioxanes:

The structure of cage silicates (silsesquioxanes), with a general formula $(XSiO_{1.5})_n$, is based on Si-O linkages forming a cage with a silicon atom at each vertex. Substituents (X) coordinate around the silicon vertices tetrahedrally. The most studied nanobrick for hybrid materials is the one containing eight silicon atoms (Figure 2.1). It exhibits an almost cubic shape with one silicon atom at each corner. The oxygen atoms are at the center of the edges, slightly shifted toward the outside.



X can be Hydrogen atoms, Organic Groups or Siloxy Groups

Figure 2.1 Schematic Diagram of Silsesquioxanes with a Cubic Shape (X₈Si₈O₁₂).

Within the general formula $(XSiO_{1.5})_n$, a classification can be made on the nature of the X groups. They can be hydrogen atoms, leading to the so-called polyhedral oligohydridosilsesquioxane (POHSS), which are commonly abbreviated as T_n^H . X can also be organic moieties bound to

silicon	
(POSS).	
groups	
the cage	
spheros	
2.1.4 S	
Polyho	
-	
oligoh	
exceed	
based	
contai	
water	
mixtu	
separa	
only b	
numer	
Prefer	
Spher	
With r	

silicon through a Si-C bond, leading to polyhedral oligosilsesquioxanes (POSS), which are commonly abbreviated as T_n . Finally, X can be siloxy groups (RR'R"SiO-). In this last case, the organic moieties are bound to the cage framework through Si-O-Si links and those nanobricks are named spherosilicates, which are commonly abbreviated as Q^n .

2.1.4 Synthesis of Silsesquioxanes:

Polyhedral Oligohydridosisesquioxane (POHSS) T_n^H:

The first report the preparation polyhedral on of а oligohydridosilsesquioxane ($H_8Si_8O_{12}$) was made in 1959 with the exceedingly small yield of 0.2%.^[15] In 1991, Agaskar proposed a method based on a biphasic reaction medium (HCl_{ag}, methanol, hexane, toluene) containing FeCl₃.^[16] In such a medium, HSiCl₃ is slowly hydrolyzed by the water released from the partially hydrated iron salt. This synthesis leads to a mixture of T_8^H and T_{10}^H , yields being 17.5% and ~8%, respectively after separation and purification. The other T_n^H compounds (n=12, 14, 16, 18) can only be prepared with very low yields $\sim 1\%$, and need to be separated through numerous and complex steps. Those low yields likely explain the preferential use of T_8^H in hybrid materials.

Spherosilicates Q_n:

The synthesis of compounds following the formula $(RMe_2SiOSiO_{1.5})_n$, with R: H, CH₃, CH=CH₂, CH₂CH=CH₂ and CH₂Cl, has been proposed in the

literature
(0\$i0 ₁ 5).
Spt
at least 2-
by treatin
good yie
propose t
The draw
T _n ^H com
reactions
Th
(0\$i0 ₁ ,
be prepa
hydrol v z
the form
ammoni
from su
Various
St.m.L
synthes.
metal a

literature from the oligohydrido $(HSiO_{1.5})_n$, or from the polyanions, $(OSiO_{1.5})_n^{n-1}$.

Spherosilicates can be prepared by reacting the T_n^H compounds with at least 2n equivalents of Me₃NOClSiMe₂R, this reagent being first obtained by treating ClSiMe₂R with anhydrous Me₃NO.^[17, 18] This reaction offers good yields of at least 50%. The need for 2n equivalents has allowed to propose the following mechanism:

 $(HSiO_{1.5})_n + Me_3NOClSiMe_2R \longrightarrow$

 $(RMe_2SiOSiO_{1.5})_n + nMe_3NClSiMe_2R + nMe_3NOHCl$

The drawback of this method, however, is that the reaction starts from the T_n^H compounds whose syntheses strongly reduce the overall yield of the reactions.

The other synthetic route uses as precursors the polyanions $(OSiO_{1.5})_n^{n-}$, which exhibits the same cage structure. These compounds can be prepared with very good yields from aqueous silicate solutions or by hydrolyzing Si(OCH₃)₄ under basic conditions.^[19, 20] In both cases, to favor the formation of the cage structures, the key point is the use of quaternary ammonium as charge compensating cations.

Spherosilicates with more complex functions can also be prepared from simple ones (R: H, vinyl...). As an example, the hydrosilylation of various unsaturated compounds by $(HMe_2SiOSiO_{1.5})_8$ has allowed to synthesize nanobricks bearing epoxy function, trimethoxysilanes groups, or metal alkoxides moieties through the complexation by a β -ketoester. ^[21, 22]

Polyhed	
Т	
skeletor	
hydroly	
where	
reactive	
oligosil	
RSiY ₃	
equatio	
H	
compli	
format	
the cor	
charac	
group	
rate of	
polyhe	
above-	
difficu	
are ver	
incomp	

Polyhedral Oligomeric Silsesquioxanes (POSS) T_n:

The most common process used to obtain polyhedral silicon-oxygen skeletons of oligosilsesquioxanes with R as an organic group is by the hydrolytic condensation of trifunctional organosilicon monomers $RSiY_3$, where R is a chemically stable organic substituent and Y is a highly reactive substituent, such as Cl, or alkoxy. The formation of oligosilsesquioxanes in the course of hydrolytic polycondensation of RSiY₃ monomers in dilute solvents can be represented by the overall equation:

 $nRSiY_3 + 1.5n H_2O$ (RSiO_{1.5})_n +3nHY

However, in reality the above reaction is a multistep and rather complicated process. The hydrolysis of $RSiY_3$ involves the consecutive formation of linear, cyclic, polycyclic, and finally polyhedral siloxane^[15].

The reaction above is strongly dependent of many factors, such as: the concentration of initial monomer in the solution; nature of the solvent; character of substituent R in the initial monomer; nature of functional group Y in the initial monomer; the type of catalyst employed, temperature, rate of addition of water and quantity of water added; and solubility of the polyhedral oligomers formed. Because of the strong mutual effects of the above-mentioned factors, the precise polycondensation process is very difficult to predict. The products of hydrolytic polycondensation of RSiY₃ are very complicated. It is a mixture of fully condensed silsesquioxanes, incompletely condensed silsesquioxanes and resins (Figure 2.2)^[23].

2

Ł

R JOH

Ľ

.



Figure 2.2: Complex Products of RSiCl₃ Hydrolytic Polycondensation Reaction

Experime

the desir

1. Fu

In

equivale

complete

cyclohe

as Viny

oxidized

variety



have a

Experimental conditions have to be optimized to favor the formation of the desired silsesquioxane product.

1. Fully Condensed Silsesquioxanes:

In general, fully condensed POSS systems (Figure 2.3) contain equivalent organic groups on each silicon atom, rendering them either completely functionalized with stable groups, for example, the cyclohexyls in Cy₈T₈, or fully functionalized with reactive groups, such as Vinyl₈T₈ ^[24, 25]. Fully functionalized POSS can be chlorinated ^[9], oxidized to spherosilicates ^[26, 27], or treated with olefins to produce a variety of hydrosilylation products ^[28-29].



Figure 2. 3: Examples of Fully Condensed POSS Systems

2. Incompletely Condensed Silsesquioxanes:

Incompletely condensed silsesquioxane frameworks (Figure 2.4) have attracted a great deal of attention. The reactivity of the silanol

groups 1 models alumino Н

conder

famili_c

additiv

agents.

groups makes the incompletely condensed POSS system of interest as models for silica ^[30-34], as ligands in homogeneous models for aluminosilicates^[35-39] and silica supported catalysts ^[40-43]. Incompletely



Figure 2. 4: Examples of Incompletely Condensed POSS Systems

condensed silsesquioxane systems are also very useful precursors to new families of graftable or polymerizable macromers that can be utilized as additives for polymers (for example: crosslinking agents, nano-reinforcing agents, and thermal modifiers) and for the preparation of POSS-based

Ŕ

frai unti

var

be p

of al

hyd*rc*

mono

oligos
polymeric systems. For example, the trisilanol functionality of the $R_7T_4D_3(OH)_3$ structure (Figure 2.5) can be corner capped with various silane coupling agents, which contain organic groups suitable for polymerization, to produce fully condensed T_8 POSS compounds with controlled functionality. Through variation of the Y group on the silane, a



Figure 2. 5: Corner Capping of R₇T₄D₃(OH)₃.

variety of functionalities can be placed off the corner of the POSS framework. Subsequent transformations of this group can be carried out until the desired functionality has been obtained.

A variety of incompletely condensed silsesquioxane frameworks can be prepared in synthetically useful quantities via hydrolytic condensations of alkyl- or aryltrichlorosilanes (Figure 2. 6). In most cases, however, trifunctional hydrolytic condensation reactions of organosilicon afford complex resins and/or fully condensed monomers oligosilsesquioxanes, rather than incompletely-condensed frameworks.



Figure 2. 6: Incompletely Condensed Silsesquioxane Prepared by the Hydrolytic Condensation of (c-C₆H₁₁)SiCl₃.

Recently, the discovery that a single Si-O-Si linkage in a fully condensed framework can be cleaved selectively by strong acids or base (e.g. HBF₄/BF₃, TfOH, and Et₄NOH) provides an important method for preparing many useful incompletely condensed frameworks ^[44-51]. For example: $R_8Si_8O_{12}$ (R=c-C₆H₁₁) reacts selectively with aqueous Et₄NOH to afford discrete incompletely condensed silsesquioxanes: it first produce $R_8Si_8O_{11}(OH)_2$, which reacts further with Et₄NOH to produce $R_7Si_7O_9(OH)_3$ (Figure 2. 7).



Figure 2. 7: Base-mediated Cleavage of Fully Condensed [C₆H₁₁)₈Si₈O₁₂]

2.2
thr
con
wit
hyb
лап
inor
2.2.
poly
poly
with
the 1
desir
macr
termi
and a
COnol.
••µ01

2.2 Polymeric Materials Containing POSS

POSS macromers can be incorporated into polymeric systems through two techniques:

1) Hybrid Polymers containing POSS: POSS macromers, which contain functional organic reactive sites, can polymerize or copolymerize with other organic species to produce a variety of organic-inorganic hybrid homopolymers or copolymers.

2) POSS/Polymer Nanoscopic Blends: POSS macromers, used as nano-reinforcing agents, blend with polymers to produce inorganic/organic nanoscopic materials.

2.2.1 Organic-Inorganic Hybrid Polymers Containing POSS

POSS macromers can be polymerized using a standard polymerization protocol (i.e. radical polymerizations, condensation polymerizations, ring opening polymerizations etc.) to provide polymers with a variety of architectures as illustrated in Figure 2. 8. Depending on the type of functionality contained on the POSS macromers and on the desired polymer architecture, POSS macromers can be introduced into macromolecular systems as either a main chain, side chain, or as chain terminus groups ^[52].

Several POSS homopolymers and copolymers have been synthesized and characterized, for example: POSS-Styryl based homopolymers and copolymers ^[53-56], methacrylates-POSS polymers ^[57, 58], norboryl- POSS

cop

[6].

sho POS

groi

poly

pha

•

55.5

copolymers ^[59], POSS-siloxane copolymers ^[60,], POSS-epoxy polymers ^[61, 62], POSS-polyurethane copolymers ^[63, 64], etc. (some examples are shown in Figures 2.9, 2.10, 2.11 and 2.12). The property studies of these POSS containing polymers showed that because the massive inorganic groups (i.e. POSS cages) are attached to polymer chains, the POSS-polymer chains act like nanoscale reinforcing fibers or like a hard block phase separated from a soft block, producing enhanced heat resistance ^[53-55, 58, 61, 63] and mechanical properties ^[55, 59, 61].











Figure 2. 8: Architecture of POSS-based Polymers

Stars

Triblocks





POSS-Methacrylate/Methacrylate Copolymer

Figure 2. 9: Polymerization of Methacrylates-POSS Homopolymer and Copolymer



Figu

.

Mezsi ()



Figure 2. 10: Free Radical Polymerization of Styryl-POSS based Copolymer



Figure 2.11: POSS-Siloxane Copolymer



Figure 2.12: Schematic of the Curing Cycle of the POSS-Epoxy System

2.2.2
POS
into
(C ₆ F
and
com
film
bler
leve
unbl
tran
ther
POS
incr
to t
enh;
the .

2.2.2 POSS/Polymer Nano-Materials:

Currently there are few literatures concerning the investigation of POSS/polymer nano-materials, where POSS macromers are incorporated into polymer by blending. Only a couple of papers are found so far.

^[57] blended $(C_6H_5)_6Si_6O_9$, Lichtenhan, Noel, Bolf and Ruth (C₆H₅)₈Si₈O₁₂, and Acrylic-POSS macromer with PMMA at 3, 6, 9, 12, 15, (w/w) level. Acrylic-POSS and 30% macromer showed better compatibility with PMMA than the other two POSS macromers. Clear films were obtained only at 3 and 6% loading levels for the $(C_6H_5)_6Si_6O_9$, and (C₆H₅)₈Si₈O₁₂ macromers. But Acrylic-POSS macromer / PMMA blends were clear throughout the 3-30% loading range. At 3-6% loading levels the TGA and DSC traces were observed to be similar to those of unblended PMMA in terms of the onset temperature of decomposition, char yield, and glass transition. This suggests that despite their transparency and apparent homogeneity there was no significant effect on thermal properties and little if any interaction between the PMMA and the POSS macromers. The visible phase-separated 15% and higher loaded blends with $(C_6H_5)_6Si_6O_9$, and $(C_6H_5)_8Si_8O_{12}$ showed a modest 5-10°C increase in glass transition by DSC over unblended PMMA, which is due to the POSS rich surface layer on the samples rather than a true property enhancement. Char yields were observed to be higher in blends containing the Acrylic-POSS macromer.

I
polypr
shear
crystal
POSS
concer
indica
of PO
shear-
that th
during
cross
chain
chain
additi
blend
of un
key j
devel
nanor

Fu, Yang, Somani, etc. ^[65] studied the crystallization of isotactic polypropylene (iPP) containing nanostructured POSS at quiescent and shear state. It was observed that the addition of POSS increased the crystallization rate of iPP at quiescent condition, which suggests that POSS crystals act as nucleating agents. However, at 30wt% POSS the crystallization rate was significantly reduced, concentration, indicating a retarded growth mechanism due to the molecular dispersion of POSS in the matrix. In situ SAXS was used to examine the behavior of shear-induced crystallization of the POSS/PP blends. The results showed that the addition of POSS significantly increased the crystallization rate during shear. The authors postulate that POSS molecules behave as weak crosslinkers in polymer melts and increase the relaxation time of iPP chains after shear. Therefore, the overall orientation of the polymer chains is improved and a faster crystallization rate is obtained with the addition of POSS.

Because the combining of POSS macromers with polymer by blending is a new approach to achieve nano-materials, there are still a lot of unknown domains that need to be investigated for this technique. The key issue in this field is to develop POSS Nano-Technology, i.e. to develop new design principles that allow to control POSS macromers at nanometer level and to achieve effective POSS-polymer interface.

PART I

INVESTIGATIONS OF POSS MACROMERS

3.1 In
10000
· · · · · ·
therm
ongoin
new c
the m
initiat
POSS
relati
syster
const
the P
Scant
n ia
*10
the P
th e d
tempe

CHAPTER 3

STRUCTURE-PROPERTY STUDIES OF POSS MACROMERS

3.1 Introduction

The recent development of POSS macromers affords a tremendous opportunity for the preparation of new polymers (thermoset, thermoplastics, and elastomers) and new polymeric blends. As part of our ongoing effort to investigate, understand, and develop these materials as a new class of nano-reinforcing fillers for polymers, an investigation into the morphology and thermal properties of these POSS macromers was initiated. This study is essential to optimizing the processing of the POSS/Polymer blends, and for understanding the structure-property relationships of the blends, since any given property of a multi-component system is some (more or less complex) function of the properties of the constituents and of the interactions between them.

In the following chapter, the morphology and thermal properties of the POSS macromers were examined, using X-ray diffraction, Differential Scanning Calorimetry (DSC), and Thermogravimeric Analysis (TGA), with special emphasis given to the effects of the organic corner groups on the POSS cages. We expect that the chemistry of the corner groups affect the degree of the orderly packing of the POSS cages, the transition temperatures, and the thermal stabilities of the POSS macromers.

3.2 3.2. diff Hyt abb Fig 3.2 3.2 (DS 3.2 eva 3.2 3.2 tar Was the

3.2 Experimental

3.2.1. POSS Macromers:

POSS Macromers used in this study so far are all T_8 cages bearing different corner groups. These POSS macromers were obtained from Hybrid Plastics Corporation. Their chemical formulae, structures, abbreviations and molecular weight (M.W.) are shown in Table 3.1 and Figure 3.1.

3.2.2 Sample Preparations:

3.2.2.1 Samples Preparations for Differential Scanning Calorimeter (DSC), and Thermogravimetric Analysis (TGA):

POSS powders were used directly for DSC, and TGA tests.

3.2.2.2 Samples Preparations for X-Ray Diffraction:

POSS macromers were dissolved in toluene for 12 hours; solvent evaporated and the samples dried under vacuum for 12 hours at 60°C.

3.2.3 Characterization Techniques:

3.2.3.1 X-ray Diffraction:

Measurements were performed using a Scintag XRD 2000 with a Cu target; 20 angle ranged from 5° to 30°; Step size and scan rate used here was 0.03° and 2° /min, respectively.

The x-ray diffraction pattern obtained from a diffractometer records the X-ray intensity as a function of diffraction angle. The inter-atomic

Table 3.1: Abbreviations, Chemical Formula and Molecular Weight of POSS Macromers , .

Abbreviations for POSS	Full Chemical Name	Chemical Formula	Molecular Weight
CpsPOSS	Octa-Cyclopentyl-POSS	C40H72Si8O12	<i>L</i> .696
Cy ₈ POSS	Octa-Cyclohexyl-POSS	C48H88Si8O12	1081.9
Styrenyl ₈ POSS	Octa-Styrenyl-POSS	C ₆₄ H ₅₆ Si ₈ O ₁₂	1241.8
Ph ₈ POSS	Octa-Phenethyl-POSS	C ₆₄ H ₇₂ Si ₈ O ₁₂	1257.9
Isobu _s POSS	Octa-Isobutyl-POSS	C ₃₂ H ₇₂ Si ₈ O ₁₂	873.6
V ₈ POSS	Octa-Vinyl-POSS	C ₁₆ H ₂₄ Si ₈ O ₁₂	633
ST ₁ Cp ₇ POSS	Styryl ₁ -Cyclopentyl ₇ -POSS	C43H70Si8O12	1003.7
Styrenyl ₁ Cp ₇ POSS	Styrenyl ₁ -Cyclopentyl ₇ -POSS	C43H70Si8O12	1003.7
V ₁ Cp ₇ POSS	Vinyl ₁ -Cyclopentyl ₇ -POSS	C ₃₇ H ₆₆ Si ₈ O ₁₂	927.6
CyHe ₁ Cp ₇ POSS	Cyclohexenyl ₁ -Cyclopentyl ₇ -POSS	C43H76Si8O12	1009.7
ST ₁ Isobu ₇ POSS	Styryl ₁ -Isobutyl7-POSS	C ₃₆ H ₇₀ Si ₈ O ₁₂	919.6
Styrenyl ₁ Isobu ₇ POSS	Styrenyl ₁ -Isobutyl ₇ -POSS	C ₃₆ H ₇₀ Si ₈ O ₁₂	919.6

Table 3.1: Abbreviations, Chemical Formula and Molecular Weight of POSS Macromers



Figure 3.1: POSS Macromers With Different Corner Groups (cont'd)





Figure 3. 1: cont'd

spacing i
<i>W</i>)
ray ($\lambda = 1$
3.2.3.2 1
T.
a Mettle
a flow
temper
3.2.3.3
2950
-00°C
T _{dec} i
^{is} the
3 -
3.3 X
dite
۲۰۰۲ fr
110m

spacing is determined by Bragg's law:

$$d = n \lambda / (2 \sin \theta)$$

Where d is the inter-atomic spacing; λ is the wavelength of the xray (λ =1.5406Å for Cu target); θ is the diffraction angle.

3.2.3.2 Determination of Transition Temperatures of POSS macromers:

Transition temperatures of POSS macromers were determined using a Mettler-Toledo 821e/400 Differential Scanning Calorimeter (DSC) under a flow of nitrogen and with a heating rate of 10°C/min. The transition temperature is taken as the maximum peak position of the transition peak.

3.2.3.3 Thermal Stability:

Thermogravimetric analysis(TGA) was carried out on a Hi-Res TGA 2950 under Nitrogen atmosphere. Temperature range used was 25 to 600° C; Heating rate utilized was 20° C/min. Decomposition Temperature T_{dec} is taken as the temperature where 5% weight loss occurred. Residue is the weight percent of the sample remains after the TGA test.

3.3 X-Ray Crystallographic Analysis of POSS Macromers

To examine the microstructures of POSS macromers, X-Ray diffraction analysis was performed. The X-ray diffraction pattern obtained from a diffractometer records the X-ray intensity as a function of the

diffra	actio
packi	ing 0.
	Thu
of co	orner
3.3.1	1 Eff
	Fig
mac	rome
diffi	ractic
the	diffri
	Ca
Cpa	POS
3.4). Ph.
3.7) mai
ma	,
ma	CIOR
ביי. בתו	CTOM
dif	from
u11	nact
	C
ma	icron.
sp;	acing.
ma	ICIOL
V	POS

diffraction angle 2 θ , and it gives the information about the orderly packing of the molecules in crystals.

The studies below mainly focused on the impacts of different kinds of corner groups on the microstructures of the POSS macromers.

3.3.1 Effects of POSS Corner Groups:

Figures 3.2 to 3.13 show the X-ray diffraction curves of POSS macromers bearing different corner groups. And their corresponding diffraction data (peak positions, inter-atomic spacing, and the 2θ width of the diffraction peaks) are listed in Table 3.2

Comparing the X-ray curves of all the R_8POSS macromers: Cp₈POSS (Figure 3.2), Cy₈POSS (Figure 3.3), Styrenyl₈POSS (Figure 3.4), Ph₈POSS (Figure 3.5), V₈POSS (Figure 3.6) and Isobu₈POSS (Figure 3.7) macromers, it can be seen that Cp₈POSS, Cy₈POSS and Isobu₈POSS macromers have more sharp peaks than Ph₈POSS and Styrenyl₈POSS macromers. Only some weak and broad peaks are found in Ph₈POSS macromer, and Styrenyl₈POSS macromer has only one weak peak in its diffraction pattern.

Comparing the $\sim 8^{\circ}2\theta$ diffraction peak of all the R₈POSS macromers, it can be seen that V₈POSS macromer has the smallest d-spacing (9.0Å. see in Table 3.2), which is due to the fact that the V₈POSS macromer has eight small vinyl groups. The high regularity of the V₈POSS macromer allows a close packing of the POSS cages. Cp₈POSS

1.6E 1.4E 1.2E 4.0 2.0 0.0 4 3

Intensity







Figure 3.3: X-ray Diffraction Profile of Cy8POSS Macromer

5.0E
4.5E
4.0E
3.5E
<u>ع 3.0E</u>
5 2.5E
± 2.0H
1.51
1.01
5.0
0.0

•

8.0 7.0 6.0

0.



Figure 3.4: X-ray Diffraction Profile of Styrenyl₈POSS Macromer



Figure 3.5: X-ray Diffraction Profile of Ph₈POSS Macromer

7.0E++
6.0E+
5.0E+
<u>≥</u> 4.0E+
tens,
= 3.0E+
2.0E+
1.0E+
0.05
0.0E-
5.0F
4.5F
4 .0F
3.5F
>3.01
1.5r
1.51 1.01
5 01
0.0 <u>1</u>
0.01



Figure 3.6: X-ray Diffraction Profile of V₈POSS Macromer



Figure 3.7: X-ray Diffraction Profile of Isobu₈POSS Macromer



Figure 3.8: X-ray Diffraction Profile of ST₁Cp₇POSS Macromer



Figure 3.9: X-ray Diffraction Profile of Styrenyl₁Cp₇POSS Macromer
5.0E-4.5E-**4**.0E-3.5E-3.0E-11122.5E-2.0E-1.5E 1.0E-5.0E **0**.0E 8 7 6 Intensity



Figure 3.10: X-ray Diffraction Profile of CyHe₁Cp₇POSS Macromer



Figure 3.11: X-ray Diffraction Profile of V₁Cp₇POSS Macromer



Figure 3. 12: X-ray Diffraction Profile of ST₁Isobu₇POSS Macromer



Figure 3. 13: X-ray Diffraction Profile of Styrenyl₁Isobu₇POSS Macromer

Table 3. 2: Peak Positions (unit: $^{o}2$ 0) and their corresponding d-spacing (as shown in parentheses, unit Å)

(3.40) (3.46) 26.2 25.7 Peak Position ($^{\circ}2$ 0), and corresponding d-Spacing (as shown in parentheses, $\dot{
m A}$) (3.61) (3.80) (3.58) (3.75) 23.8 23.4 24.6 23.7 (4.00) 22.9 (3.88) 22.2 (4.42) (4.22) 19.3 (4.6) 21.1 20.1 (4.64) (4.85) (4.61) (4.77) (4.78) (4.78) (4.57) (4.87) (4.61) 18.6 18.5 18.5 19.4 18.2 18.3 19.2 19.2 19.1 (5.40) (5.71) (6.74) (5.65) 16.4 15.5 15.7 13.1 12.2 (7.25) (8.04) (8.04) (7.89) 11.2 (69)() 11.5 11 Π (10.92) (10.02) 9.8 (0.6) 8.8 8.0 (10.72) (10.68) (10.72) (10.68) (10.15)8.3 8.3 8.2 8.2 8.7 8.1 (11.6) (11.47) (11.6) (11.47)(11.6) (11.3)(11.2)7.6 7.6 7.6 7.8 7.9 1.7 7.7 Isobu₇POSS [sobu₈POSS] V₁Cp,POSS Macromers CyHe₁Cp₇ POSS ST₁Isobu₇ POSS Styrenyl_s POSS **CysPOSS** Cp,POSS **Styrenyl**₁ **CpsPOSS Ph**_sPOSS V₈POSS **Styrenyl**₁ ST₁Cp₇ POSS POSS

Table 3. 2: Peak Positions (unit: °2 θ) and their corresponding d-spacing (as shown in parentheses, unit $\dot{
m A}$) of POSS Macromers (Summarized from their X-ray diffraction curves)

at h.

ii S

.

and Cy₈POSS macromers have similar X-ray curves, however, Cy₈POSS has larger d-spacing (Table 3.2) than Cp₈POSS, which is probably introduced by the additional methylene unit in the cyclohexyl group. Styrenyl₈POSS macromer is the least ordered macromer among all the R_8POSS macromers, which is due to its huge and rigid corner group.

The replacement of one corner group (R) in the R₈POSS macromers with a different chemical group alters the morphology of the POSS macromers. Comparing the X-ray curves of ST₁CP₇POSS (Figure 3.8), Styrenyl₁Cp₇POSS (Figure 3.9), CyHe₁CP₇POSS (Figure 3.10), and V_1Cp_7POSS (Figure 3.11) macromers with the diffraction curve of the Cp₈POSS (Figure 3.2) macromer, we observed that ST₁Cp₇POSS, Styrenyl₁Cp₇POSS, CyHe₁CP₇POSS, and V₁Cp₇POSS macromers have fewer and less sharp peaks than Cp₈POSS, indicating that ST₁Cp₇POSS, Styrenyl₁Cp₇POSS, CyHe₁CP₇POSS, and V₁Cp₇POSS macromers are less ordered than Cp₈POSS macromer. This is because that the introduction of one styryl / styrenyl/ cyclohexenyl/or vinyl group into Cp₈POSS reduces the symmetry and regularity of the POSS cage structure, and hence hinders the close packing of ST_1Cp_7POSS , $Styrenyl_1Cp_7POSS$, V_1Cp_7POSS and $CyHe_1CP_7POSS$ macromers. The same results are also observed in the X-ray diffraction patterns of ST₁Isobu₇POSS (Figure 3.11), Styrenyl₁Isobu₇POSS (Figure 3.12), in comparison with the X-ray diffraction of Isobu₈POSS macromer (Figure 3.6).

The above discussion is only a simple comparison of the structures of POSS macromer with different corner groups. A complete crystallographic analysis of theses POSS macromers is beyond the scope of this work and will be the subject of a future research.

3.3.2 Summary:

The chemistry of the corner groups on the POSS cage affects the morphological structures of the POSS macromers. The higher the symmetry and regularity of the POSS macromers, and the smaller the size of the corner groups, the more ordered the POSS macromers.

Among the 12 POSS macromers investigated, Cp_8POSS , Cy_8POSS , V_8POSS , and Isobu_8POSS are more ordered than Ph_8POSS, Styrenyl_8POSS, ST_1Cp_7POSS, Styrenyl_1Cp_7POSS, CyHe_1Cp_7POSS, V_1Cp_7POSS, ST_1Isobu_7POSS and Styrenyl_1Sobu_7POSS.

3.4 Thermal Stabilities of POSS Macromers

Thermal stability studies on the POSS macromers bearing different corner groups were conducted. This type of information provides insight into the understanding of the thermal stabilities of POSS/Polymer blends.

In this experiment, Thermogravimeric Analysis (TGA) is used to determine the decomposition temperature (T_{dec}) , and weight loss (or residue) of the POSS macromers.

Т		
the dec		
the T_{de}		
as the		
bonds.		
inorga		
molec		
chemi		
loss.		
which		
of 45		
kJ/m		
(abo		
kJ/m		
size		
Me.		
POS		
the		
are		
the		

Thermal stability of a matter can be embodied by two parameters: the decomposition temperature (T_{dec}) and weight loss. The magnitude of the T_{dec} is mainly determined by the chemical structure of the matter, such as the bond energy, defects inside the molecule and reactivity of the bonds. Weight loss is decided by the content of organic elements and inorganic elements in the molecules, and whether there are more stable molecules formed during the decomposition pathway as a result of a chemical reaction. The higher the carbon element, the larger the weight loss.

POSS macromers are composed of a silica-like inorganic core, which is surrounded by organic groups. The Si-O bond has a bond energy of 451 kJ/mole, which is higher than the bond energy of the C-C (345 kJ/mole) in organic materials ^[66]. However, the bond energy of Si-C (about 318 kJ/mole) is much lower than the bond energy of Si-O (451 kJ/mole), and the bond energies of Si-alkyl bonds become smaller as the size of the alkyl group is increased. For example, the bond energies of Si-Me, Si-Et, and Si-Pr are 331, 211, 192 kJ/mole respectively^[66]. Because POSS macromers consist of both organic and inorganic components, therefore, it is expected that the thermal stabilities of POSS macromers are primarily influenced by the stabilities of the organic corner groups on the POSS cage.

3.

di

0

·

3.4.1 Effects of POSS Corner Groups:

Figures 3.14 to 3.25 show the TGA curves of POSS macromers with different corner groups. The values of the T_{dec} , weight loss, and residues of these POSS macromers, which are obtained from their TGA curves are tabulated in Table 3.3. Table 3.4 lists the molecular weight of the POSS macromers, their weight percentages of the inorganic Si-O portion, and the organic C-H portion.

3.4.1.1 Decomposition Temperatures (T_{dec}) of POSS Macromers:

During the TGA experiments, the decomposition temperature (T_{dec}) is taken as the temperature where 5% weight loss occurred. It can be seen from Figures 3.14 to 3.25 that the order of the T_{dec} of POSS macromers from high to low is: Ph₈POSS (487.97°C, Figure 3.17), Styrenyl₈POSS (458.18°C, Figure 3.16), Cy₈POSS (397.5°C, Figure 3.15), ST₁Cp₇POSS (381.22°C, Figure 3.20), Styrenyl₁Cp₇POSS (374.62°C, Figure 3.21), Cp₈POSS (371.56°C, Figure 3.14), V₁Cp₇POSS (369.05°C, Figure 3.22), CyHe₁Cp₇POSS (348.14°C, Figure 3.23), Styrenyl₁Isobu₇POSS (301.2°C, Figure 3.25), ST₁Isobu₇POSS (284.96°C, Figure 3.24), Isobu₈POSS (267.58°C, Figure 3.18), and V₈POSS (251.28°C, Figure 3.19). It is noticed that this sequence is nearly the same as the sequence of the molecular weight of these POSS macromers from high to low as shown in Table 3.4, except for CyHe₁Cp₇POSS macromer.

Comparing the TGA curves of all the R₈POSS macromers (Figure 3. 26), we can see that Ph₈POSS (487.97°C) and Styrenyl₈POSS (458.2°C)

macro macro mode (251.) isobu (369 Isob Сун (Fig styr Cps wit . V_1 (Wit rep sty fo th m

macromers have significantly higher T_{dec} than the other R₈POSS macromers. Cy₈POSS (397.5°C) and Cp₈POSS (371.56°C) macromers have moderate thermal stabilities. Isobu₈POSS (267.58°C), and V₈POSS (251.28°C) have the lowest T_{dec} among all the R₈POSS macromers.

We also observed that POSS macromers containing vinyl /or isobutyl corner groups have relatively low T_{dec} , for example: V_1Cp_7POSS (369.05°C), Styrenyl₁Isobu₇POSS (301.2°C), ST₁Isobu₇POSS (284.96°C), Isobu₈POSS (267.58°C), and V₈POSS (251.28°C).

Comparing the T_{dec} of ST_1Cp_7POSS , $Styrenyl_1Cp_7POSS$, CyHe₁Cp₇POSS, and V₁Cp₇POSS macromers with that of Cp₈POSS (Figure 3.27), we can see that the replacement of one cyclopentyl with styryl increases the T_{dec} by about 10°C (ST_1Cp_7POSS), while, the T_{dec} of Cp₈POSS decreases by 23°C when replacing one of its cyclopentyl groups with cyclohexenyl group (CyHe₁Cp₇POSS). Styrenyl₁Cp₇POSS and V₁Cp₇POSS macromers have nearly the same T_{dec} as Cp₈POSS macromer.

By comparing the T_{dec} of ST_1Isobu_7POSS and $Styrenyl_1Isobu_7POSS$ with that of $Isobu_8POSS$ macromer (Figure 3.28), it can be seen that the replacements of one isobutyl group in $Isobu_8POSS$ with styryl group and styrenyl group increase the T_{dec} by $17^{\circ}C$ (for ST_1Isobu_7POSS), and $34^{\circ}C$ for (Styrenyl_1Isobu_7POSS).

The above results showed that the chemistry of the corner groups on the POSS cages significantly affected the thermal stabilities of the POSS macromers. As stated in the beginning of this section, the T_{dec}







Figure3. 15: TGA curve of Cy₈POSS Macromer







Figure 3. 17: TGA Curve of Ph₈POSS Macromer

Weight (%)

.



Figure 3. 18: TGA Curve of Isobu₈POSS Macromer



Figure 3. 19: TGA Curve of V₈POSS Macromer

1 Weight (%)

,

Weight (%)



Figure 3. 20: TGA Curve of ST₁Cp₇OSS Macromer



Figure 3. 21: TGA Curve of Styrenyl₁Cp₇POSS Macromer

100-
120
100-
100
80
(%)
ਦ ਸੂ60
Veiç
4(
2
1
1
(°)
() T
'aiat
3







Figure 3. 23: TGA Curve of V₁Cp₇POSS Macromer

Weight (%)

Weight (%)



Figure 3. 24: TGA Curve of ST₁Isobu₇POSS Macromer



Figure 3. 25: TGA Curve of Styrenyl₁Isobu₇POSS Macromer













	5
ſ	
ſ	
	S

Table 3.3: Thermal Stabilities of POSS Macromerswith different Corner Groups (TGA results)

POSS Macromers	DECOMPOSITION TEMPERATURE (at 5% Weight Loss, °C)	WEIGHT CHANGE (%)	RESIDUE (%)
Cp ₈ POSS	371.5	94.35	5.644
Cy ₈ POSS	397.5	85.28	14.73
Styrenyl ₈ POSS	458.1	20.88	79.12
Ph ₈ POSS	487.9	47.29	52.71
Isobu ₈ POSS	267.5	94.64	5.36
V ₈ POSS	251.2	52.13	47.87
ST ₁ CP ₇ POSS	381.2	60.19	39.8
Styrenyl ₁ Cp ₇ POSS	374.6	67.66	32.32
CyHe ₁ Cp ₇ POSS	348.1	96.07	3.93
V ₁ Cp ₇ POSS	369.0	79.51	20.49
ST ₁ Isobu ₇ POSS	284.9	89.50	10.50
Styrenyl ₁ Isobu ₇ POSS	301.2	96.45	3.6

POSS Macromers	Molecular Weight	Cage (wt%)	Si (wt%)	0 (w1%)	C-H (wt%)	C (wt%)	(%1M) H	T _{dec} at 5wt% Loss	TGA 1st Plateau Residue (wt%)	TGA Final Residue (wt%)
Ph ₈ POSS	1257.9	33.12	17.86	15.26	66.88	61.11	5.77	487.97		52.71
Styrenyl ₈ POSS	1241.8	33.55	18.09	15.46	66.45	61.90	4.55	458.18		79.12
CysPOSS	1081.9	38.51	20.77	17.74	61.49	53.29	8.20	397.50	20.46	14.73
CyHe ₁ Cp ₇ OSS	1009.7	41.85	22.25	19.60	57.35	49.96	7.39	348.14		3.93
ST ₁ Cp ₇ POSS	1003.7	41.51	22.39	19.12	58.49	51.46	7.03	381.22	50.09	39.82
Styrenyl ₁ Cp ₇ OSS	1003.7	41.52	22.39	19.13	58.49	51.46	7.03	374.62	45.19	32.32
CpsPOSS	969.7	42.97	23.17	19.80	57.03	49.55	7.48	371.56		5.64
V ₁ C _{P7} OSS	927.6	44.92	24.22	20.70	55.08	47.91	7.17	369.05	47.52	20.5
ST ₁ Isobu ₇ POSS	919.6	45.31	24.43	20.88	54.69	47.02	7.67	289.56		6.24
Styrenyl ₁ Isobu ₇ POSS	919.6	45.31	24.43	20.88	54.69	47.02	7.67	301.20		3.6
Isobu ₈ POSS	873.6	47.7	25.72	21.98	52.30	44.00	8.31	267.58	38.89	5.36
V ₈ POSS	633	65.82	35.50	30.32	34.18	30.36	3.82	251.28		47.87

п	nagn
S	uch
i	bond
	the 1
	indi
	chei
	POS
	stał
	Stv
	010
	5.
	3.
.	0.
	01
	ſ
	(
	(
	(
]

magnitude of a material is mainly determined by its chemical structure, such as the bond energy, defects inside the molecule and reactivity of the bonds. The degradation of POSS macromers starts from initial cleavage of the C-C and Si-C bonds in the corner groups. The above TGA results indicate the C-C and Si-C bond energies on the POSS cages vary with the chemistry of the corner groups. The more stable the corner groups on the POSS cage, the higher the T_{dec} of POSS macromer. The order of thermal stabilities of the organic groups from high to low is: Phenethyl, Styryl, Styrenyl, Cyclohexyl, Cyclopentyl, Isobutyl, Vinyl and Cyclohexenyl groups.

3.4.1.2 Residues of the POSS Macromers:

Residue of the POSS macromers is taken as the weight percentage of the sample remains after the TGA test. We can see from Table 3.3 that the order of the POSS residue yields from high to low is: Styrenyl₈POSS (79.12wt%), Ph₈POSS (59.71wt%), V₈POSS (47.87wt%), ST₁Cp₇POSS (39.80wt%), Styrenyl₁Cp₇POSS (32.32wt%), V₁Cp₇POSS (20.50wt%) Cy₈POSS (14.73wt%), ST₁Isobu₇POSS (10.50wt%), Cp₈POSS (5.64wt%), Isobu₈POSS (5.36wt%), CyHe₁Cp₇POSS (3.93wt%), and Styrenyl₁Isobu₇POSS (3.6wt%).

Among all the R_8POSS macromers (Figure 3.26), POSS macromers containing benzene rings and/or double bonds in their corner groups have higher residue yields. For example, the residues of the Styrenyl₈POSS

(79. are and Cys of t resi C p Sty ex Cp re PC **S**7 in CI S ۴ (79.12wt%), Ph₈POSS (52.71wt%), and V₈POSS (47.87wt%) macromers are higher than those of the Cy₈POSS (14.73wt%), Cp₈POSS (5.64wt%), and Isobu₈POSS (5.36wt%). Comparing the residues of the Cp₈POSS, Cy₈POSS and Isobu₈POSS macromers, we can see that the larger the mass of the corner groups on the POSS cage, the higher their residue yield: the residue of the Cy₈POSS macromer (14.73wt%) is higher than those of Cp₈POSS (5.644wt%) and Isobu₈POSS (5.36wt%) macromers.

As shown in Figure 3.27, the ST_1Cp_7POSS (39.80wt%), Styrenyl₁Cp₇POSS (32.32wt%) and V₁Cp₇POSS (20.50wt%) macromers exhibit significantly increased residue yields when compared with Cp₈POSS (5.64wt%), while, CyHe₁Cp₇POSS (3.93wt%) displays a lower residue than Cp₈POSS (5.64wt%). However, we didn't see this trend in the POSS macromers containing isobutyl groups (Figure 3.28): the residues of ST₁Isobu₇POSS (10.50wt%) and Styrenyl₁Isobu₇POSS (3.6wt%) are about in the same order as Isobu₈POSS (5.36wt%).

The above results showed that the chemistry of POSS has considerable impacts on the residue yields of the POSS macromers. As stated earlier, the residue of a matter is decided by the content of organic elements and inorganic elements in the molecules, and if there are more stable molecules formed during the decomposition pathway as a result of a chemical reaction. This principle also applies to POSS macromers. As shown in Table 3.4, the weight percentages of the inorganic Si-O cages in
the POS
of the c
It
Ph,POS
notice
inorgan
results
reporte
chemic
Ph₄PO§
:
(39.82)
macror
of the
respec
their c
the sy
of PC
chemi
(14.75
Isobu
Styre-

the POSS macromers are between 33~65wt%, depending on the chemistry of the corner groups.

It is noticeable in Table 3.4 that Styrenyl₈POSS (79.12wt%) and Ph₈POSS (52.71wt%) macromers have considerably high residues. We notice that these values are higher than the weight percentages of their inorganic Si-O (~33wt%) content. Based on this fact and also on the results that the loss of POSS cages takes place around 450 to 600°C, as reported by Mantz, Jones, etc ^[67], we postulate that at high temperatures chemical crosslinking reactions might occur in the Styrenyl₈POSS and Ph₈POSS macormers that results in the formation POSS resin.

As seen in Table 3.4, the residue yields of the ST_1Cp_7POSS (39.82wt%), Styrenyl₁Cp₇POSS (32.32wt%) and V₈POSS (47.87wt%) macromers are similar to or somewhat lower than the weight percentages of their inorganic Si-O content: 41.51wt%, 41.51wt%, and 65.82wt% respectively. We presume that in these POSS macromers, partial losses of their organic corner groups and also their inorganic Si-O cages occur in the systems; and the experimental fact that there are still some remaining of POSS macromers even at temperatures above 450°C is because chemical reactions might take place among some of the POSS cages.

Table 3.4 also reveals that V_1Cp_7POSS (20.5wt%), Cy_8POSS (14.73wt%), ST_1Isobu_7POSS (6.24wt%), Cp_8POSS (5.64wt%),Isobu_8POSS (5.36wt%), $CyHe_1Cp_7POSS$ (3.93wt%), andStyrenyl_1Isobu_7POSS (3.6wt%) macromers have very low residues

(3-20		
their		
in the		
clear		
resid		
resid		
3.4.		
is t		
two		
Cv		
Iso		
C v		
e,		
2.		
5		
6,		
۲. ۲		
t		

(3~20wt%). These values are much lower than the weight percentages of their inorganic Si-O cages (40~45wt%), indicating that most of Si-O cages in these POSS macromers are lost during the heating. However, it is not clear why ST₁Isobu₇POSS and Styrenyl₁Isobu₇POSS have very low residues, while, ST₁Cp₇POSS, and Styrenyl₁Cp₇POSS have very high residues.

3.4.1.3 Two Mass-Loss Regions:

Another feature noticed in the TGA curves of the POSS macromers is that during the decomposition process, some POSS macromers display two mass-loss regions.

Two clear mass-loss regions are observed in the TGA curves of Cy_8POSS (350-436°C, and 506-550°C, as shown in Figure 3.15), Isobu_8POSS (250-300°C, and 370-450°C, as shown in Figure 3.18), $CyHe_1Cp_7POSS$ (350-410°C, and 470-600°C, as shown in Figure 3.22), and V_1Cp_7POSS (300-400°C, and 450-500°C, as shown in Figure 3.23). ST_1Cp_7POSS (Figure 3. 20), and Styrenyl_1Cp_7POSS (Figure 3. 21) also exhibit two mass-loss regions, but less distinctive.

The presence of two mass-loss regions suggests that the above POSS macromers have more complicated thermal decomposing processes than other POSS macromers.

The mechanism of POSS decomposition, which can be developed by analyzing the gas-phase product and chars of the samples, is beyond the scope of this research. More detail studies on the thermolysis of POSS macromers can be found in references [59-61].

3.4.2 Summary:

The chemistry of the organic corner groups on the POSS cages plays an important role in determining the thermal stabilities of POSS macromers. The POSS macromers with functionalities, which may undergo chemical crosslinking reactions, possess high thermal stability, for example: Styrenyl₈POSS and Ph₈POSS macromers. Among all the 12 POSS macromers investigated, the Styrenyl₈POSS (T_{dec} : 458.18°C, Residue: 79.12wt%) and Ph₈POSS (T_{dec} : 487.97°C, Residue: 52.71wt%) macromers have significantly high decomposition temperatures and residues.

The order of the POSS decomposition temperature from high to low is: Ph_8POSS (487.97°C), $Styrenyl_8POSS$ (458.18°C), Cy_8POSS (397.5°C), ST_1Cp_7POSS (381.22°C), $Styrenyl_1Cp_7POSS$ (374.62°C), Cp_8POSS (371.56°C), V_1Cp_7POSS (369.05°C), $CyHe_1Cp_7POSS$ (348.14°C), $Styrenyl_1Isobu_7POSS$ (301.2°C), ST_1Isobu_7POSS (284.96°C), $Isobu_8POSS$ (267.58°C), and V_8POSS (251.28°C).

The order of the POSS residue yields from high to low is: Styrenyl₈POSS (79.12wt%), Ph₈POSS (59.71wt%), V₈POSS (47.87wt%),

ST (20 (5. St 3.5 3.5 tra Tł te in 80 th (t fı (] tr С S l P ST_1Cp_7POSS (39.80wt%), $Styrenyl_1Cp_7POSS$ (32.32wt%), V_1Cp_7POSS (20.50wt%), Cy_8POSS (14.73wt%), ST_1Isobu_7POSS (10.50wt%), Cp_8POSS (5.64wt%), $Isobu_8POSS$ (5.36wt%), $CyHe_1Cp_7POSS$ (3.93wt%), and $Styrenyl_1Isobu_7POSS$ (3.6wt%).

3.5 Transition Temperatures of POSS Macromers

3.5.1 Effects of POSS Corner Groups:

Differential Scanning Calorimetry (DSC) was used to test the transition temperatures of POSS macromers with different corner groups. The DSC results are showed in Figures 3.29 to 3.40, and the transition temperature data are listed in Table 3.5. Some of these transitions shown in the DSC figures are the fusions of POSS crystalline structures, and some of them are the destruction of POSS weak associations. The heats of these fusions or disassociations of POSS macromers are very weak (between 2~40J/g), except that V₈POSS has a relatively high heat of fusion, which is about 135.4J/g.

We can see that the Cp₈POSS (Figures 3.29), Styrenyl₈POSS (Figure 3.32), and Isobu₈POSS (Figure 3.34) macromers all have two transition peaks: 12.5° C (disassociation) and 29.9° C (disassociation) for Cp₈POSS; 189.1°C (disassociation) and 274.3°C (melting) for Styrenyl₈POSS; and 49.6°C (disassociation) and 272.1°C (melting) for Isobu₈POSS. The disassociation temperatures of the Cy₈POSS and Ph₈POSS macromers are 23.7°C and 76.5°C, respectively. V₈POSS,



Figure 3.29: DSC Curve of Cp₈POSS Macromer



Figure 3.30: DSC Curve of Cy₈POSS Macromer



Figure 3.31: DSC Curve of Styrenyl₈POSS Macromer



Figure 3.32: DSC Curve of Ph₈POSS Macromer







Figure 3.34: DSC Curve of Isobu₈POSS Macromer







Figure 3.36: DSC Curve of Styrenyl₁Cp₇POSS Macromer



Figure 3.38: DSC Curve of V₁Cp₇POSS Macromer



Figure 3.39: DSC Curve of ST₁Isobu₇POSS Macromer



Figure 3.40: DSC Curve of Styrenyl₁Isobu₇POSS Macromer

POSS	Transition Temperature		Heat of	Dissociation
Macromers			1	(J/g) 2
Cp ₈ POSS	12.5	29.9	4.4	6.2
Cy ₈ POSS	23.7	~	2.5	~
Styrenyl ₈ POSS	189.1	274.3	4.5	29.6
Ph ₈ POSS	76.5	~	37.8	~
Isobu ₈ POSS	49.6	272.1	14.6	10.2
V ₈ POSS	349.1	~	135.4	~
Styrenyl ₁ Cp ₇ OSS	~	~	~	~
ST ₁ Cp ₇ POSS	~	~	~	~
CyHe ₁ Cp ₇ POSS	339.1	~	15.9	~
V ₁ Cp ₇ OSS	~	~	~	~
Styrenyl ₁ Isobu ₇ POSS	169.3	~	22.0	~
ST ₁ Isobu ₇ POSS	~	~	~	~

 Table 3.5: Transition Temperatures of POSS Macromers (DSC Results)

CyHe₁Cp₇POSS and Styrenyl₁Isobu₇POSS macromers have a melting temperature at 349.1°C, 339.1°C and 169.3°C respectively. It is also noticed that the melting temperatures of Isobu₈POSS (Figure 3.34), CyHe₁Cp₇POSS (Figure 3.37), and Styrenyl₁Isobu₇POSS (Figure 3.40) are very close to their decomposition zones.

No transition peaks were found in ST_1Cp_7POSS (Figure 3.34), Styrenyl₁Cp₇POSS (Figure 3.36), V₁Cp₇POSS (Figure 3.38), and ST_1Isobu_7POSS (Figure 3.39) macromers. However, both ST_1Cp_7POSS and ST_1Isobu_7POSS macromers have one upward peak, at 160°C and 229°C respectively, which indicates that an exothermal reaction takes place during heating.

melting transitions of V_8POSS . Only the Isobu₈POSS, Styrenyl₈POSS, and CyHe₁Cp₇POSS macromers are observed in the DSC experiments. Even thought the melting peaks of Cp₈POSS, Cy₈POSS, Ph₈POSS. Styrenyl₁Cp₇POSS, ST_1Cp_7POSS , V_1Cp_7POSS , and ST₁Isobu₇POSS macromers are not observed in their DSC curves, we assume that it is because that their melting temperatures are higher than their decomposition temperatures. The small disassociation peaks found in Styrenyl₈POSS, Ph₈POSS, Cp₈POSS, Cy_8POSS , and Isobu₈POSS macromers are thought to be a destruction of weak aggregations in these POSS macromers.

3.5.2 Summary:

The melting temperatures of Styrenyl₈POSS, Isobu₈POSS, V₈POSS, CyHe₁Cp₇POSS and Styrenyl₁Isobu₇POSS macromers are 274.3°C, 272.1°C, 349.1°C, 339.1°C and 169.3°C, respectively. The melting peaks of Cp₈POSS, Cy₈POSS, Ph₈POSS, Styrenyl₁Cp₇POSS, ST₁Cp₇POSS, V₁Cp₇POSS, and ST₁Isobu₇POSS macromers are not observed because their melting temperatures are higher than their decomposition temperatures. ST₁Cp₇POSS and ST₁Isobu₇POSS macromers have one upward peak, at 160°C and 229°C respectively, which indicates that an exothermal reaction takes place during heating.

Weak associations are observed in Cp₈POSS, Cy₈POSS, Styrenyl₈POSS, Ph₈POSS, and Isobu₈POSS macromers.

PART II

INVESTIGATIONS OF POSS/POLYMER BLENDS

PREFACE

The following two chapters describe a study where POSS macromers were incorporated by mixing into traditional polymers to prepare POSS/Polymer blends. Two kinds of polymers were used. Polystyrene (PS), one of most commonly used thermoplastics, was selected as one of the model polymers. Another one, chosen from polysiloxane polymers, was Polydimethyl Siloxane (PDMS).

Compared to other inorganic fillers, POSS macromers possess greater potential as a nano-reinforcing filler. As stated in Chapter 1, POSS macromers have two unique features. First, the chemical composition is a hybrid: POSS macromers have an inorganic silica-like core, which is surrounded by organic groups. The organic groups surrounding the POSS framework can be made to be compatible with polymers to form blends of nano-reinforced blends. Second, the physical size of POSS macromers is about 1.5 nm ^[11], which is nearly equivalent in size to most polymer segments and coils. Because of these two characteristics of POSS macromers, it is expected that nano-dispersed POSS/polymer blends can be fabricated for nearly every type of polymer matrix by modifying the chemistry of the corner groups.

The following research is intended to answer the question of how POSS macromers can be "molecularly" dispersed in polymer matrix to

form	
struct	
it is d	
two ce	
ргоре	
physi	
morp	
homo	
mor	
para	
inte	
fun	
bet	
COL	
dis	
Sig	
pro	
W }	
ал	
th	

form a nanoscopic material, and to determine what are the structure/property relationships of the POSS/polymer blends.

In general, in order to achieve the optimum performance of a blend, it is crucial that its morphology of the blends and interface between the two components be carefully controlled.

The morphology of a blend plays a key role in determining its properties. Both the response to an applied mechanical stress and the physical properties exhibited by the blend will depend markedly on its morphology, such as: the amount of phase separation, the sample homogeneity, and the domain size in a phase-separated system. The morphological structure of a multi-component blend is affected by many parameters, such as the complex interplay of rheology, diffusion, interfacial forces and time-scale of processing. However, the decisive fundamental factor in determining its morphology is the compatibility between the components. With increasing compatibility between its components, the morphology of a blend becomes more homogeneously dispersion.

The interfaces between the two components in a blend also have a significant influence on the performance of the material. Mechanical properties in filled systems are limited by the strength of the interface, which is often the weakest element of a blend. A favorable chemical and/or physical interaction between the two constituents usually enhances the mechanical properties of the blend.

Because of the above reasons, an investigation on the morphology and interaction between POSS and polymeric matrix was initiated. TEM and X-ray diffractometer were utilized to characterize the morphologies of the POSS/polymer blends. The interactions between POSS macromers and polymers were analyzed by monitoring the changes of the glass transitions of the polymer chains, which were detected by DSC.

An examination of the performance of POSS/polymer blends was followed after their morphology studies. Properties investigated in this paper included thermal stability and rheological properties. Thermal stability is one of the important advantages that organic materials can obtain by combining with inorganic materials. TGA was employed to test the thermal stability of the POSS/polymer blends. The interaction between POSS with varying organic groups and polymer matrix was examined using rheological techniques, which were carried out with a Universal Dynamic Spectrometer. Because of the limited quantities of POSS materials, only the rheological properties of POSS/PDMS blends were conducted.

Based on the above morphology and performance studies of the POSS/polymer blends, we generated the structure and property relationships of the blends.

=		
4.1		
T		
pl		
in		
С		
S		
g		
I		
F		
I		
I		
ł		
C		
I		
I		
t		

CHAPTER 4

MORPHOLOGY, INTERACTION AND THERMAL STABILITY STUDIES OF POSS/POLYSTYRENE (PS) BLENDS

4.1 Introduction:

The morphology, interaction and thermal stability of POSS/PS blends were investigated. The studies were mainly focused on the influence of POSS chemistry on the morphologies of the POSS/PS blends.

Polystyrene (PS) is one of the most commonly used thermoplastics. Composed of only carbon and hydrogen atoms, PS is a good model for studying the effects of POSS macromers bearing different organic corner groups on the compatibilities, and hence the morphologies, of the blends. In this study, TEM was utilized to characterize the morphologies of the POSS/PS blends, and X-ray diffractometer was employed to identify the morphological changes of POSS macromers after they were blended with PS. It is expected that POSS macromers, which have less crystallinity and bear organic corner groups chemically similar to PS, will be more compatible with PS and hence more homogeneously dispersed in the PS matrix.

The interactions between POSS macromers and PS were analyzed by monitoring the changes of polymer glass transition, which were detected by DSC. It is thought that because there are no strong interaction forces

bet not the sta 4.2 4.: 4. PS pı 4. in V S il

between POSS macromers and PS, the molecular mobility of PS chains is not much affected by the addition of POSS macromers.

Because of the limited quantities of POSS macromers, only the thermal stability of the POSS/PS blends was conducted. Thermal stabilities of the POSS/PS blends were characterized by TGA.

4.2 Experimental:

4.2.1. Materials:

4.2.1.1 Polystyrene (PS):

Monodispersed PS was obtained from Aldrich Chemical Company. PS2M: Mw=2316000, PS2K. Mw=216,000.

Poly-dispersed PS (PS1M: Mw=1,600,00, $Mw/Mn \le 1.16$) was purchased from Pressure Chemical.

4.2.1.2 POSS Macromers:

POSS Macromers used for the experiments described in this chapter included Cp₈POSS, Cy₈POSS, Styrenyl₈POSS, Ph₈POSS, Isobu₈POSS, V₈POSS, ST₁Cp₇POSS, Styrenyl₁Cp₇POSS, CyHe₁Cp₇POSS, V₁Cp₇POSS, ST₁Isobu₇POSS, and Styrenyl₁Isobu₇POSS. Their chemical structures are illustrated in Table 3.1 and Figure 3.1.

POSS Loadings in PS were 20wt%, 50wt%, and 80wt%.

4.2.2 Sample Preparations:

4.2.2.1 Transmission Electron Microscope (TEM) Samples Preparation:

PS and POSS macromer were dissolve in THF for more than 4 hours. The concentration of the solution was approximately 0.5%. The solution was then dropped onto a glass slide and let to dry in the air. The film was removed from the glass slide by slowly immersing the slide into a vessel of water at a 45° angle to the surface. Next, the grids were dropped onto the film and the whole piece of film with grids on the surface was lifted out of the water using a section a paper. The grids were dried on filter paper and subsequently carbon coated to increase their beam stability.

4.2.2.2 Samples Preparations for Differential Scanning Calorimeter (DSC), Thermogravimetric Analysis (TGA) and X-Ray Diffraction:

Preparations of POSS/PS blends were performed by dissolving PS and POSS macromer in toluene for 12 hours; evaporating the solvent, and then by drying the samples under vacuum for more than 12 hours at 60° C.

4.2.3 Characterization Techniques:

4.2.3.1 Transmission Electron Microscope (TEM):

Thin films were observed on JEOL 100CX TEM using an acceleration voltage of 120kv.

4.2.3.2 X-ray Diffraction:

Measurements were performed using a Scintag XRD 2000 with a Cu target; 20 angle ranged from 5° to 30°; Step size and scan rate used here was 0.03° and 2° /min, respectively.

the spac () () 4.5 4.5 4.5 4.5

The x-ray diffraction pattern obtained from a diffractometer records the X-ray intensity as a function of diffraction angle. The inter-atomic spacing is determined by Bragg's law:

$$d = n\lambda / (2\sin\theta)$$

Where d is the inter-atomic spacing; λ is the wavelength of the x-ray (λ =1.5406Å for Cu target); θ is the diffraction angle.

4.2.3.3 Thermal Stability:

Thermogravimetric analysis was carried out on a Hi-Res TGA 2950 under Nitrogen atmosphere. Temperature range used was 25 to 600° C; Heating rate utilized was 20° C/min. T_{dec} is taken as the temperature where 5% weight loss occurred. Residue is the weight percent of the sample remains after the TGA test.

4.2.3.4 Determination of Glass Transition Temperature (Tg):

Glass transitions were determined using a Mettler-Toledo 821e/400 Differential Scanning Calorimeter (DSC) under a flow of nitrogen and with a heating rate of 10° C/min. The glass transition temperature was taken as the inflection point of the glass transition region. The glass transition width is the temperature span between the onset of the transition and the endset of the transition.

4.3 Ele ble fu: we 4)

4.3 Morphological Studies of POSS/PS Blends By Transmission Electronic Microscope (TEM)

This section presents the morphological structures of POSS/PS blends observed by TEM. We have investigated the effects of different functionalized POSS macromers, POSS concentration, and molecular weights of PS on the morphological structures of the blends.

4.3.1 Effects of POSS Macromers with Different Corner Groups on the Morphologies of POSS/PS2M Blends (50wt% POSS Loading):

Figures 4.1 to 4.8 show the TEM photographs of blends of PS2M with Cp₈POSS, ST₁Cp₇POSS, Styrenyl₈POSS, Ph₈POSS, Cy₈POSS, V₈POSS, CyHe₁Cp₇POSS and V₁Cp₇POSS (POSS Loading: 50wt%; PS molecular weight: 2316000). The phase characteristics of these blends are summarized in Table 4.1.

As shown in Figure 4.1, the Cp₈POSS/PS2M blend has two phases with PS as the continuous phase and snowflake like Cp₈POSS macromers as the disperse phase. The dimensions of the Cp₈POSS aggregates are around 140-2000nm. The replacement of one cyclopentyl group with one styryl group (ST₁Cp₇POSS) changes the pattern and the dimensions of the POSS aggregates. ST₁Cp₇POSS aggregates in ST₁Cp₇POSS /PS2M blends are roughly round shape, and their sizes are approximately 70-600nm (Figure 4.2). Because of the less crystallinity

POSS/PS2M (50 wt%)	Phases	Continuous Phase	Dispersion Phase	Dimensions of the dispersion phase
Cp ₈ POSS	Two	PS	POSS	140-2000nm
Cy ₈ POSS	Two	PS	POSS	microns
Styrenyl ₈ POSS	Two	POSS+PS	PS	50-200nm
Ph ₈ POSS	One	~	~	~
V ₈ POSS	Two	PS	POSS	microns
ST ₁ Cp ₇ POSS	Two	PS	POSS	70-600nm
CyHe ₁ Cp ₇ POSS	Two	POSS+PS	POSS+PS	microns
V ₁ Cp ₇ POSS	Two	PS	POSS	microns

Table 4. 1: Phase Characteristics of the POSS/PS2M Blends (50 wt% POSS)



Figure 4. 1: TEM Image of Cp8POSS/PS2M Blend (50 wt% POSS)



Figure 4. 2: TEM Image of ST1Cp7POSS/PS2M Blend (50 wt% POSS)

of the and S increa enhan↓ ma in dis an of the ST₁Cp₇POSS, and also the more chemical similarity between PS and ST₁Cp₇POSS, the introduction of one styryl group into Cp₈POSS increases the compatibility between ST₁Cp₇POSS and PS, and therefore, enhances the dispersion of the POSS macromer.



Figure 4. 3: TEM Image of Styrenyl₈POSS/PS2M Blend (50 wt% POSS)

The substitution of all the cyclopentyl groups in the Cp₈POSS macromer with styrenyl groups (Styrenyl₈POSS) renders a phase inversion in the Styrenyl₈POSS/PS2M blend: PS (white round particles) becomes the disperse phase, and the continuous phase is a mixture of Styrenyl₈POSS and PS (Figure 4.3).



Figure 4. 4: TEM Image of PhaPOSS/PS2M Blend (50 wt% POSS)

The replacement of all the cyclopentyl groups in Cp_8POSS macromer with phenethyl groups dramatically improves the compatibility between Ph_8POSS and PS. The Ph_8POSS macromer is homogeneously dispersed in the PS matrix. There is no phase separation in the $Ph_8POSS/PS2M$ blend (Figure 4.4).

Phase separations are observed in $Cy_8POSS/PS2M$ (Figure 4.5), V₈POSS/PS2M (Figure 4.6), CyHe₁Cp₇POSS /PS2M (Figure 4.7) and V₁Cp₇POSS /PS2M (Figure 4.8) blends, with POSS being the disperse phase, PS as the continuous phase. The dimensions of POSS aggregates in these blends are in the range of microns (Table 4.1).



Figure 4. 5: TEM Image of Cy8POSS/PS2M Blend (50 wt% POSS)



Figure 4. 6: TEM Image of V₈POSS/PS2M Blend (50 wt% POSS)



Figure 4. 7: TEM Image of CyHe₁Cp₇POSS/PS2M Blend (50 wt% POSS)



Figure 4. 8: TEM Image of V1Cp7POSS/PS2M Blend (50 wt% POSS)
4.3.
Ble
-
Sty
PS
fo
oc
C
v
Н
b
10
C
I
1
5

4.3.2 Effects of POSS Loading on the Morphologies of POSS/PS2M Blends:

The morphologies of the blends of PS2M with Cp₈POSS, Cy₈POSS, Styrenyl₈POSS, Ph₈POSS, V₈POSS, and ST₁Cp₇POSS (20wt% POSS loading, PS molecular weight: 2316000) are displayed in Figures 4.9 to 4.14.

As with the 50wt% Ph₈POSS/PS2M blend, no phase separation is found in the 20wt% Ph₈POSS/PS2M blend. Yet, phase separations still occur in the 20wt% POSS loading blends of Cp₈POSS/PS2M (Figure 4.9), Cy₈POSS/PS2M (Figure 4.10), Styrenyl₈POSS/PS2M (Figure 4.11), V_8 POSS/PS2M (Figure 4.13), and ST₁Cp₇POSS/PS2M (Figure 4.14). However, compared to the 50wt% blends, POSS macromers in the 20wt% blends are more homogeneously dispersed and the phase boundaries are less distinctive. This effect is a consequence associated with the kinetics of the phase separation, which occurs during the TEM sample preparation process. During this process, when POSS macromers and PS have only a limited compatibility, the POSS macromers tend to aggregate and phaseseparate from the PS matrix to form their own phase. As the PS content is increased, more PS molecules present in the system hinder the POSS macromers from migrating towards each other, leading to a decrease in the diffusion rate of the POSS macromers. Therefore, POSS macromers in the low POSS loading POSS/PS blends are more homogeneously dispersed POSS in the PS matrix than those in the high loading blends. After the solvent evaporates, POSS clusters are frozen in the PS matrix.



Figure 4. 9: TEM Image of Cp₈POSS/PS2M Blend (20 wt%)



Figure 4. 10: TEM Image of Cy8POSS/PS2M Blend (20 wt%)



Figure 4. 11: TEM Image of StyrenylsPOSS/PS2M (20 wt%)



Figure 4. 12:TEM Image of Ph₈POSS/PS2M Blend (20 wt%)



Figure 4. 13: TEM Image of V₈POSS/PS2M Blend (20 wt%)



Figure 4. 14: TEM Image of ST1Cp7POSS/PS2M Blend (20 wt%)

4.3.3 Effects of PS Molecular Weight on the Morphologies of PhsPOSS/PS Blends:



Figure 4. 15: TEM Image of Ph₈POSS/PS216K Blend (20 wt%)

The morphological structure of the Ph₈POSS/PS216K blend (20wt% POSS loading; PS molecular weight: 216,000) is shown in Figure 4.15. The TEM image reveals that phase separation occurs in the Ph₈POSS/PS blend with a low molecular weight PS. From a thermodynamic point of view, in a given composition at a particular temperature, reducing the molecular weight of the polymer enhances the miscibility between the POSS and the polymer, which should lead to a more homogeneously dispersed POSS phase. However, the morphology of a blend also depends on the rheology of the components. Based on kinetic theory consideration, if the components of a blend are not truly miscible at the molecular level, phase separation will occur faster in the low molecular weight (low viscosity) matrix than in the high molecular weight matrix (high viscosity). Therefore, a two-phase structure appears in the low molecular weight blend: Ph₈POSS/PS216K. While a single-phase structure is formed in the high molecular weight blend: Ph₈POSS/PS2M.

4.3.4 Discussion:

The morphology of a blend depends on the compatibility between the two components, the type of molecular interaction and the resultant interface, the rheology of the components and the processing history.

For POSS/Polymer blends, the following factors influence the compatibility between the two components, and hence the morphologies of the blends:

 The chemistry of POSS: The chemical structures of the corner groups on the POSS cage greatly influence the compatibility between POSS and polymers.

The above studies showed that the compatibilities between POSS and PS varied with different POSS chemical structures. Notably, among the eight POSS macromers studied, the Ph_8POSS macromer is the most compatible one with PS and, hence, it is the one which can be homogenously dispersed in the PS matrix.

The degree of the crystallinity of POSS macromers also affects the morphologies of the POSS/PS blends. The potential for achieving miscible blends in which one or both components are crystalline is low because of the heat of fusion which would have to be overcome to achieve the necessary thermodynamic criteria for mixing. High crystallinity POSS does not favor the formation of homogeneous dispersion of the POSS. POSS macromers with a strong tendency to crystallize are inclined to aggregate and phase separate from the polymer host.

- 2. Composition of the mixture: The above TEM results showed that the low POSS loading blends have a more homogeneously dispersed POSS phase than the high POSS loading blends. This is because with increasing polymer content, more polymer chains interfere with the migration of the POSS macromers, leading to a more homogeneity of the blends.
- 3. The molecular weight of the polymer: In a given composition at a particular temperature, from a thermodynamic view, reducing the molecular weight of polymer enhances the miscibility between POSS and the polymer. However, the morphology of a blend is also affected by the rheology of the components. Kinetically, because the viscosity of the polymer drops with a decrease of its molecular weight, POSS macromers are more easily to aggregate in low molecular weight matrix during the sample preparation process, especially when the two

components are not truly miscible at the molecular level. Therefore, phase separation of the components occurs relatively easily in the low molecular weight polymer blends.

4.3.5 Summary:

The chemistry of POSS macromers plays an important role in determining the morphologies of the POSS/PS blends. Depending on the attached chemical groups on the POSS macromer, the morphologies of POSS/PS blends ranged from a complete phase separation between POSS and PS to a homogeneous dispersion of POSS in the PS matrix in a nanoscopic scale. Among the eight POSS macromers used, Ph₈POSS is the most compatible one with PS and can be homogeneously dispersed in PS matrix. All other POSS/PS blends display a certain amount of phase separation to a various degrees.

The POSS concentration and PS molecular weight also influence the morphologies of the POSS/PS blends. With a decrease of POSS loading and increasing of PS molecular weight, POSS macromers are more homogeneously dispersed in the PS matrix.

4.4 X-Ray Crystallographic Analysis of POSS/PS Blends

In this section, X-ray diffraction techniques were employed to characterize the morphologies of POSS/PS blends. The effects of the PS on the crystalline structures of POSS macromers were studied by

comparing the X-ray diffraction patterns of the POSS macromers in the POSS/PS blends with those of the neat POSS macromers. The results reflect the degree of compatibility between the POSS macromers and PS.

In the X-ray curve, the crystallography of a matter is characterized by the positions and the 2θ widths of the diffraction peaks.

4.4.1 Effects of POSS Chemistry and POSS Loading:

Figure 4.16 shows the X-ray diffraction curves of Cp₈POSS macromer and Cp₈POSS/PS2M blends (20 and 50wt% POSS loading). The numbers in the plot are the 2 θ positions of the peaks. Their respective d-spacing and 2 θ width are listed in Table 4.2. Comparing the X-ray curve of Cp₈POSS macromer with that of the 50wt% POSS loading blend, we can see that there are two well-defined crystalline peaks in Cp₈POSS macromer,



Figure 4. 16: X-Ray Diffraction Profile of Cp₈POSS/PS2M Blends

Sample	PEAK	POSITI	ON (° 2θ)	
Cp ₈ POSS	8.2 (10.77, 0.32)	11 (8.04)	19.1 (4.64, 0.37)	24.6 (3.61)
Cp8POSS/PS (50/50)	7.5 (11.78, 0.8)	10.5 (8.42)	18.8 (4.72, 0.88)	
Cp8POSS/PS (20/80)	6.6 (13.55, 1.35)		18.5 (4.79, 0.78)	

 Table 4. 2: Comparison of Peak Positions of Cp₈POSS and Cp₈POSS/PS2M

 Blends (from X-ray Diffraction Curves in Figure 4.16)

Note: In Tables 4.2 to 4.9, the first number in the parentheses is the d Spacing of the peak (unit Å). The second number in the parentheses is the 2θ width of the peak (°).

and these two peaks shift to the left and broaden after Cp₈POSS is blended with PS. The peak positions are 8.2°20 and 19.1 °20 for the 7.5 °2θ 18.8 unmixed Cp₈POSS macromer. and and °20 for Cp₈POSS/PS2M (50%) blend. The peak shifting of Cp₈POSS macromer to left after it is blended with PS indicates the that the corresponding inter-planary d spacing of the Cp₈POSS crystal increases (Table 4.2): from 10.77 Å to 11.78 Å for peak 8.2°20, and from 4.64 to 4.72Å for peak 19.1 °20. Furthermore, the 20 width of these two peaks increases from 0.325° to 0.8° for peak 8.2°20, and from 0.375° to 0.88° for peak 19.1 °20, implying that the sizes of the crystal become small and there are more defects in the crystals. The comparison between the 20 wt% and 50 wt% POSS loading blends of Cp₈POSS/PS2M shows that with a decrease of POSS loading, the diffraction peaks of Cp₈POSS macromer shift further to the left and broaden more (Table 4.2). The above results reveal that the addition of PS interrupts the crystallization of Cp₈POSS macromer, and modifies the crystalline structures of the Cp₈POSS

macromer. The degree of crystallinity of the Cp₈POSS macromer in the POSS/PS blends decreases with increasing of PS content.

The X-ray Diffraction curves of Cy_8POSS and $Cy_8POSS/PS2M$ (20 and 50wt% POSS loading) are presented in Figure 4.17. Table 4.3 lists the d-spacing and the 20 width of the diffraction peaks in Figure 4.17.



Figure 4.17: X-Ray Diffraction Profile of Cy₈POSS/PS2M Blends

Table 4. 3: Comparison of Peak Positions of Cy8POSS and Cy8POSS/PS2M Blends(from X-ray Diffraction Curves in Figure 4.17)

Sample		PEAK	POSITION	(° :	20)
Cy ₈ POSS	7.8	(11.32, 0.22)	15.5 (5.71)	18.2 (4.87)	23.4 (3.80)
Cy8POSS/PS (50/50)	8.2	(10.77, 0.44)	11.8 (7.49)	18.5 (4.79)	
Cy8POSS/PS (20/80)			10.1 (8.75)		

We can see from Figure 4.17 that there are two well-defined peaks in the x-ray curve of Cy₈POSS/PS2M (50wt%) blend. These peaks correspond to the two peaks in the neat Cy₈POSS macromers, but with the peak positions shifting to the right. This indicates that Cy₈POSS macromer form more close packing crystals (i.e. smaller d-spacing as shown in Table 4.3) when it blended with PS. However, there is only one small peak (10.1°20) in the x-ray curve of Cy₈POSS/PS2M (20wt%), implying that Cy₈POSS macromer can be more well-dispersed in PS matrix with a low POSS loading.



Figure 4.18: X-Ray Diffraction Profile of Styrenyl₈POSS/PS2M Blends

As shown in Figure 4.18, there is only one small sharp peak in all the X-ray diffraction curves of Styrenyl₈POSS and Styrenyl₈POSS/PS2M

Sample	PEAK	POSITION	(° 2 0)
Styrenyl ₈ POSS	5	3.3 (10.68, 0.24)	
Styrenyl ₈ POSS/PS (50/50)		6.8 (12.99, 0.4)	
Styrenyl ₈ POSS/PS (20/80)		5.9 (14.97, 0.5)	_

 Table 4.4: Comparison of Peak Positions of StyrenylsPOSS and

 StyrenylsPOSS/PS2M Blends (from X-ray Diffraction Curves in Figure 4.18)

(20 and 50wt% POSS loading). The 2 θ position of this peak is 8.3 for Styrenyl₈POSS, 6.8 for Styrenyl₈POSS/PS2M (50wt%) and 4.9 for Styrenyl₈POSS/PS2M (20wt%). It can be seen that with the addition of PS, the diffraction peak of the Styrenyl₈POSS shifts to the left and the 2 θ width of the peak broadens (Table 4.4). The 20wt% POSS loading blend has larger d-spacing and wider 2 θ width than the 50 wt% POSS loading blend, indicating that in the low loading POSS blend, the crystalline structures of POSS macromer are more impaired.



Figure 4. 19: X-Ray Diffraction Profile of Ph₈POSS/PS2M Blends

Sample	PEAK	POSITION	(° 2 0)
	8.1 (10.92)	8.8 (10.02)	18.3 (4.85)
Ph ₈ POSS	20.1 (4.42)	22.2 (4.0)	26.2 (3.40)
Ph ₈ POSS/PS (50/50)	10.4 (8.5)		
Ph ₈ POSS/PS (20/80)	6.3 (14.0)		

Table 4.5: Comparison of Peak Positions of Ph₈POSS and Ph₈POSS/PS2M Blends (from X-ray Diffraction Curves in Figure 4.19)

The X-ray diffraction curves of the Ph₈POSS and Ph₈POSS/PS2M (20 and 50wt% POSS loading) are shown in Figure 4.19 and their corresponding d-spacing and the 20 width of the diffraction peaks are listed in Table 4.5. There are many small peaks in the unmixed Ph₈POSS macromer ($8.1^{\circ}2\theta$, $8.8^{\circ}2\theta$, $13.2^{\circ}2\theta$, $16.5^{\circ}2\theta$, $18.3^{\circ}2\theta$, $20.1^{\circ}2\theta$, $22.2^{\circ}2\theta$, $22.9^{\circ}2\theta$, and $26.2^{\circ}2\theta$). However, only a very broad peak is observed in Ph₈POSS /PS2M (20 and 50wt%) blends, indicating that the Ph₈POSS macromers are well-dispersed in the PS matrix.

The X-ray diffraction profiles of the V₈POSS macromer and V₈POSS/PS2M blends (20 and 50wt% POSS loading) are displayed in Figure 4.20 and their corresponding d-spacing and the 20 width of the diffraction peaks are tabulated in Table 4.6. The 20 and 50wt% POSS loading blends still retain the 9.8°20 diffraction peaks with a little shifting. In the 50wt% POSS loading blend, this diffraction peak shifts to the right, and its corresponding d-spacing decreases (Table 4.20), while, in the 20wt% POSS loading blend, this diffraction peaks shifts to the left, and its

corresponding d-spacing increases. The above results manifest that with the decreasing of V_8 POSS loading, V_8 POSS and PS become more compatible.



Figure 4. 20: X-Ray Diffraction Profile of V₈POSS/PS2M Blends

Table 4.6: Comparison of Peak Positions of V₈POSS and V₈POSS/PS2M Blends(from X-ray Diffraction Curves in Figure 4.20)

Sample	PEAK		POSITION		(° 2 0)	
V ₈ POSS	9.8	13.1	19.7	21.1	22.9	23.7
	(9.0, 0.48)	(6.74)	(4.50)	(4.22)	(3.88)	(3.75)
V ₈ POSS/PS (50/50)	10.8	13.9	20.6	21.9	23.9	24.6
	(8.19, 0.7)	(6.37)	(4.31)	(4.06)	(3.72)	(3.62)
V ₈ POSS/PS (20/80)	9.4 (9.4, 0.20)			22.5 (3.95)	23.3 (3.81)	

Figure 4.21 shows the X-ray diffraction curves of ST_1Cp_7POSS and its blends with PS2M (20 and 50wt% POSS loading). There are two welldefined peaks in all the three specimens. The peak positions are $8.2^{\circ}2\theta$ and $19.2^{\circ}2\theta$ for the neat ST_1Cp_7POSS macromer, 7.8 °20 and 18.8 °20 for ST₁Cp₇POSS /PS2M (50wt%), and 7.5 °2 θ and 18.9 °2 θ for ST₁Cp₇POSS /PS2M (20wt%). As shown in Table 4.7, the corresponding interplanary d spacing of the ST₁Cp₇POSS diffraction peaks increases after it is blended with PS: from 10.72 Å to 11.33 Å (for 50wt% loading blend), and to 11.78 Å (for 20wt% loading blend) for the peak 8.2°2 θ , and from 4.61 Å to 4.72 Å (for the 50wt% blend) and, to 4.69Å (for the 20wt% blend) for peak 19.2°2 θ . The 2 θ width of the first peak expands from 0.375° to 0.59° (for the 50wt% blend), and to 1.5° (for the 20wt% blend). This expansion reveals that PS modifies the morphology of the ST₁Cp₇POSS when they are blended together.



Figure 4.21: X-Ray Diffraction Profile of ST₁Cp₇POSS/PS2M Blends

Sample	PEAK	POSITION	(° 2 0)
ST ₁ Cp ₇ POSS	8.2 (10.72, 0.375)	11 (8.04)	19.2 (4.61)
ST1Cp7POSS /PS (50/50)	7.8 (11.33, 0.59)	10.8 (8.19)	18.8 (4.72)
ST ₁ Cp ₇ POSS (20/80)	7.5 (11.78, 1.50)		18.9 (4.69)

 Table 4.7: Comparison of Peak Positions of ST1Cp7POSS and ST1Cp7POSS /PS2M

 Blends (from X-ray Diffraction Curves in Figure 4.21)

The X-ray diffraction profile of V_1Cp_7POSS and $V_1Cp_7POSS/PS2M$ (20 and 50wt% POSS loading), as shown in Figure 4.22 and Table 4.8) manifests that after blending with PS, the V_1Cp_7POSS macromer in the blend maintains similar peak features to the neat V_1Cp_7POSS macromer. These three curves all have diffraction peaks with similar peak positions.



Figure 4.22: X-Ray Diffraction Profile of V₁Cp₇POSS/PS2M Blends

Sample	PEAK PO	SITION	(°2 0)
V ₁ Cp ₇ POSS	7.5 (11.7, 0.34)	10.3 (8.58)	18.5 (4.78)
V ₁ Cp ₇ POSS /PS (50/50)	7.7 (11.47, 0.5)	10.4 (8.50)	18.7 (4.74)
V ₁ Cp ₇ POSS /PS (20/80)	7.8 (11.33, 0.21)		18.9 (4.69)

Table 4.8: Comparison of Peak Positions of V1Cp7POSS and V1Cp7POSS /PS2MBlends (from X-ray Diffraction Curves in Figure 4.22)

The X-ray diffraction curves of $CyHe_1Cp_7POSS$ and $CyHe_1Cp_7POSS$ /PS2M (20 and 50wt% POSS loading) are shown in Figure 4.23, and their corresponding d-spacing and the 20 width of the diffraction peaks are listed in Table 4.9. Figure 4.23 reveals that after blending with PS, the diffraction peaks of CyHe_1Cp_7POSS macromers maintain similar features to the unmixed CyHe_1Cp_7POSS macromers.



Figure 4.23: X-Ray Diffraction Profile of CyHe₁Cp₇POSS/PS2M Blends

Table 4.9: Comparison of Peak Positions of CyHe₁Cp₇POSS and CyHe₁Cp₇POSS /PS2M Blends (from X-ray Diffraction Curves in Figure 4.23)

Sample	PEAK P	OSITION	(°20)	
CyHe ₁ Cp ₇ POSS	7.7 (11.47)	8.6 (10.27)	18.6 (4.77)	19.3 (4.60)
CyHe ₁ Cp ₇ POSS /PS (50/50)		8.6 (10.27, 0.84)		19.6 (4.53)
CyHe ₁ Cp ₇ POSS /PS (20/80)	7.7 (11.47, 1.8)		18.4 (4.82)	

The above results suggest that the addition of PS modifies the crystalline structures of the POSS macromers, and the degree of modification depends on the compatibility level between the two components. The higher the compatibility between POSS and PS, the less the crystallinity of the POSS macromers. When POSS and PS are miscible, POSS disperses homogeneously in the PS matrix, such as in the case of Ph₈POSS/PS blends, where Ph₈POSS is amorphous in the PS matrix. When POSS macromers and PS are partially compatible, the d-spacing and widths of the diffraction peaks of the POSS macromers increase after they are blended with PS.

POSS loading also has effects on the crystalline structures of the POSS macromers in the POSS/PS blends. Because POSS macromers in the 20wt% POSS loading blends have better compatibility with PS than those in the 50wt% POSS loading blends, the POSS macromers in the low loading blends are less ordered.

4.4.2 Effects of PS Molecular Weight:

Figures 4.24 and 4.25 present the effects of the PS molecular weight on the microstructures of the POSS/PS blends (20wt% POSS loading). Compared to the diffraction peaks of the high molecular weight PS2M/Cp₈POSS and PS2M/ST₁Cp₇POSS blends, the diffraction peaks of the low molecular weight PS216K/Cp₈POSS and PS216K/ST₁Cp₇POSS blends are more distinctive, implying that POSS macromers are more ordered in the low molecular weight PS matrix than in the high molecular weight PS matrix. As we explained earlier, this is because POSS macromers are easier to phase separate from the low molecular weight (low viscosity) matrix than from the high molecular weight matrix (high viscosity).



(20wt% POSS Loading) with Different Molecular Weight PS



Figure 4.25: X-ray Diffraction Profiles of ST₁Cp₇POSS/ PS Blends (20wt% POSS Loading) with Different Molecular Weight PS

4.4.3 Summary:

1. The crystallography of POSS macromers in the POSS/PS blends depends on the compatibility between the two components. The more compatible POSS and PS are, the less crystalline the POSS macromer becomes when it blend with PS. When the two are miscible, the POSS macromer disperses components homogeneously in the PS matrix. Among the eight POSS macromers studied, Ph₈POSS is the most compatible one with PS. All the other POSS macromers: ST_1Cp_7POSS , Styrenyl₈POSS, Cy₈POSS, Cp₈POSS, V₈POSS, V₁Cp₇POSS, and CyHe₁Cp₇POSS are partially compatible with PS.

- 2. With decreasing of POSS loading, POSS macromers are more well-dispersed in the PS matrix.
- 3. POSS macromers are more ordered in the low molecular weight polymer matrix than in the high molecular weight one.

4. 5 Glass Transition Behaviors of POSS/PS Blends

This section examines the glass transition characteristics of a series of POSS/PS blends. The intention is to see how the addition of POSS macromers modifies the microenvironment of the polymer chains, and how this modification affects the molecular motion of the polymer chain segments: retarding the chain motion, enhancing the chain motion or no impact? The information reflects the compatibility and interaction between POSS macromer and polymer.

The glass transition temperature (T_g) , obtained from DSC, is used here to characterize the motion of the polymer chain segments.

4.5.1 Effects of POSS Chemistry and POSS Loading:

Figures 4.26 to 4.41 show the influence of different POSS macromers on the T_g behaviors of POSS/PS1M blends (PS: Mw=1600,000). Their results are listed in Table 4.10. Comparing the T_g values of POSS/PS blends with that of the neat PS, we can see that the additionof POSS macromers lowers the T_g value of PS and also broadens the transition width, irrespective of the types of POSS macromers. **Table 4.10 Glass Transition Behaviors of POSS/PS1M Blends**

PS/POSS Blends				POSS		Loading			
(PS: $Mw=1600000$, $Tg = 112.2^{\circ}C$, $Breadth = 5.4^{\circ}C$)		20%			50%			80%	
POSS Types	Tg (°C)	Width (°C)	Tg Change	Tg (°C)	Width (°C)	Tg Change	Tg (°C)	Width (°C)	Tg Change
CpsPOSS	78.1	7.9	-30.4%	89.8	21.3	-20.0%	108.9	9.7	-2.9%
ST ₁ Cp ₇ POSS	105.8	29.7	-5.7%	105.1	25.8	-6.3%	109.4	10.8	-2.5%
Isobu ₈ POSS	87.5	20	-22.0%	107.7	26.4	-4.0%	110.7	1.11	-1.3%
Ph ₈ POSS	48.4	16.6	-56.9%	37.2	20	-66.8%	-8.1	18.1	-107.2%
Styrenyl ₈ POSS	89.4	14.3	-20.3%	106.8	18	-4.8%	105.5	13.8	-6.0%







Figure 4.27: DSC Curve of PS1M/Cp₈POSS (20wt% POSS Loading)



Figure 4.28: DSC Curve of PS1M/Cp₈POSS (50wt% POSS Loading)



Figure 4.29: DSC Curve of PS1M/Cp₈POSS (80wt% POSS Loading)



Figure 4.30: DSC Curve of PS1M/Styrenyl₈POSS (20wt% POSS Loading)



Figure 4.31: DSC Curve of PS1M/Styrenyl₈POSS (50wt% POSS Loading)



Figure 4.32: DSC Curve of PS1M/Styrenyl₈POSS (80wt% POSS Loading)



Figure 4.33: DSC Curve of PS1M/Ph₈POSS (20wt% POSS Loading)



Figure 4.34: DSC Curve of PS1M/Ph₈POSS (50wt% POSS Loading)



Figure 4.35: DSC Curve of PS1M/Ph₈POSS (80wt% POSS Loading)



Figure 4.36: DSC Curve of PS1M/Isobu₈POSS (20wt% POSS Loading)



Figure 4.37: DSC Curve of PS1M/Isobu₈POSS (50wt% POSS Loading)



Figure 4.38: DSC Curve of PS1M/Isobu₈POSS (80wt% POSS Loading)



Figure 4.39: DSC Curve of PS1M/ST₁Cp₇POSS (20wt% POSS Loading)



Figure 4.40: DSC Curve of PS1M/ST₁Cp₇POSS (50wt% POSS Loading)



Figure 4.41: DSC Curve of PS1M/ST₁Cp₈POSS (80wt% POSS Loading)

Among all of the POSS/PS blends studied, Ph₈POSS/PS1M blends (Figures 4.33, 4.34, and 4.35) have the most dramatic drop in T_g at all compositions. The reductions in T_g values are 56.9%, 66.8% and 107.2%, for the 20, 50, and 80 wt% Ph₈POSS loading blends respectively (Table 4.10), while the ST₁Cp₇POSS/PS1M blends (Figures 4.39, 4.40, 4.41 and Table 4.10) have a very small decline in T_g at all compositions---only about 2~6%.

Comparing the T_g values of all the 20wt% POSS loading blends (Table 4.10), the T_g of ST_1Cp_7POSS /PS1M blend decreases only 5.7%, Τg drops Cp₈POSS/PS1M (30.4%), much less than the of Isobu₈POSS/PS1M (22.0%),Ph₈POSS/PS1M (56.9%),and Styrenyl₈POSS/PS1M (20.3%).

As seen in Table 4.10, for all the 50wt% POSS loading blends, the T_g values of blends $ST_1Cp_7POSS/PS1M$, Isobu₈POSS/PS1M, and Styrenyl₈POSS/PS1M decrease only about 5%, while the T_g values of Cp₈POSS/PS1M, and Ph₈POSS/PS1M fall significantly more, 20% and 66.8%, respectively. Among the 80wt% POSS loading blends, the T_g value of all the blends is close to the T_g of unmixed PS, except for the Ph₈POSS/PS1M blend.

It can be seen from Table 4.10 that with the increasing of POSS loading the T_g values of the POSS/PS1M blends are more close to the T_g of the neat PS, but with one exception: for Ph₈POSS/PS blends, the T_g values decrease with increasing POSS loading.

In comparison with the glass transition zone width of the neat PS, the transition widths broaden in all the POSS/PS1M blends. However, the 50wt% loading POSS blends have broader transition zones than the 20wt% and 80wt% blends.

4.5.2 Discussion

The above results manifest that POSS macromers behave like plasticizers in the PS matrix. The addition of POSS macromers into PS decreases the T_g and broadens the transition zone of the PS.

How POSS macromers influence the polymer chain motions depends mainly on the following two factors:

First is the interaction force between POSS macromers and polymer chains. One extreme case is there are no any kind of interactions between POSS and polymers. In this case, POSS macromers have no effect on the mobility of the polymer chains. Another extreme case is when the POSS macromers are attached to polymer chains. In this case, the mobility of the polymer chains is retarded due to the massive POSS cage.

The second factor is the compatibility between the polymer and the POSS macromers. Good compatibility results in thorough dispersion of the POSS macromers in the polymer matrix, and fineness of the dispersion sizes. The degree of dispersion of the POSS macromers is the fundamental factor that decides if POSS macromers affect the mobility of the polymer chains.

When POSS macromers have a high degree of compatibility but weak interactions with PS, the blending of POSS macromers into PS causes a dramatic drop in the T_g value of the PS. This is because that the high degree of compatibility between the two components assures a homogeneous dispersion of POSS macromers in the matrix (i.e. they don't aggregate), and the absence of favorable interactions between the POSS macromers and the polymer chains renders POSS macromers acting like plasticizers in the polymer matrix. As a result, the addition of POSS macromers expands the distance between polymer chains, and increases the free volumes of the polymer chains, leading to a temperature drop and width broadening of the glass transition. The more the compatible the two components are, the more the T_g drops (such as in the case of . Ph₈POSS/PS blends).

The addition of POSS macromers, with poor compatibility with PS, into PS also decreases the T_g of the PS, but significantly less than the drop in T_g observed for POSS/PS blends with good compatibility. Since POSS macromers with low compatibility aggregate in PS matrix, polymer chains are not effectively affected by the POSS macromers owing to the severe phase separation.

4.5.3 Summary:

The proceeding results indicate that there is no favorable interaction between POSS macromers and polymeric chains. POSS

macromers behave like plasticizers in the PS matrix, which results in the decrease of the glass transition temperature of the PS and the broadening of the transition zone of the PS.

The more compatible between the POSS macromer and the polymer, the more the T_g drops. Among the five POSS/PS blends studied (Cp₈POSS/PS, Styrenyl₈POSS/PS, Ph₈POSS/PS, Isobu₈POSS/PS, ST₁Cp₇POSS/PS), the Ph₈POSS/PS blend has the lowest T_g .

4.6 Thermal Stability Studies of POSS/PS Blends:

4.6.1 Effects of POSS Chemistry and POSS Loading:

Figures 4.42 to 4.49 are the TGA curves of POSS/PS2M blends (PS Mw: 2316000, 20 and 50wt% POSS loading).

As shown in Figures 4.42 to 4.47, the T_{dec} values of the 20 and 50wt% loading blends of Cp₈POSS/PS2M, Cy₈POSS/PS2M, V₈POSS/PS2M, ST₁CP₇POSS/PS2M, V₁Cp₇POSS/PS2M, and CyHe₁Cp₇POSS/PS2M are all lower than the T_{dec} values of their neat components. Styrenyl₈POSS/PS2M blends (20wt% and 50wt%) (Figure 4.48) have T_{dec} values higher than the T_{dec} of PS but lower than the T_{dec} of Styrenyl₈POSS. As shown in Figure 4.49, the 20wt% Ph₈POSS/PS2M blend has a lower T_{dec} than the PS and Ph₈POSS, while the T_{dec} of the 50wt% blend falls between the T_{dec} values of PS and Ph₈POSS. Comparing the T_{dec} values of the 50wt% blends with those of the 20wt% blends, we can see that all the 50wt% POSS loading blends have higher T_{dec} than their corresponding 20wt% POSS loading blends.






Figure 4.43: TGA Curves of PS2M/Cy₈POSS Blends.







Figure 4. 45: TGA Curves of PS2M/ST₁Cp₇POSS Blends.



Figure 4.46: TGA Curves of PS2M/V₁Cp₇POSS Blends.



Figure 4. 47: TGA Curves of PS2M/CyHe₁Cp₇POSS Blends.





Figure 4.49: TGA Curves of PS2M/Ph₈POSS Blends.

The addition of POSS macromers into PS renders the POSS/PS blend higher residues than the neat PS. As seen in Figures 4.42 to 4.49, the residues of all the POSS/PS blends fall between the residues of the unmixed POSS and PS. The 50wt% POSS loading blends have higher residues than their corresponding 20wt% POSS loading blends.

Comparing the TGA curves of all the POSS/PS blends with those of their neat components, we can see that the decomposition paths of the blends are different from those of their unmixed components and vary with the types of POSS macromers.

At the early decomposition stage (before 380°C), all the POSS/PS blends start losing weight at lower temperatures than both the POSS macromers and PS, even though the 50wt% blends exhibit better thermal stabilities than the 20wt% blends.

However, in the middle stage of the decomposition, the decomposition paths of the POSS/PS blends exhibit two cases. Firstly, for blends in which the T_{dec} of POSS macromer is higher than the T_{dec} of PS, their decomposition curves fall between the curves of the unmixed components, such as Cy₈POSS/PS (Figure 4.43), ST₁CP₇POSS/PS (Figure 4.45), Styrenyl₈POSS /PS (Figure 4.48), and Ph₈POSS/PS (Figure 4.49) blends, and the 50wt% blends have better thermal stabilities than their corresponding 20wt% blends. Secondly, for blends in which the T_{dec} of POSS macromer is lower than the T_{dec} of PS, their decomposition paths are somewhat complicated: during one temperature range, the thermal

stabilities of the blends fall between those of the unmixed components, while at another temperature range, the thermal stabilities of the blends are better than both the neat components, such as the Cp₈POSS/PS (Figure 4.42), CyHe₁Cp₇POSS/PS (Figure 4.47), V₁Cp₇POSS/PS (Figure 4.46), V₈POSS/PS (Figure 4.44) blends. However, in the second case, the 20wt% blends exhibit higher thermal stabilities than their corresponding 50wt% blends.

At the final stage of decomposition, the TGA curves of all the POSS/PS blends fall between the TGA curves of the pure POSS macromers and PS. The 50wt% POSS loading blends have higher stability than their corresponding 20wt% POSS loading blends.

4.6.2 Summary:

POSS/PS blends exhibit improved thermal stability when using POSS macromers with higher decomposition temperatures and residue yields than PS. Styrenyl₈POSS/PS and Ph₈POSS/PS blends exhibit better thermal stabilities than other POSS/PS blends.

CHAPTER 5

MORPHOLOGY AND PROPERTIES OF POSS/POLYDIMETHYL SILOXANE (PDMS) BLENDS

5.1 Introduction:

The morphology and performance of the POSS/PDMS blends were next examined. Our research studies mainly focused on their rheological properties.

The compositions of polysiloxanes include both inorganic and organic portions. The polymer backbone is composed of alternate silicon and oxygen atoms. Each silicon atom has two organic groups attached to it. The chain-end silicon atoms have a third group (organic, hydroxyl, or alkoxy group) to satisfy silicon's fourth valence.

Polydimethyl siloxane (PDMS), which was used in this study, consists of methyl group substitution and can be represented as in Figure 5.1.



Where R can be an organic, hydroxyl, or alkoxy group.

Figure 5.1: Chemical Structure of Polydimethyl Siloxane (PDMS)

There are two reasons why we have chosen PDMS as one of the polymer models for the studying of POSS/polymer blends. First, because

of their similarity in chemical compositions, POSS macromers have better compatibility with PDMS than with other polymers, and good compatibility is a crucial requirement for fabricating multi-component systems with specific properties. Second, POSS macromer has the potential to be a reinforcing filler for PDMS. The tensile strength of a cross-linked non-reinforced high molecular weight PDMS is in the range of about 0.34 MPa^[68]. This value is too low to satisfy the property requirements of most applications, hence, the reinforcement of PDMS is necessary. We expect that because of their organic/inorganic feature and the nanometer-size of the POSS macromers, POSS macromers would have significant potential as a nano-reinforcing filler for PDMS.

In the following studies, X-ray diffraction was utilized to characterize the morphologies of the POSS/PDMS blends. Thermal stability of the POSS/PDMS blends was studied by TGA, and the rheological measurements of POSS/PDMS blends were carried out with a Universal Dynamic Spectrometer.

5.2 Experimental:

5.2.1 Materials:

5.2.1.1 Polydimethyl siloxanes (PDMS):

A number of different molecular weight PDMS were provided by the Silicone Division at General Electric Company. Their characteristics are presented in Table 5.1.

Product Name	Chemical Name	Average Molecular Weight ^[1]	Viscosity ^[1] (centistokes) 25°C
SE72	polydimethylsiloxane gum	525,000	~
Visc100M	polydimethylsiloxane fluids	139,000	100000
Visc60M	polydimethylsiloxane fluids	116,500	60000
Visc30M	polydimethylsiloxane fluids	91,700	30000

 Table 5.1: Characteristics of Polydimethyl Silioxane (PDMS)

Note: (1) Provided by GE Silicone.

5.2.1.2 POSS Macromers:

POSS macromers used for the experiments described in this chapter include Cp_8POSS , Isobu₈POSS, V₈POSS, ST₁Cp₇POSS, Styrenyl₁Cp₇POSS, CyHe₁Cp₇POSS, V₁Cp₇POSS, ST₁Isobu₇POSS, and Styrenyl₁Isobu₇POSS.

See Table 3.1 and Figure 3.1 for their chemical structures.

5.2.2 Sample Preparation:

5.2.2.1 Samples Preparations for Thermogravimetric Analysis (TGA) and X-Ray Diffraction:

Preparations of POSS/PDMS blends were performed by dissolving PDMS and POSS macromer in toluene for 12 hours; evaporating the solvent, and then by drying the samples under vacuum for more than 12 hours at 60°C. 5.2.2.2 Samples Preparations for Rheology tests:

POSS and PDMS were dissolved in toluene for 12 hours. The solution was then poured into methanol, causing the POSS/PDMS blend to precipitate. This precipitate then was vacuum-dried for 24 hours at 60°C.

5.2.3 Characterization Techniques:

5.2.3.1. Morphology Characterization:

The morphologies of POSS/PDMS blends were characterized by X-ray diffraction techniques. X-ray diffraction measurements were performed using a Scintag XRD 2000 with a Cu target; 2 θ angle ranged from 5° to 30°; Step size and scan rate used here was 0.03° and 2° /min, respectively.

The x-ray diffraction pattern obtained from a diffractometer records the X-ray intensity as a function of diffraction angle. The inter-atomic spacing is determined by Bragg's law: $d = n\lambda / (2\sin\theta)$

Where d is the inter-atomic spacing; λ is the wavelength of the x-ray (λ =1.5406Å for Cu target); θ is the diffraction angle.

5.2.3.2 Thermal Stability Characterization:

Thermogravimetric analysis was carried out on a Hi-Res TGA 2950 under Nitrogen atmosphere. Temperature range used was 25 to 600°C; Heating rate utilized was 20°C/min. T_{dec} is taken as the temperature where 5% weight loss occurred. Residue is the weight percent of the sample remains after the TGA test.

5.2.3.3 Rheology Test:

The rheological properties of POSS/PDMS blends were determined using a stress-controlled rheometer, Paar-Physica UDS-200, equipped with a force-air oven with temperature ranged from -150° C to 600° C. A 25mm diameter cone-and-plate with an angle of 2° was used in this study.

The existence and extent of the linear viscoelastic (LVE) regime was determined by measuring the dynamic storage modulus, (G'), as a function of shear stress (test range is 24~2480Pa) at a constant frequency of 5Hz. The results showed that the POSS/PDMS blends exhibit linear viscoelasticity in the experimental conditions tested.

Measurements were performed in a temperature range from 30°C to 200°C. The experimental protocol used was as follows. The sample was loaded at 30°C and then the temperature was step-wise gradually increased until the desired annealing temperature was reached. Frequency sweep experiments were performed at each chosen temperature. Prior to each measurement, the temperature was held for 15 minutes to allow for equilibration. Upon reaching the desired annealing temperature, frequency sweep sweep experiments were performed as a function of annealing time.

Creep tests were conducted for the un-gelled (i.e. before annealing) and gelled (i.e. after annealing) POSS/PDMS blends at 30°C.

The following types of measurements were utilized in this research:

---Frequency Sweep: 0.315-315 rad/s at a Shear Stress 245 Pa;

---Shear Stress Sweep: 24-2480 Pa at a frequency 5Hz (31.4 rad/s);

---Strain ([©]) Sweep: 1-200% at a frequency 10Hz (62.9 rad/s);

---Steady State: Shear Rate: 0.01-100s⁻¹;

---Creep test: A constant shear stress is imposed on the sample, and time-dependent rheological information is recorded.

5.3 Morphological Structures of POSS/PDMS Blends

Because the glass transition of PDMS (T_g =-120°C) is well below ambient temperature, the specimens of POSS/PDMS blends are very soft. The TEM sample preparations of the POSS/PDMS blends require a special technique, which included sample micro-toming with a diamond knife at near liquid nitrogen temperatures (-150°C). Due to this complexity of the TEM sample preparations, in this section, we only employed X-ray diffraction technique to characterize the morphological structures of the POSS/PDMS blends.

The x-ray diffraction curves of Cp₈POSS/SE72, V₈POSS/SE72, Isobu₈POSS/SE72, ST₁Cp₇POSS/SE72, Styrenyl₁Cp₇POSS/SE72, CyHe₁Cp₇POSS/SE72, V₁Cp₇POSS/SE72, ST₁Isobu₇POSS/SE72, and Styrenyl₁Isobu₇POSS/SE72 blends (20wt% POSS loading) are shown in Figures 5.2 to 5.10. These figures show that compared to the x-ray diffraction curves of their neat POSS macromers, the microstructures of the POSS macromers are all modified to a various degree after they are mixed with PDMS.

As shown in Figure 5.2 and 5.3, after Cp_8POSS , and V_8POSS macromers are blended with PDMS, they still retain similar diffraction features to their corresponding neat POSS macromers, indicating that these two POSS macromers form their own phases, and their microstructures are not greatly affected by PDMS.



Figure 5.2: X-ray Profile of SE72/Cp₈POSS Blend (20 wt% POSS loading)



Figure 5.3: X-ray Profile of SE72/V₈POSS Blend (20 wt% POSS loading)



Figure 5.4 X-ray Profile of SE72/Isobu₈POSS Blend (20 wt% POSS loading)



Figure 5.5: X-ray Profile of SE72/ST₁Cp₇POSS Blend (20 wt% POSS loading)



Figure 5.6: X-ray Profile of SE72/Styrenyl₁Cp₇POSS Blend (20 wt% POSS loading)



Figure 5.7: X-ray Profile of SE72/CyHe₁Cp₇POSS Blend (20 wt% POSS loading)



Figure 5.8: X-ray Profile of SE72/V₁Cp₇POSS Blend (20 wt% POSS loading)



Figure 5.9: X-ray Profile of SE72/ST₁Isobu₇POSS Blend (20 wt% POSS loading)



Figure 5.10: X-ray Profile of SE72/Styrenyl₁Isobu₇POSS Blend (20 wt% POSS loading)

Figures 5.4 and 5.8 show that after Isobu₈POSS and V₁Cp₇POSS macromers blended with PDMS (SE72), they still retain the low 2 θ -angle diffraction peaks, which are similar to their corresponding neat POSS macromers. However, the crystalline peaks at the high 2 θ diffraction angles, as observed in the x-ray diffraction curves of the neat Isobu₈POSS and V₁Cp₇POSS macromers, disappear after they are blended with PDMS. This indicates that after Isobu₈POSS and V₁Cp₇POSS macromers are mixed with PDMS, only large scale ordered POSS structures are formed.

As seen in Figures 5.5, 5.6, 5.9, and 5.10, ST_1Cp_7POSS , Styrenyl₁Cp₇POSS, ST_1 Isobu₇POSS, and Styrenyl₁Isobu₇POSS macromers show less ordered structures after blended with PDMS, indicating a higher

degree of compatibility with PDMS than Cp_8POSS , V_8POSS , Isobu₈POSS, CyHe₁Cp₇POSS, and V₁Cp₇POSS.

In summary, the X-ray diffraction studies of POSS/PDMS (SE72) blends reveal that the less ordered POSS macromers have better compatibility with PDMS than the ordered POSS macromers.

5.4 Thermal Stability of POSS/PDMS Blends:

Figures 5.11 to 5.19 are the TGA curves of Cp₈POSS/SE72, V₈POSS/SE72, Isobu₈POSS/SE72, ST₁Cp₇POSS/SE72, Styrenyl₁Cp₇POSS/SE72, CyHe₁Cp₇POSS/SE72, V₁Cp₇POSS/SE72, ST₁Isobu₇POSS/SE72, and Styrenyl₁Isobu₇POSS/SE72 blends (20wt% POSS loading).

It can be seen in Figure 5.11 that the TGA curve of $Cp_8POSS/SE72$ blend locates below the TGA curves of both the neat components. This indicates that the blending of Cp_8POSS and PDMS decreases the thermal stabilities of both the neat components.

The TGA curves of $Isobu_8POSS/SE72$ (Figure 5.13), Styrenyl₁Cp₇POSS/SE72 (Figure 5.15), CyHe₁Cp₇POSS/SE72 (Figure 5.16) and V₁Cp₇POSS/SE72 (Figure 5.17) blends show that at the early stage of decomposition, these curves locate between the TGA curves of their corresponding neat components, while, after a certain temperature, the TGA curves of these blends fall below the TGA curves of their corresponding neat components.

As shown in Figures 5.11 and 5.19, during most of the temperature range investigated, the TGA curve of the Cp₈POSS/SE72 blend is below the TGA curves of both of the neat components, while the TGA curve of Styrenyl₁Isobu₇POSS/SE72 blend is between the TGA curves of their corresponding neat components. We can see from Figure 5.12 that the thermal stability of the V₈POSS/SE72 blend is between the thermal stabilities of their neat components: below a temperature of 510°C, the TGA curve of V₈POSS/SE72 blend is below the TGA curve of SE72 but above that of the V₈POSS macromer, while above 510°C, the TGA curve of this blend is below of V₈POSS macromer but above that of the SE72.



Figure 5.11: TGA Curve of SE72/Cp₈POSS Blend (20 wt% POSS loading)



Figure 5.12: TGA Curve of SE72/V₈POSS Blend (20 wt% POSS loading)



Figure 5.13: TGA Curve of SE72/Isobu₈POSS Blend (20 wt% POSS loading)

The thermal stability behaviors of the $ST_1Cp_7POSS/SE72$ and $ST_1Isobu_7POSS/SE72$ blends, as shown in Figure 5.14 and 5.18, are of more interest.

The $ST_1Cp_7POSS/SE72$ blend (Figure 5.14) exhibits higher decomposition temperature than both of their neat components. Below a temperature of 580°C, the TGA curve of $ST_1Cp_7POSS/SE72$ is above both the TGA curves of ST_1Cp_7POSS macromer and SE72. When the temperatures are higher than 580°C, the TGA curve of the $ST_1Cp_7POSS/SE72$ blend falls between the TGA curves of ST_1Cp_7POSS macromer and SE72. It is assumed that this thermal stability improvement might be due to the chemical reactions that occur between ST_1Cp_7POSS macromer and PDMS at elevated temperature. The attachment of POSS cages to the PDMS polymer chains, as a result of these chemical reactions, would then lead to the excellent thermal stability of the $ST_1Cp_7POSS/SE72$ blend.

Thermal stability improvement is also observed in the ST₁Isobu₇POSS/SE72 blend. As shown in Figure 5.18, although below a temperature of 490°C, the TGA curve of the ST₁Isobu₇POSS/SE72 blend is between the TGA curves of their neat components, when temperatures are in the range of 490°C to 580°C, the TGA curve of the blend is above both the TGA curves of the ST₁Isobu₇POSS macromer and SE72, indicating that ST₁Isobu₇POSS/SE72 blend has a better thermal stability than both of the neat components. After the temperature exceeds 580°C, the TGA curve of the blend again falls between the TGA curves of the ST₁Isobu₇POSS macromer and SE72.



Figure 5.14: TGA Curve of SE72/ST₁Cp₇POSS Blend (20 wt% POSS loading)



Figure 5.15: TGA Curve of SE72/Styrenyl₁Cp₇POSS Blend (20 wt% POSS loading)



Figure 5.16: TGA Curve of SE72/CyHe₁Cp₇POSS Blend (20 wt% POSS loading)



Figure 5.17: TGA Curve of SE72/V₁Cp₇POSS Blend (20 wt% POSS loading)



Figure 5.18: TGA Curve of SE72/ST₁Isobu₇POSS Blend (20 wt% POSS loading)



Figure 5.19: TGA Curve of SE72/Styrenyl₁Isobu₇POSS Blend (20 wt% POSS loading)

In summary, the TGA results reveal that only when POSS macromers with the proper reactive corner groups (such as a styryl group), induce chemical reactions between POSS and PDMS, will there be a significant enhancement of the thermal stability of the POSS/PDMS blends. The attachment of POSS massive cages to polymer chains renders POSS/PDMS blends with excellent heat resistance.

5.5 Rheological Behavior of POSS /PDMS Blends:

5.5.1 Effects of POSS Macromers on the Rheological Behaviors of PDMS:

Figure 5.20 shows the storage modulus of the various POSS/PDMS blends, versus angular frequency, at 30°C.

We can see from Figure 5.20 that the addition of Cp₈POSS, V₁Cp₇POSS, and ST₁Cp₇POSS macromers into PDMS (SE72) increases the storage modulus of the PDMS, while, the storage modulus of CyHe₁Cp₇POSS/SE72, Isobu₈POSS/SE72, Styrenyl₁Cp₇POSS/SE72, V₈POSS/SE72, ST₁Isobu₇POSS/SE72, and Styrenyl₁Isobu₇POSS/SE72 blends are similar to that of the SE72.

The above results indicate that the addition of POSS into PDMS doesn't significantly increase the storage modulus of the polymer. It is assumed that because there is no favorable interaction between these two components, POSS macromers behave like inert fillers which have no reinforcement to the polymer.





5.5.2 Gelation Process of POSS/PDMS Blends:

This section describes the gelation phenomenon of POSS/PDMS blends, which was discovered during the rheological measurements under elevated temperature. Gelation of the POSS/PDMS blends results in a rheological behavior change from that of a viscous liquid to that of an elastic solid.

5.5.2.1 Background of Gelation:

The term "gelation" is used here to describe the conversion of a liquid to a disordered solid by the formation of a network of chemical or physical bonds between the molecules or particles composing the liquid. In different situations, scientists use different terms to describe this phenomenon: such as association, cross-linking, vulcanization, flocculation, agglomeration, aggregation, clumping, or thickening.

Physical gelation occurs as a result of intermolecular association. Intermolecular associations are weak bonds produced by Van der Waals forces, electrostatic attractions, or hydrogen bonds. Chemical gelation takes place as a result of chemical bonds, which are covalent attachments between two atoms. Both physical gelation and chemical gelation lead to a formation of a network in the system, rendering a rheological property change from that of a viscous liquid to that of an elastic solid.

There are two major categories involved in gelation: polymeric gels, and particulate gels.

Polymeric Gels: Polymeric chemical gel is formed when a precursor liquid, composed of either small molecules or polymers, is cross-linked to form a gel, as occurs for example, during the curing of elastomers and thermoset plastics. Polymeric physical gelation is formed as a result of any one of the following interactions: locally helical structures whereby one molecule winds around another; microcrystallites; or nodular domains in which the chain is chemically heterogeneous, and association occurs only at preferred sites along the chain.

Particulate Gels: Particulate gelation is the conversion of an initially stable sol composed of colloidal particles to a solid-like gel phase by the formation of a network of particles. It occurs as a result of intermolecular association, which draws particles into near contact, producing a filler network. It has been postulated that the mechanical behavior of a filled blend material in response to the applied deformation is dominated by the formation, maintenance, and destruction of the filler network.

In filled polymer compounds, because of the high viscosity of polymers, filler particles dispersed in the polymeric matrix are in a relatively stable state. It is assumed that the reinforcement of elastomers due to reinforcing fillers (such as carbon black, fumed silica) is due to a formation of network structures among filler aggregates and the polymeric molecules. The network is held together by filler-filler interactions and filler-polymer-filler bridge bonds between the filler aggregates. Long

polymer molecules that are strongly adsorbed to the particle surfaces can induce gelation by bridging the gap between neighboring particles. The rheological properties of mixtures of particles and adsorbing polymers bear a resemblance to those of polymeric physical gels, wherein the particles play the role of cross-linkers, binding different polymer molecules together.

It has been found that appreciable carbon black gelation occurred in filled rubber stocks during storage or vulcanization in the absence of shear ^[69, 70]. The carbon black aggregates in the polymer matrix tended to agglomerate, and at high concentrations it was hypothesized that they form a continuous filler network structure, which was held together by relatively weak Van der Waals forces. Additionally, it was observed that these network structures broke up with increasing dynamic strain amplitude. The dissociation of the filler structure, also called the Payne effect, resulted in the removal of a significant part of the filler reinforcement, leading to a drop in the storage modulus G'. Furthermore, with the removal of the applied strain, the network was at least partially restored.

Fumed silica is widely used in industry as an active filler for reinforcement of elastomers, as a rheological additive in fluids, and as a free flow agent in powders. Fumed silica reinforced polydimethylsiloxane (PDMS) polymers have been extensively studied by scientists. Since its T_g is -123°C, PDMS is amorphous/rubbery at ambient temperatures and

above. When cross-linked, PDMS has a tensile strength of only about 0.35 MPa, hence it requires reinforcement to exhibit useful mechanical properties. ^[68] Amorphous silica, particularly fumed silica, is the primary reinforcing filler used in silicone elastomers. Studies ^[68, 71, 72] showed that the silanol groups and strained Si-O-Si bonds on the surface of fumed silica interact with the terminal chain silanol groups and the $-(CH_3)_2Si$ -O-Si(CH₃)₂- segments of the PDMS chains to form hydrogen bonding and Van der Waals forces. It is believed that the intermolecular interactions between fumed silica particles and PDMS render the formation of the silica-PDMS network and is responsible for the reinforcement effects. The network is held together by silica-silica interactions and silica-polymersilica bridge bonds between the silica aggregates. Increasing the silica loading, surface area, and structure level increases the number of interactions and hence the network strength.

One common problem in the studies of filled polymer gelation is reproducibility. Because these gels are disordered materials that are kinetically frozen, the method of preparation strongly influences the properties obtained. As a result, reproducibility is often a major problem with such materials; for example, the sample can "age", or change slowly over time. Therefore, the rheological properties of filled polymeric gels are, on the whole, not yet well-understood, in part because of their sensitivity to preparation and poor reproducibility.

Gelation phenomenon also has been observed in POSS/PDMS blends. In this study, we examined the rheological property changes during the gelation process of POSS/PDMS blends, the rheological behavior of the gelled POSS/PDMS blends, and the influence of POSS types, POSS concentration, polymer molecular weight, and annealing temperatures on the kinetics of the gelation process. Based on the experimental results, the gelation mechanics of the POSS/PDMS blends is postulated. During the entire experiments, the sample preparations were kept controlled at the same conditions as much as possible.

5.5.2.2 Gelation Process of POSS/PDMS Blends:

Figure 5.21 shows that the storage modulus, loss modulus and loss tangent (tan δ) changes of Isobu₈POSS/SE72 (10wt% POSS loading) before annealing and after 60hr annealing at 200°C. We can see from Figure 5.21 that the storage modulus of the un-annealed Isobu₈POSS/SE72 blend has a crossover with its loss modulus, while this crossover disappear in the annealed Isobu₈POSS/SE72 blend: the storage modulus of the annealed blend is higher than its loss modulus. It is also found that the loss tangent $(\tan \delta)$ of the annealed Isobu₈POSS/SE72 blend is lower than that of the un-annealed Isobu₈POSS/SE72 blend, and their values are less than 1. These results indicate that the rheological behavior of the Isobu₈POSS/SE72 blend changed from that of a viscous liquid to that of an elastic solid after annealing.



Figure 5.21: Comparison of Modulus (G' and G''), and Loss Tangent (tanô), as a function of frequency, of IsobusPOSS/SE72 Blend (10wt% POSS Loading) before annealing (open symbols) and after annealed for 60 hours at 200°C (filled symbols).

The whole annealing process of the Isobu₈POSS/SE72 blend (10wt% POSS loading) is shown in Figure 5.22, which describes the gradual changes of storage modulus (G'), loss tangent (tan δ), and complex viscosity of the blend with annealing time at 200°C. As shown in Figure 5.22 (a), with annealing time the storage Modulus (G') gradually increases and becomes less frequency-dependent. Furthermore, the changes of G' in the low frequency range are more dramatic than those in the high frequency range. At the high frequency end, G' remains basically constant after an initial drop at the beginning of the annealing. This indicates that the during the annealing process, the large-scale chain architecture of the polymer chain changes over annealing time, which has a profound effect on the storage modulus in the low frequency range.





Figure 5.22: Rheological Properties Changes of the 10weight % Loading Isobu₈POSS/SE72 Blend with Annealing Time at 200°C (cont'd)



b. Loss tangent $(tan \delta)$



c. Complex Viscosity

Figure 5.22: (cont'd)

The loss tangent and the complex viscosity behaviors of the $Isobu_8POSS/SE72$ blend with annealing time, as shown in Figure 5.22 (b) and (c), manifest that the loss tangent of the blend drops with annealing time and after 50 hrs, tan δ is less than 1, while the complex viscosity of the blend becomes more frequency-dependent with annealing time.

The rheological experiment of PDMS (SE72) was also conducted (Figure 5.23). The annealing of PDMS (SE72) sample at elevated temperatures showed no modulus increase; instead the modulus of SE72 decreases with annealing time at 200°C. It is believed that this reduction in modulus is caused by the thermal degradation of PDMS macromolecules at elevated temperatures.



Figure 5.23: Comparison of the Storage Modulus (G') and Loss Modulus (G''), as a function of frequency, of PDMS (SE72) at different annealing time at 200°C

All of the previous results indicate that gelation occurs in the Isobu₈POSS/SE72 blend (10wt%POSS loading) under elevated temperatures, which leads to the rheological behavior change of the blend from liquid-like to solid-like. No gelation found in SE72 manifests that the gelation of the Isobu₈POSS/SE72 blend is caused by the addition of POSS macromer.

5.5.3 Rheological Properties of Gelled POSS/PDMS Blends:

Figures 5.24 (a), (b) and (c) are the modulus, loss tangent, and complex viscosity, as a function of frequency, of the un-gelled and gelled Isobu₈POSS/Visc100M blend (10wt% POSS loading) at 30°C. These figures show that the gelled POSS/PDMS blends have the rheological features of "solid-like" materials.

Before the gelation, the storage modulus of the blend has a crossover with its loss modulus (Figure 5.24(a)). After the network is formed, the storage modulus of the blend is higher than its loss modulus and the elastic storage modulus, G', is less frequency dependent over a wide range of frequencies, which suggests that even for long-timerelaxation (or terminal) regions, the gelled blend behaves elastically.

As noted in Figure 5.24(b), the loss tangent of the gelled blend is lower than that of the un-gelled blend, and their values are less than 1, which is the characteristic behavior of a solid-like fluid.


Figure 5.24: Comparison of Rheological Properties, as a function of frequency, of un-gelled and gelled Isobu₈POSS/Visc100M (10wt%) blend at 30°C (cont'd).



Figure 5.24: cont'd

As shown in Figure 5.24(c), the complex viscosity of the gelled blends is more frequency dependent. The viscosity of the gelled blend falls off greatly with increasing frequency. In the low frequency range, the gelled blend has much higher viscosity than the un-gelled one. However, near the high frequency end, it approaches the un-gelled blend, whose viscosity is low and nearly constant throughout the frequency range.

In addition, the rheological properties of the gelled POSS/polymer blends show more non-linearity than the un-gelled blends. Figure 5.25 shows the low-frequency modulus, versus strain, of Isobu₈POSS/Visc100M (10wt% POSS) before and after gelation. Compared to the un-gelled Isobu₈POSS/Visc100M blend, the gelled blend

exhibits an earlier drop at a smaller strain of 40%. The modulus of the gelled blend tends to be highly strain-dependent, with linear behavior confined to a low strain amplitude.



Figure 5.25: Storage Modulus, as a function of strain, for un-gelled and gelled Isobu₈POSS/Visc100M blends of 10wt% POSS loading. The experiment was performed at 30°C and with angular frequency of 62.9 1/s.

Furthermore, the gelled POSS/PDMS blends are more creep resistant than the un-gelled blends. Figure 5.26 is the strain, versus time, of Visc30M/Isobu₈POSS blend (20wt% POSS) under shear stress of 500Pa at 30°C. During the creep phase, the strain of the un-gelled blend increases with time at a nearly constant rate, while the strain of the gelled blend, which is much lower than the strain of the un-gelled blend, is independent of time after loading. During the creep recovery phase, the strain of the un-gelled blend exhibits no recovery upon unloading, while the strain of the gelled blend goes immediately to nearly zero with unloading. The above creep results imply that the un-gelled blend behaves like a Newtonian liquid, and the gelled one bears the features of Hookean solid. We think that this high creep resistance behavior of the gelled POSS/PDMS is a result of POSS macromers acting like anchors, which constrain the mobility of the polymer chains.



Figure 5.26: Creep Behavior of the un-gelled and gelled Isobu₈POSS/Visc30M (20wt% POSS) blends. The experiment was conducted at 30°C, and shear stress of 500Pa.

5.5.4 Physical Nature of POSS/PDMS Gelation:

As we mentioned before, gelation can be physical (which occurs as a result of intermolecular association), or chemical (which takes place as a result of chemical bonds). Both physical gelation and chemical gelation lead to a formation of a network in the system, rendering a rheological property change from that of a viscous liquid to that of an elastic solid. The question here is: "What is the nature of the POSS/PDMS gelation: physical or chemical?" Through the investigations in the following experiments, we conclude that the gelation of the POSS/PDMS blends is physical.

5.5.4.1 DSC Result of POSS/PDMS Blend:

We expect that because the chemical composition of SE72 is polydimethyl silicone (PDMS), it is unlikely that chemical reaction would occur between POSS and PDMS. The DSC result of the Isobu₈POSS/SE72 (20wt% POSS loading) blend also proves that there is no chemical reaction between the two components. Although, as shown later in Figure 5.37, the rheology test manifests that the Isobu₈POSS/SE72 blend (20wt% POSS) gels after 6 hours at 200°C, however, the DSC result (Figure 5.27) of this blend, which was heated under isothermal condition (200°C) for 6 hours, shows that no chemical reaction was detected. In addition, the TGA result of Isobu₈POSS/SE72 blend (20 wt% POSS loading), as shown previously in Figure 5.13, also indicated that there is no chemical reaction occurred in the blend under elevated temperatures. Therefore, based on the above analysis, we suggest that the structure change in the POSS/PDMS blends is a physical association between the two components.



Figure 5.27: DSC Result of Isobu₈POSS/SE72 (20wt% POSS Loading) Blend under 200°C Isothermal Condition for 6hr.

5.5.4.2. Creep Tests --- Gelation Destruction and Re-forming of the Gelled POSS/PDMS Blends

Because physical gelation occurs as a result of intermolecular associations, which are weak Van der Waals forces and hydrogen bonds, it can be destroyed by large stress or strain and re-formed at gelation conditions. In the next experiment, the creep test is used to prove this physical nature of the POSS/PDMS gelation.

1. Destruction of POSS/PDMS Gelation:

The behavior of a sudden decrease in viscosity above a critical shear stress is often referred to as yield, and the critical stress is called the yield stress. In a filled polymeric gel, the yielding of the gel is related to the destruction of the filler-filler and/or the filler-polymer network. In this study, creep tests were used to determine the yielding of POSS/PDMS blends. Creep tests are useful for detesting the yielding of a material, since if the imposed stress is below the yielding point, the steadystate shear rate will be zero.



Figure 5.28: Creep Compliances of gelled Isobu₈POSS/Visc30M (10 wt% POSS loading) Blends under shear stresses of 5 and 10 KPa at 30°C

Figure 5.28 shows the creep compliances of the gelled $Isobu_8POSS/Visc30M$ (10wt% POSS) blend under constant shear stresses of 5KPa and 10 KPa respectively, at 30°C. Under a shear stress of 5KPa, the creep compliance of the gelled $Isobu_8POSS/Visc30M$ blend remains constant, however, under a 10KPa shear stress, the creep compliance of the gelled blend increases dramatically after 90 seconds.



Figure 5.29: Shear Rate of Gelled Isobu₈POSS/Visc30M Blends (10wt% POSS loading) during creep test (under shear stresses of 5 and 10 KPa at 30°C)



Figure 5.30: Viscosity, versus time, of Gelled Isobu₈POSS/Visc30M Blends (10wt% POSS loading) during creep test (under shear stresses of 5 and 10 KPa at 30°C)

During the 5 and 10 KPa creep tests, changes of shear rate and viscosity were also observed (Figure 5.29 and Figure 5.30). The results show that under the 5KPa shear stress, the shear rate of the gelled Isobu₈POSS/Visc30M blend retains zero, and its viscosity remains constant; while under the 10KPa shear stress, the shear rate of the gelled blend is no longer zero, and the viscosity has a sudden decrease. All the above results indicate that yielding of the gelled Isobu₈POSS/Visc30M blend takes place during the 10KPa creep test.

The frequency sweeps of the gelled $Isobu_8POSS/Visc30M$ blends before and after the 5 and 10 KPa creep tests were also conducted. Figures 5.31 and 5.32 are the modulus of the gelled $Isobu_8POSS/Visc30M$ blends (10wt% POSS loading) before and after the creep tests of 5KPa and 10KPa, respectively.



Figure 5.31: Modulus Comparison of the Gelled Isobu₈POSS/Visc30M Blend (10 wt% POSS loading) before and after the 5 KPa creep test

As shown in Figure 5.31, the modulus measured after the 5KPa creep test is almost coincident with the modulus before the creep test. It is also noticed that after the 5KPa creep test, the storage modulus of the blend still remains greater than its loss modulus, which indicates that the network structure is not destroyed by the shear stress.

Figure 5.32 shows that the un-crept Isobu₈POSS/Visc30M gel blend has the rheological features of an elastic solid, where the storage modulus is higher than its loss modulus. While the crept Isobu₈POSS/Visc30M blend behaves like a Newtonian liquid. The storage modulus of the blend measured after the 10KPa creep test has a crossover with its loss modulus. This result implies that the gelled blend has gone through a dissociation process during the 10KPa creep test, leading to the rheological behavior change of the gel from an elastic solid to a viscous liquid.



Figure 5.32: Modulus, as a function of frequency, of Gelled Isobu₈POSS/Visc30M Blends (10wt% POSS) before and after the 10 KPa creep

2. Re-Gelation Process:

When placing the destroyed Isobu₈POSS/Visc30M blend (10wt% POSS) at an elevated temperature of 200°C, the POSS-PDMS network can be restored (Figure 5.33). The re-gelation process is very fast; it even occurs during the heating phase. The storage modulus of the Isobu₈POSS/Visc30M blend is already higher than its loss modulus upon reach 200°C. This effect is probably because the destruction of the gelation is partial, and the POSS/PDMS blend needs less time to gel.



Figure 5.33: Re-Gelation of Isobu₈POSS/Visc30M Blend (10wt%POSS) at 200°C

Figure 5.34 shows the modulus, versus frequency, of the re-gelled Isobu₈POSS/Visc30M blend (10wt % POSS) at 30°C. Compared to the G', and G" curves before re-gelation (the curves with filled symbols as shown in Figure 5.32), the re-gelled blend has the rheological features of an elastic solid: its storage modulus G' is higher than its loss modulus G".



Figure 5.34: Modulus, as a function of frequency, of Re-gelled Isobu₈POSS/Visc30M Blend (10wt% POSS) 30°C.

3. Discussion:

The above results indicate that yielding of the gelled POSS/PDMS blends takes place during the 10KPa creep test, which reflects a dissociation process of the POSS/PDMS gels. The yielding mechanism of the gelled POSS/PDMS blends during the creep test is described as follow: Imagine that a POSS/PDMS gel is subjected to a shear stress that homogeneously displaces the particles and polymer chains from their positions of static equilibrium. Pairs of POSS aggregates, and pairs of POSS-PDMS would be pulled apart by this stress, and the separation distances among the POSS aggregates and polymer chains would increase. A force would be produced by this increased separation between the POSS particles and the adsorbed polymer chains that would tent to restore the original inter-particle spacing if the shear stress were removed. In this case, the gel would maintain its mechanical stability. But if the stress exceeds a certain point, any further stress would produce a decreasing force, and the POSS-PDMS network structure would break apart. This stress limit corresponds to the point of yielding.

Results of the creep tests (Figure 5.28) reveal that under the 5KPa yield stress, the creep strain of the gelled POSS/PDMS blends retains constant (independent of time after loading), which indicates that the gelled blends behave like a Hookean solid, and the associations between the POSS and the adsorbed PDMS chains are not destroyed. Under the 10KPa yield stress, the gelled POSS/PDMS blend responds elastically in the beginning (about 90 seconds). During this period, the POSS and PDMS polymer chains, which are confined in the gel network and entangled by surrounding chains, equilibrate in the deformed state. As a result, the creep strain retains a basically constant value. However, when the POSS and PDMS chains begin to relax locally and the polymer chains extricate themselves from the constraining POSS particles and mesh of surrounding chains, the POSS-PDMS network breaks down. Consequently, as shown in Figure 5.28, the strain increases dramatically.

When the destroyed POSS/PDMS gel is placed under an elevated temperature, the POSS-PDMS network structure is re-formed (Figure 5.33).

5.5.4.3 Physical Nature of the POSS/PDMS Gelation:

The above DSC and creep tests show that the gelation of the POSS/PDMS blend is physical. No chemical reaction is observed during the POSS/PDMS gelation process. The associations between POSS and PDMS are weak Van der Waals forces, and they can be destroyed by large stress or strain and re-formed at elevated temperatures.

The detail gelation mechanism will be discussed later in 5.5.6.1.

5.5.5 Effects of Compositions and Experimental Conditions on the Gelation Processes of the POSS/PDMS Blends:

In the following text, the effects of the POSS chemistry, POSS loading, PDMS molecular weights and annealing temperatures on the gelation rates of the POSS/PDMS blends are discussed.

First, we need to define a parameter which can properly characterize the gelation rates of the POSS/PDMS blends.

5.5.5.1 Rate of Storage Modulus Change (R_G) ---Characterization of the Gelation Rates of the POSS/PDMS Blends:

Because the gelation process of a POSS/PDMS blend is affected by the chemistry of the components, the composition and the experimental conditions etc., it is necessary to find a parameter that defines the gelation rate of the blend. Since the storage modulus of the POSS/PDMS blend in the low-frequency range changes dramatically with annealing time during its association, the rate of storage modulus change (in the low frequency range) --- R_G , is used to characterize the gelation rate of the POSS/PDMS blend.

The Rate of Storage Modulus Change (R_G) is defined as:

$$R_{G}(t, T) = \frac{G'(t, T) - G'(0, T)}{t}$$

where t is the annealing time; G'(t, T) is the storage modulus of the blend at annealing time t and annealing temperature T under a constant frequency f; and G'(0, T) is the initial storage modulus of the blend at

annealing temperature T under a constant frequency f. In this study, angular frequency f is chosen as 1 rad/s.

5.5.5.2 Effects of the POSS Chemistry on the Gelation Processes of the POSS/ PDMS Blends:

Figure 5.35 is the rates of storage modulus change (R_G) of the blends of PDMS (SE72) with POSS macromers bearing different corner groups (20wt% POSS loading).

We can see from Figure 5.35 that among the three R_8POSS macromers: Cp_8POSS , V_8POSS , and $Isobu_8POSS$, gelation occurs in the $Isobu_8POSS/SE72$ blend, but no gelations are found in the $Cp_8POSS/SE72$, $V_8POSS/SE72$ blends.

Although there is no gelation in the Cp₈POSS/SE72 blend, however, with one of its cyclopentyl corner groups replaced, gelation takes place in the blends of V₁Cp₇POSS /SE72, ST₁CP₇POSS /SE72, CyHe₁Cp₇POSS /SE72, and Styrenyl₁Cp₇POSS/SE72. The order of gelation rates, from fast to slow, is Styrenyl₁Cp₇POSS/SE72, CyHe₁Cp₇POSS/SE72, ST₁CP₇POSS /SE72, and V₁Cp₇POSS/SE72.

Similar results can be arrived at when comparing the gelation rates of the blends of SE72 with POSS macromers bearing isobutyl groups as their corner groups. As shown in Figure 5.35, the gelation rates of the Styrenyl₁Isobu₇POSS/SE72 and ST₁Isobu₇POSS/SE72 blends are significantly higher than that of the Isobu₈POSS/SE72 blend. The order of





gelation rates, from fast to slow, is Styrenyl₁Isobu₇POSS/SE72, ST₁Isobu₇POSS/SE72 and Isobu₈POSS/SE72.

We also notice that the gelation rates of POSS macromers with isobutyl corner groups (such as: Isobu₈POSS/SE72, Styrenyl₁Isobu₇POSS/SE72 and ST₁Isobu₇POSS/SE72) are higher than the gelation rates of their corresponding POSS macromers bearing cyclopentyl corner groups (for example: Cp₈POSS/SE72, Styrenyl₁Cp₇POSS/SE72, and ST₁CP₇POSS /SE72). The Isobu₈POSS/SE72, Styrenyl₁Isobu₇POSS/SE72 and ST₁Isobu₇POSS/SE72 blends gel faster than the Cp₈POSS/SE72, Styrenyl₁Cp₇POSS/SE72, and ST₁CP₇POSS/SE72 blends, respectively.

The above results reveal that the chemistry of the organic corner groups on the POSS cages has dramatic effects on the gelation rates of the POSS/PDMS blends. It is thought that the compatibility between POSS and PDMS, the dispersion of the POSS in PDMS and the interactions between POSS and PDMS influence the gelation processes of the POSS/PDMS blends.

Because of their good compatibilities with PDMS, Isobu₈POSS, Styrenyl₁Isobu₇POSS, ST₁Isobu₇POSS, Styrenyl₁Cp₇POSS, ST₁CP₇POSS, and CyHe₁Cp₇POSS macromers are well dispersed in the host and form stable colloidal dispersions. At elevated temperatures, polymer chains diffuse to POSS particle surfaces and form POSS-polymer associations.

However, since Cp_8POSS and V_8POSS macromers have relatively poor compatibility with PDMS, these two POSS macromers are not well-

dispersed and have a larger domain phase in the PDMS matrix. This severe aggregation of POSS macromers dramatically decreases the POSS surface areas that polymer chains can interact with, leading to a less effective use of the POSS macromers.

In summary, the gelation rates of the POSS/PDMS blends depend on the chemistry and structures of the POSS corner groups. Our studies manifest that POSS macromers which have good compatibilities with PDMS have a stronger tendency to gel under elevated temperatures than those with poor compatibility. Good compatibility ensures thorough dispersions of the POSS macromers in the PDMS matrix and sufficient interactions between POSS and PDMS, which result in the formation of POSS-PDMS network. While for POSS macromers which are incompatible with the PDMS host, POSS-PDMS networks are less likely to form in the blends because of the reduced interacting surfaces of the POSS macromers.

5.5.5.3 Gelation Behaviors of POSS/PDMS Blends with Different POSS Concentrations:

Figure 5.36 is the rate of storage modulus change (R_G) , versus annealing time, of Isobu₈POSS/Visc100M blends with different POSS loadings. The results show that with increasing POSS loading, the gelation rates of the blends increase. It is assumed that increasing the POSS concentration increases the number of anchors (interaction sites) for polymer chains to interact with, and hence the gelation rates of the blends.



Figure 5.36: Effects of POSS Loading on the Gelation Rates of Isobu₈POSS/ PDMS (Visc100M) Blends

5.5.5.4 Influence of PDMS Molecular Weight on the Gelation Rates of POSS/PDMS Blends:

Figure 5.37 shows the effect of PDMS molecular weight on the gelation rates of Isobu₈POSS/PDMS blends (20wt% loading). Comparing the gelation rates of the blends of Isobu₈POSS with Visc30M, Visc60M, and Visc100M, we can see that with increasing of PDMS molecular weight, the gelation process slows down. Such an inverse dependence on molecular weight or indirectly on viscosity would be expected in a diffusion-controlled gelation process. Increasing the molecular weight of PDMS enhances the entanglement of the polymer chains, hence reduces the diffusion rate of the polymer chains towards POSS particles. However, the gelation rate of the Isobu₈POSS/SE72 blend is higher than those of the Isobu₈POSS/Visc60M and Isobu₈POSS/Visc100M blends. We assume that it is because POSS macromers are better dispersed in the high molecular weigh PDMS gum (SE72) than in the PDMS fluid (Visc), as stated in Chapter 4. This dispersion effect ensures POSS macromers have more surface areas that PDMS chains can interact with.





5.5.5.5 Effects of Annealing Temperatures on the Gelation Rates of POSS/PDMS Blends:

The rates of storage modulus change (R_G) of Isobu₈POSS/Visc30M (10wt% POSS loading) blends at different annealing temperatures are shown in Figure 5.38. The results show that decreasing the annealing temperatures results in an enormous drop in the gelation rates of the POSS/PDMS blends. This phenomenon can be explained by realizing that the annealing temperature has a tremendous impact on the diffusion rate of the polymer chains. Raising the temperature increases the mobility of the polymer chains by expanding the free volume and boosting the thermal energy of the polymer chains. As a result, the diffusion rate of polymer chains towards POSS macromers increases, leading to a faster gelation



Figure 5.38: Effects of Annealing Temperatures on the Gelation Rates of Isobu₈POSS/PDMS (Visc30M) Blends (10wt% POSS Loading)

5.5.6 Discussion

5.5.6.1 Gelation Mechanism of the POSS/PDMS Blends

From the above rheological results, we can see that under elevated temperatures gelation occurs in POSS/PDMS blends. The interactions between PDMS and POSS macromers, which lead to the formation of POSS-POSS or/and POSS-PDMS network, take place and progress further upon aging (annealing) at elevated temperatures. The nature of these interactions is physical, as stated earlier.

There are two possible physical interactions, which may contribute to the network strength of the POSS/PDMS blends:

- 1) Interactions between POSS and POSS macromers, which lead to the flocculation of the POSS macromer.
- 2) Interactions between POSS and Polymer, which result in POSSpolymer associations.

In the first case, POSS particles, assumed well-dispersed in polymeric matrix, diffuse toward each other to form particle pairs, triplets, and so on. This growth process continues until filler network is formed. In this situation, the domains of POSS aggregates after gelation would be bigger than those of POSS aggregates before gelation, and there would be a tendency toward larger phase separation. However, as shown in Figures 5.39, and 5.40, the X-ray diffraction curves of the Styryl₁Isobu₇POSS/SE72 and Styrenyl₁Isobu₇POSS/SE72 blends (20wt% POSS loading) after gelation shows little difference from the X-ray diffraction curves of these blends



Figure 5.39: X-ray Diffraction Profiles of ST₁Isobu₇POSS/PDMS (SE72) Blends (20wt% POSS Loading) Before and After Gelation



Figure 5.40: X-ray Diffraction Profiles of Styrenyl₁Isobu₇POSS/ PDMS (SE72) Blends (20wt% POSS Loading) Before and After Gelation

before gelation, indicating that the gelled blends are still homogenous and no phase separation occurs. Also it is observed that during the experiments, the gelled Styryl₁Isobu₇POSS/SE72, and Styrenyl₁Isobu₇POSS/SE72 blends samples still remain transparent. Therefore it is postulated that POSS flocculation is not the main gelation mechanism of the POSS/PDMS blends.

In the second case, interactions, similar to those found in fumed silica filled PDMS, occur between PDMS and POSS when the Si-O-Si bonds on the surface of POSS particles interact with the $-(CH_3)_2Si$ -O-Si $(CH_3)_2$ - segments of the PDMS chains resulting in Van der Waals interactions. Although the adsorptive interactions in POSS-polymer blends are weak, there is, however, considerable evidence that the elastomer molecules are affected by even weak interactions arising from adsorptive or dispersion forces. As a result of these weak interactions between filler and polymer chains, the molecular mobility of polymers is decreased in the vicinity of filler surfaces ^[68, 71,72].

It is postulated that long polymer molecules are adsorbed to the surfaces of POSS particles, inducing the formation of a gel network by bridging the gap between the neighboring POSS particles. The bridging can be a single polymer chain, which is attached to two or more adjacent POSS aggregates, forming a POSS-polymer-POSS bond bridge (Figure 5.41(a)), or two single polymer chains entangle together, each of which is attached to a different single POSS aggregate, (Figure 5.41(b)),



A single polymer chain is attached to two or more adjacent POSS aggregates, forming a POSS-polymer-POSS bond

Two single polymer chains entangle together, each of which is attached to a different single POSS aggregate,

A single polymer chain, which is attached to a single POSS aggregate, entangle with other free bulk polymer chains in the system

POSS Aggregate

PDMS polymer chains

Figure 5.41: Schematic Diagram of the Formation of the POSS-PDMS Network

or a single polymer chain, which is attached to a single POSS aggregate entangle with other free bulk polymer chains in the system (Figure 5.41(c)). The rheological properties of the mixture of POSS particles and adsorbing polymers bear a close resemblance to those of polymeric physical gels, wherein the POSS particles play the role of cross-linkers, binding different polymer molecules together.

In summary, the gelation of the POSS/PDMS blends occurs as a result of intermolecular associations between the POSS filler and polymer chains, leading to the formation of a POSS-PDMS network. The interaction between POSS and polymer chains is mainly due to Van de Waals force. However, the precise nature and origin of the gelation process for POSS/Polymer blends still needs further investigation.

5.5.6.2 Gelation Process of POSS/PDMS Blends:

In our study, the storage modulus change at the low frequency range is used to characterize the gelation rate of the POSS/PDMS blend. Although the gelation rates of POSS/PDMS blends vary with the composition of the blends and experimental conditions etc., the gelation process generally includes four stages, as shown in Figure 5.42: (1) an induction period, (2) an acceleration stage, (3) a plateau stage, and (4) a deceleration stage. Although the previous rheology tests show that some POSS/PDMS blends exhibit virtually no induction period, while others have little or no tendency toward slowing down or have a very short plateau stage, most blends can clearly manifest all these four stages at proper temperatures.



Figure 5.42: Schematic Illustration of the Gelation Process of POSS/Polymer Blends

The induction period represents the time interval, during which no measurable gelation can be observed at the annealing temperature. During this stage, polymer chains near the POSS aggregates diffuse further toward the surfaces of POSS particles, but there are no interactions formed between them. Following the induction period, gelation occurs at a rate which is dependent on temperature and the nature of the composition. In this stage, an embryo of POSS-polymer network forms and the storage modulus of the blend dramatically increase. As the generation of the POSpolymer network culminates, the rate of storage modulus increase reaches a constant and the gelation process comes to a plateau period. After the POSS-polymer network is mostly completed, the gelation process reaches its deceleration stage. At this stage, the rate of modulus increase drops and gelation process slows down.

The gelation processes of POSS/PDMS blends are affected by the POSS chemistry, POSS loading, PDMS molecular weight, and annealing temperatures. With increasing of the compatibility between POSS and PDMS, POSS loading, and annealing temperatures, and decreasing of PDMS molecular weight, the gelation rates of the POSS/PDMS blends increase.

5.5.7 Summary:

1. Rheological Features of Gelled POSS/PDMS Blends:

The rheological properties of the gelled POSS/PDMS blends bear the features of elastic solids. The storage modulus G' of the gelled blends is higher than their loss modulus G", and G' is nearly independent of frequency.

For these solid-like POSS/PDMS gels, their loss tangent, tan[®], is less than 1 and their shear viscosity decreases with increasing frequency.

In addition, the gelled POSS/PDMS blends display stronger nonlinear rheological behaviors than the un-gelled blends. The storage modulus of the gelled blends has an earlier drop at a smaller strain than the un-gelled blends.

Furthermore, the Gelled POSS/PDMS blends have significantly improved creep resistance.

2.Gelation Rates of the POSS/PDMS Blends:

The studies of the effects of POSS chemistry on the POSS/PDMS gelation reveal that the POSS-PDMS associations tend to occur in blends where POSS macromers are well dispersed in PDMS matrix, i.e. where POSS macromers have good compatibility with PDMS. The gelation rates of the POSS/PDMS blends are enhanced with increasing of the annealing temperatures and POSS loading.

3. Gelation Mechanism of the POSS/PDMS Blends:

The gelation of the POSS/PDMS blends occurs as a result of intermolecular association between the POSS filler and the PDMS chains, leading to the formation of a POSS-PDMS network. The interactions between POSS and polymer chains are mainly Van de Waal forces. The POSS-PDMS network can be destroyed under large stress or strain and be re-formed at elevated temperatures.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions:

In this study, POSS macromers were incorporated into polymeric system by blending. Systematic studies on the POSS/polymer nanoscopic materials were, for the first time, conducted. The results of this work are concluded as follows:

1. The microstructures and thermal stability studies of POSS macromers show that the morphologies and properties of POSS macromers vary with the chemistry of the corner groups on the POSS cages.

a). Microstructural studies of POSS macromers by X-ray diffraction show that the higher the symmetry and regularity of the POSS macromers, and the smaller the size of the corner groups, the more ordered the POSS macromers. Among the 12 POSS macromers investigated, Cp₈POSS, Cy₈POSS, V₈POSS, and Isobu₈POSS are more ordered than Ph₈POSS, Styrenyl₈POSS, ST₁Cp₇POSS, Styrenyl₁Cp₇POSS, CyHe₁Cp₇POSS, V₁Cp₇POSS, ST₁Isobu₇POSS and Styrenyl₁Isobu₇POSS.

b). The chemistry of the organic corner groups on the POSS cages plays an important role in determining the thermal stabilities of POSS macromers. The POSS macromers with functionalities, which may undergo chemical cross-linking reactions, possess high thermal stability, for example: among all the 12 POSS macromers investigated, the

Styrenyl₈POSS (T_{dec} : 458.18°C, Residue: 79.12wt%) and Ph₈POSS (T_{dec} : 487.97°C, Residue: 52.71wt%) macromers have significantly high decomposition temperatures and residues.

The order of the POSS decomposition temperature from high to low is: Ph_8POSS (487.97°C), Styrenyl₈POSS (458.18°C), Cy₈POSS (397.5°C), ST₁Cp₇POSS (381.22°C), Styrenyl₁Cp₇POSS (374.62°C), Cp₈POSS (371.56°C), V₁Cp₇POSS (369.05°C), CyHe₁Cp₇POSS (348.14°C), Styrenyl₁Isobu₇POSS (301.2°C), ST₁Isobu₇POSS (284.96°C), Isobu₈POSS (267.58°C), and V₈POSS (251.28°C).

The order of the POSS residue yields from high to low is: Styrenyl₈POSS (79.12wt%), Ph₈POSS (59.71wt%), V₈POSS (47.87wt%), ST₁Cp₇POSS (39.80wt%), Styrenyl₁Cp₇POSS (32.32wt%), V₁Cp₇POSS (20.50wt%), Cy₈POSS (14.73wt%), ST₁Isobu₇POSS (10.50wt%), Cp₈POSS (5.64wt%), Isobu₈POSS (5.36wt%), CyHe₁Cp₇POSS (3.93wt%), and Styrenyl₁Isobu₇POSS (3.6wt%).

c). The DSC results of the POSS macromers show that the chemistry of the corner groups on POSS cages influences the transition temperatures of the POSS macromers.

The melting temperatures of Styrenyl₈POSS, Isobu₈POSS, V₈POSS, CyHe₁Cp₇POSS and Styrenyl₁Isobu₇POSS macromers are 274.3°C, 272.1°C, 349.1°C, 339.1°C and 169.3°C, respectively. The melting peaks of Cp₈POSS, Cy₈POSS, Ph₈POSS, Styrenyl₁Cp₇POSS, ST₁Cp₇POSS,

 V_1Cp_7POSS , and ST_1Isobu_7POSS macromers are not observed because their melting temperatures are higher than their decomposition temperatures.

Weak associations are also observed in Cp₈POSS, Cy₈POSS, Styrenyl₈POSS, Ph₈POSS, and Isobu₈POSS macromers.

2. Morphological structures of POSS/PS and POSS/PDMS blends were conducted by using TEM and X-ray diffraction. The results are summarized as follow:

a). The morphology studies of POSS/PS blends by TEM show that the chemistry of POSS macromers plays an important role in determining the morphologies of the POSS/PS blends. Depending on the attached chemical groups on the POSS macromer, the morphologies of POSS/PS blends ranged from a complete phase separation between POSS and PS to a homogeneous dispersion of POSS in the PS matrix in a nanoscopic scale. Among the eight POSS macromers used, Ph₈POSS is the most compatible one with PS and can be homogeneously dispersed in PS matrix. All other POSS/PS blends display a certain amount of phase separation to a various degrees.

The POSS concentration and PS molecular weight also influence the morphologies of the POSS/PS blends. With a decrease of POSS loading and increasing of PS molecular weight, POSS macromers are more homogeneously dispersed in the PS matrix.

b). The X-ray diffraction studies of POSS/PS blends show that the crystallography of POSS macromers in the POSS/PS blends depends on the compatibility between the two components. The more compatible POSS and PS are, the less crystalline the POSS macromer becomes when it blend with PS. When the two components are miscible, the POSS macromer disperses homogeneously in the PS matrix. Among the eight POSS macromers studied, Ph₈POSS is the most compatible one with PS. All the other POSS macromers: ST_1Cp_7POSS , $Styrenyl_8POSS$, Cy_8POSS , Cp_8POSS , V_8POSS , V_1Cp_7POSS , and $CyHe_1Cp_7POSS$ are partially compatible with PS.

With decreasing of POSS loading and increasing of PDMS molecular weight, POSS macromers are more well-dispersed in the PS matrix.

c). The morphology studies of POSS/PDMS blends by X-ray diffraction show that the less ordered POSS macromers have better compatibility with PDMS than the ordered POSS macromers.

3. Interaction studies of the POSS/PS blends show that there is no favorable interaction between macromers and polymeric chains. The POSS macromers behave like plasticizers in the PS matrix, which results in the decrease of the glass transition temperature of the PS and the broadening of the transition zone of the PS.

The more compatible between the POSS macromer and PS, the more the T_g drops and the more the transition width broadens. Among the five POSS/PS blends studied (Cp₈POSS/PS, Styrenyl₈POSS/PS, Ph₈POSS/PS, Isobu₈POSS/PS, ST₁Cp₇POSS/PS), the T_g of the Ph₈POSS/PS blend is the lowest.

4. Thermal stability studies of POSS/PS blends indicate that POSS/PS blends exhibit improved thermal stability when using POSS macromers with higher decomposition temperatures and residue yields than PS.

Thermal stability studies of POSS/PDMS blends reveal that only when POSS macromers with the proper reactive corner groups (such as: styryl group), which induce chemical reactions between POSS and PDMS, can significantly enhance the thermal stability of the POSS/PDMS blends. The attachment of POSS massive cage to the PDMS chains renders POSS/PDMS blends with excellent heat resistance.

5. The rheological investigations of POSS/PDMS blends show that under elevated temperatures, a network forms between POSS macromers and PDMS polymer chains, resulting in the gelation of the POSS/PDMS blends. It is postulated that this gelation of the POSS/PDMS blends occurs as a result of intermolecular association between POSS macromers and PDMS polymer chains.

The formation of gelation between POSS and PDMS endows the POSS/PDMS blends with a solid-like behavior. The gelled POSS/PDMS blends have high modulus, and significantly improved creep resistance. They also display stronger nonlinear rheological behaviors than the ungelled blends.

Because of its physical nature, the gelation formed in the POSS/PDMS blends can be destroyed under large stain or stress and reformed at elevated temperatures.

The studies of the effects of POSS chemistry on the gelation of the POSS/PDMS blends reveal that the associations tend to occur in blends where POSS macromers are well dispersed in polymer matrix, i.e. where POSS macromers have good compatibility with polymer.

It was also found that the gelation rates of POSS/PDMS blends are enhanced with increasing of the annealing temperatures and the POSS concentrations.

In summary, the crucial parameters in developing POSS/polymer nanoscopic materials with the desired properties are the compatibility and interactions between the two components, which determine the morphology and interface of the POSS/polymer blends. Good compatibility and strong interactions between POSS macromer and polymers result in a nano-dispersed POSS/polymer blend with an
enhanced performance, and these two requirements may be achieved by selecting POSS macromers with desired functional corner groups.

6.2 Recommendations:

A lot of efforts have been put into the above investigations on the POSS/polymer blends. However, since this research was just the beginning exploration of POSS macromers as reinforcing fillers for polymers, some of the structure/property relationships of POSS/polymer blends were still not completely clear and fully understood. The author suggests that the following further investigations should be conducted to make the current research work more thorough and complete.

1. During the TGA experiments of POSS/PDMS blends, it was found that $ST_1Cp_7POSS/PDMS$, and $ST_1Isobu_7POSS/PDMS$ blends exhibit significantly improved thermal stability. We assumed this improvement is due to the chemical reactions between POSS macromers and PDMS. However, further inspections need to be done in order to prove the mechanism of this improvement.

2. To develop POSS macromers as a reinforcing filler for silicone gum, the mechanical properties of the POSS/PDMS blends, the effects of the addition of curing agents in PDMS on the gelation of POSS/PDMS blends and so on need to be examined.

196

3. Studies on the gelation of other POSS/polymer blends need to be carried out in the future. Through these further investigations, we can find out that if gelation occurs in other POSS/polymer systems and if these POSS/Polymer pairs have the same gelation mechanism as the POSS/PDMS blends.

4. The morphologies and properties (mechanical properties, flame retardation, and oxygen permeability) studies of the blends of POSS macromers with other types of polymers (for example: PP, PE, Nylon, Epoxy, NR, EPR...) need to be investigated. Through these studies, we can test if the structure/property relationships developed in this work apply for other POSS/polymer systems.

5. Because the limited amount of POSS macromers available, this work only studied the morphologies and properties of solution blended POSS/polymer blends. The author suggests that the investigation of the morphologies and properties of the mechanical blended POSS/polymer blends (such as extruder, internal mixer) need to be conducted in the future.

197

REFERENCES

REFERENCES

- 1. J. Schwab, and J. D. Lichtenhan, Appl. Organometal. Chem, 12, 707 (1998).
- 2. T. S. Haddad, and J. D. Lichtenhan, Macromolecules, 29, 7302 (1996).
- 3. A. Ladenburg, Ann. 173, 143 (1874).
- 4. J. A. Meads and F. S. Kipping, J. Chem. Soc., 107, 459 (1915).
- 5. J. F. Brown and L. H. Vogot, J. Am. Chem., 87, 4313 (1965).
- 6. J. F. Brown, J. of Am. Chem. Soc., 87, 4317 (1965).
- 7. M. G. Voronkov, T. N. Martynova, R. G. Mirskov and V. I. Belyi, Zh. Obshch. Khim., 49, 1522 (1979).
- 8. T. N. Martynova, V.P. Korchkov and P. P. Swmyannikov. J. Organomet. Chem., 258, 277 (1983).
- 9. V. W. Day, W. G. Klemperer, V. V. Mainz and D. M. Miller, J. Am. Chem. Soc., 107, 8262 (1985).
- 10. F. J. Feher, T. A. Budzichowski, J. Organomet. Chem., 379, 33 (1989).
- 11. R. Weidner, N. Zeller, B. Deubzer and V. Frey, U.S. Pat., 5 047 492, (1991).
- 12. C. Zhang and R. M. Laine, J. Organomet. Chem., 521, 199 (1996).
- 13. F. J. Feher, D. Soulivoung and A. G. Eklund, K. D. Wyndham, Chem, Commun., 1185 (1997).
- 14. U. Dittmar, B. J. Hendan, U. Florke and H. C. Marsmann, J. Organomet. Chem., 489, 185 (1995).
- 15. R. Muller, R. Kohne, S. Sliwinski, J. Prakt. Chem., 9, 71 (1959).
- 16. P. A. Agaskar, Inorg. Chem. 30, 2707 (1991).
- 17. P. A. Agaskar, V.W. Day, W.G. Klemperer, J. Am. Chem. Soc. 109, 5554 (1987).
- 18. P. A. Agaskar, J. Am. Chem. Soc. 111, 6858, (1989).

- 19. D. Hoebbel, W. Wieker, Z. Anorg. Allg. Chem., 384, 43 (1971).
- 20. I. Hasegawa, S. Sakka, Y. Sugahara, K. Kuroda, C. Kato, J. Chem. Soc., Chem. Commun. 208 (1989).
- 21. C. Zhang, R. M. Laine, J. Organomet. Chem, 521, 199 (1996).
- 22. D. Hoebbel, K. Endres, T. Reinert, H. Schmidt, Mat. Res. Soc. Symp. Pro. 346, 863 (1994)
- 23. P. G. Harrison, J. Organomet. Chem., 542, 141 (1997).
- 24. C. L. Frye and W. T. Collins, J. Am. Chem. Soc., 92, 5586 (1970)
- 25. P. A. Agaskar, Inorg. Chem., 30, 2707 (1991).
- 26. P. A. Agaskar, V. W. Day, W. G. Klemperer, J. Am. Chem. Soc., 109, 5554 (1987).
- 27. A. R. Bassindale and T. Gentle, J. Organomet. Chem., 521, 391 (1996).
- 28. T. E. Gentle and A. R. Bassindale, J. Inorg. Organomet. Pol., 5, 281 (1995).
- 29. J. V. Crivello and R. Malik, J. Polym. Sci., Part A: Polym. Chem., 35, 407 (1997).
- 30. F. J. Feher, D. A. Newman, J. F. Walzer, J. Am. Chem. Soc., 111, 1741 (1989).
- 31. F. J. Feher, D. A. Newman, J. Am. Chem. Soc., 112, 1931 (1990).
- 32. F. J. Feher, T. A. Budzichowski, K. Rahimian, J. W. Ziller, J. Am. Chem. Soc., 114, 3859 (1992).
- 33. F. J. Feher, S. H. Phillips, J. Organomet. Chem. 521, 401 (1996).
- 34. F. J. Feher, S. H. Phillips, J. W. Ziller, Chem. Commun. 829 (1997).
- 35. F. J. Feher, T. A. Budzichowski, K. J. Weller, J. Am. Chem. Soc., 111, 7288 (1989).
- 36. F. J. Feher, K. J. Weller, Organometallics, 9, 2638 (1990).
- 37. F. J. Feher, K. J. Weller, J. W. Ziller, J. Am. Chem. Soc. 114, 9686 (1992).

- M. L. Montero, I. Uson, H. W. Roesky, Angew. Chem., Int. Ed. Engl. 33, 2103 (1994).
- 39. F. J. Feher, and T. A. Budzichowski, Polyhedron, 14, 3239 (1995).
- 40. F. J. Feher, R. L. Blanski, J. Chem. Soc., Chem. Commun. 1614 (1990).
- 41. F. J. Feher, J. F. Walzer, Inorg. Chem. 30, 1689(1991).
- 42. F. J. Feher, J. F. Walzer, R. L. Blanski, J. Am. Chem. Soc. 113, 3618 (1991).
- 43. F. J. Feher, R. L. Blanski, J. Am. Chem. Soc. 114, 5886(1992).
- 44. F. J. Feher, D. Soulivong and G. T. Lewis, J. Am. Chem. Soc., 119, 11323 (1997).
- 45. F. J. Feher, D. Soulivong and A. E. Eklund, Chem. Commun., 399 (1998).
- 46. F. J. Feher, J. J. Schwab, D. M. Tellers and A. Burstein, Main Group Chem., 2, 169 (1998).
- 47. F. J. Feher, D. Soulivong and F. Nguyen, Chem. Commun., 1279 (1998).
- 48. F. J. Feher, F. Nguyen, D. Soulivong and J. W. Ziller, Chem. Commun., 1705 (1999).
- 49. F. J. Feher, R. Terroba and J. W. Ziller, Chem. Commun., 2153 (1999).
- 50. F. J. Feher, R. Terroba and J. W. Ziller, Chem. Commun., 2309 (1999).
- 51. F. J. Feher, R. Terroba and R.-Z. Jin, Chem. Commun., 2513 (1999).
- 52. J.D. Lichtenhan, Comments Inorg. Chem., 17, 115 (1995).
- 53. T. S. Haddad, and J. D. Lichtenhan, Macromolecules, 29, 7302 (1996).
- 54. T. S. Haddad, E. Choe, J. D. Lichtenhan, Mat. Res. Soc. Symp. Proc., 435, 25 (1996).
- 55. A. Romo-Uribe, P. T. Mather, T. S. Haddad, and J. D. Lichtenhan, J. of Polymer Science: Part B: Polymer Physics, 36, 1857 (1998).
- 56. T. S. Haddad, J. Schwab, P. T. Mather, A. Romo-Uribe, Y. Otonari, M. J. Carr, J. D. Lichtenhan, ANTEC, 610, 1814 (1997).

- 57. J. D. Lichtenhan, C. J. Noel, A. G. Bolf, P. N. Ruth, Mat. Res. Soc. Symp. Proc., 435, 3 (1996).
- 58. J. D. Lichtenhan, Y. A. Otonari, and M. J. Carr, Macromolecules, 28, 8435 (1995).
- 59. P. T. Mather, H. G. Jeon, A. Romo-Uribe, T. S. Haddad, and J. D. Lichtenhan, Macromolecules, 32, 1194 (1999).
- 60. J. W. Gilman, D. S. Schlitzer, and J. D. Lichtenhan, J. of Applied Polymer Science, 60, 591 (1996).
- 61. A. Y. Lee, and J. D. Lichtenhan, Macromolecules, 31, 4970 (1998).
- 62. A. Lee, J. D. Lichtenhan, J. Appl. Polym. Sci., 73, 1993 (1999).
- 63. B. S. Hsiao, X. Fu, P. T. Mather, K. P. Chaffee, H. Jeon, H. White, M. Rafailovich, J. D. Lichtenhan, and J. J. Schwab, Polym. Mater. Sci. Eng., 79, 389 (1998).
- 64. J. Schwab, J. D. Lichtenhan, M. J. Carr, K. P. Chaffee, P. T. Mather, and A. Romo-Uribe; Polym. Mater. Sci. Eng., 77, 549 (1997).
- 65. B. X. Fu, L. Yang, R. H. Somani, S. X. Zong, B. S. Hsiao, S. Phillips, R. Blanski, and P. Ruth, J. Polym. Sci.: Part B: Polym. Phys., 39, 2727 (2001).
- 66. K. E. Polmanteer, Rubber Chem. and Technol., 54, 1051 (1981).
- 67. R. A. Mantz, P. F. Chaffee, J. D. Lichtenhan, and J. W. Gilman, Chem. Mater., 8, 1250 (1996).
- 68. E. L. Warrick, O. R. Pierce, K. E. Polmanteer, and J. C. Saam, Rubber Chem. Technol. 52, 437 (1979).
- 69. K. Yurekli, R. Krishnamoorti, M. F. TSE, K. O. Mcelrath, A. H. Tsou, H.-C. Wang, J. Polym. Sci.: Part B: Polym. Phys., 39, 256 (2001).
- 70. G. Bohm and M. Nguyen, J. Appl. Polym. Sci., 55, 1041 (1995).
- 71. H. Cochrane and C. S. Lin, Rubber Chem. Technol., 66, 48 (1993).
- 72. M. P. Wagner, Rubber Chem. Technol., 49, 703 (1976).

