ABSTRACT

CAYDAMLI, YAVUZ. Development of POSS Structure-Matrix Polymer Property Relations. (Under the direction of Dr. Alan E. Tonelli, and Dr. Dr. Richard J. Spontak).

Polyhedral Oligomeric Silsesquioxanes (POSS) are 3D inorganic-organic hybrid cage-like molecules with the general formula \((RSiO_{1.5})_n\). Their unique structure makes them the smallest silica particles. Due to organic groups on the corners of each molecule, POSS has countless types of molecular compositions and applications. From this dissertation, we would like to gain a basic understanding between different POSS structures and polymer matrices by systematically changing the organic groups of POSS. It is important that we can predict how a particular POSS type and polymer will behave in terms of phase behavior. POSS structures should have a direct effect on almost every major property of their nanocomposites and functions.

In the first chapter, we introduce POSS, with its major types, application areas, and usage in fibrous structures. In the second chapter, we compare three types of POSS behavior in the same polymer matrix (PEO). Each POSS has non-functional hydrocarbon chains varying systematically in length. Besides experimental work, we also compared them with computational studies and tried to have drawn mathematical conclusions. In the third chapter, we compare PEO/POSS composites with POSS molecules varying only in one functional group. Likewise, we compared their observed behaviors with computational calculations as well and found important correlations.

In the fourth chapter, we probe the results of the third chapter further by doing both experimental and computational studies. As a result, we gained a deeper understanding of the effects of POSS chemical structure on their composites with PEO. In the fifth and last experimental chapter, we introduced a new polymer to the polymer-POSS composite blend that is compatible with POSS. We discussed its success in this role by doing several experimental analyses.
Development of POSS Structure - Matrix Polymer Relations

by
Yavuz Caydamli

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Fiber and Polymer Science

Raleigh, North Carolina
2017

APPROVED BY:

________________________________________  _______________________________________
Dr. Alan E. Tonelli                                    Dr. Richard J. Spontak
Co-Chair of Advisory Committee                          Co-Chair of Advisory Committee

________________________________________  _______________________________________
Dr. Melissa A. Pasquinelli                                Dr. Samuel M. Hudson
DEDICATION

To my beloved family
Yavuz Caydamli was born and raised in the third largest city of Turkey: Izmir. He received both B.Sc. and M.Sc. degrees in Textile Engineering at Dokuz Eylul University (Izmir, Turkey).

After being awarded with Fulbright Scholarship, he started his PhD degree at NC State University-Fiber and Polymer Science program under direction of Dr. Alan E. Tonelli, and Dr. Richard J. Spontak. Besides his research efforts, which resulted in three research awards and three research image awards, he taught a course for five consecutive academic terms, completed the certificate of accomplishment in teaching (CoAT) program and received the outstanding graduate student teachers award for two consecutive years.
ACKNOWLEDGMENT

I am grateful to my advisors, Dr. Alan E. Tonelli, and Dr. Richard J. Spontak for their continuous support throughout my doctoral study.

I would also like to thank my committee members, Dr. Melissa A. Pasquinelli, Dr. Samuel M. Hudson, and Dr. Denis Fourches for their precious time, helpful feedbacks, and assistance. I am thankful to Dr. Erol Yildirim, who joined to NC State University as a post-doctoral researcher in Dr. Pasquinelli’s research group, for his continuous help, teaching, and support to me especially on the computational modeling part of this dissertation.

I am thankful to all my former and current group members: Jialong Shen, Xiaomeng Fang, Shanshan Li, Alper Gurarslan, Hui Yang, Abhay Sham Joijode, Ganesh Narayanan, Rana Gurarslan, and all M3G group members for their timely discussions and help.

I would also like to express gratitude to Charles Mooney, and Judy Elson for their helpful training on various instruments.

As a Fulbrighter, I thank Fulbright Scholarship very much not only for monetary support but also for the friendly contacts and assistance whenever I needed.

Finally, very special thanks go to my family especially my parents Lale and Ali Caydamli, my brother Selim, my aunt Yasemin Barbaros, and my beloved grandmothers Sermin Barbaros and Mukaddes Caydamli for their great support, love, and trust in me.
TABLE OF CONTENTS

LIST OF TABLES ......................................................................................................................... ix

LIST OF FIGURES ...................................................................................................................... x

Chapter 1  Introduction .................................................................................................................. 1
  1.1 Background .............................................................................................................................. 1
  1.2 History of POSS ......................................................................................................................... 4
  1.3 Production of POSS .................................................................................................................... 5
  1.4 Hydrosilylation ............................................................................................................................ 6
  1.5 Metallasilsesquioxanes ............................................................................................................... 7
  1.6 POSS in Polymers ....................................................................................................................... 9
  1.7 Applications of POSS with Polymers ...................................................................................... 10
    1.7.1 Electronics and Energy Applications ............................................................................... 12
    1.7.2 Space Applications ............................................................................................................ 14
    1.7.3 Biomaterial Applications ................................................................................................. 14
  1.8 Fiber Applications with POSS ............................................................................................... 15
  1.9 POSS in PEO ........................................................................................................................... 20

Chapter 2  Investigation of POSS molecules with different hydrocarbon side chains .......................... 23
  2.1 Materials and Methods ............................................................................................................. 24
    2.1.1 Polarized optical light microscopy ................................................................................. 25
2.1.2  Confocal Laser-Scanning Microscopy .................................................. 25
2.1.3  Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS) ................................................................. 25
2.1.4  Thermogravimetric Analysis (TGA) ........................................................ 26
2.1.5  Mechanical Testing .............................................................................. 26
2.1.6  Methodology of Computational Calculations .......................................... 26
2.2  Results and Discussion ........................................................................... 29
  2.2.1  Polarized Optical Light Microscopy ...................................................... 29
  2.2.2  Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) Map ............................................................. 35
  2.2.3  Confocal-Laser Scanning Microscopy (CLSM) ..................................... 45
  2.2.4  Computational Calculations ................................................................. 52
  2.2.5  Thermogravimetric Analysis ............................................................... 54
  2.2.6  Mechanical Analyses ......................................................................... 55
2.3  Conclusion .............................................................................................. 56

Chapter 3  Investigation of Isobutyl POSS molecules with mono-substituted functional groups ........................................................................... 57
  3.1  Materials and Methods .......................................................................... 58
    3.1.1  Polarized optical light microscope ................................................... 60
    3.1.2  Confocal Laser-Scanning Microscope .............................................. 60
3.1.3 Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDS) ................................................................. 60
3.1.4 Thermogravimetric Analysis .................................................................................................................. 60
3.1.5 Mechanical Tests .................................................................................................................................. 60
3.1.6 Methodology of Computational Calculations ....................................................................................... 61
3.2 Results and Discussion ............................................................................................................................ 63
  3.2.1 Polarized Optical Light Microscope .................................................................................................. 64
  3.2.2 Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) Map .................................................. 70
  3.2.3 Confocal-Laser Scanning Microscope (CLSM) ................................................................................. 82
  3.2.4 Computational Calculations ........................................................................................................... 84
  3.2.5 Thermogravimetric Analysis .......................................................................................................... 92
  3.2.6 Mechanical Analyses ...................................................................................................................... 92
3.3 Conclusion .................................................................................................................................................. 94
Chapter 4 Understanding Allyl isobutyl POSS behavior ........................................................................... 95
  4.1.1 Computational Calculations ........................................................................................................... 106
  4.2 Conclusions and Future work ............................................................................................................. 108
Chapter 5 Use of compatibilizer polymer in an immiscible polymer-POSS blend ...................................... 110
Chapter 6 Conclusions and Future work .................................................................................................. 132
LIST OF TABLES

Table 1.1 Properties of carbon fibers used in unsaturated polyester composites [79,81,84,85,120] ........................................................................................................................................... 19
Table 2.1 List of interaction energies between PEO and POSS samples ................. 52
Table 2.2 List of interaction energies between POSS and POSS samples .............. 53
Table 2.3 Summary of interaction energies* including the ΔE/RT normalized interaction parameter ...................................................................................................................................... 54
Table 3.1 List of interaction energies between PEO and POSS samples ............... 85
Table 3.2 List of interaction energies between POSS and POSS samples ............ 86
Table 3.3 Summary of interaction energies* including the ΔE/RT normalized interaction parameter ...................................................................................................................................... 87
Table 5.1 Molecular interaction energy results for several POSS-Polymer couples using Monte Carlo computer simulations .............................................................................................................. 111
Table 5.2 Sample set and recipes ........................................................................... 116
LIST OF FIGURES

Figure 1.1 General structure of POSS [3]................................................................. 2
Figure 1.2 Types of silsesquioxanes and difference between T8 and Q8 [7]........... 2
Figure 1.3 Different cage structures of POSS based on number of silicon atoms. [7] 3
Figure 1.4 The number of patents and publications about silsesquioxanes before foundation of Hybrid Plastics [6]................................................................. 5
Figure 1.5 Hydrolytic condensation of trifunctional organosilanes resulting with POSS formation [8]................................................................. 6
Figure 1.6 Possible outcomes of hydrosilylation reaction: α- and β- additions [8] ..... 6
Figure 1.7 Three different ways to synthesize mono-substituted POSS molecules. [8] ............................................................................................................... 7
Figure 1.8 Synthesis of the titanasilsesquioxanes [29,36]................................. 8
Figure 1.9 Molecular models that mimic the various types of silanol groups of a silica surface [37,38] ......................................................................................... 9
Figure 1.10 POSS-Polymer configurations [21].............................................. 10
Figure 1.11 Molecular structure of T8 POSS, list of important properties and applications [14]...................................................................................... 12
Figure 1.12 Dumbbell shaped main chain LC polymer [11]............................... 13
Figure 1.13 Molecular Structures of MEH-PPV-POSS and PFO-POSS [46]....... 13
Figure 1.14 Synthesis route of POSS-functionalized polyfluorene [47]............. 14
Figure 1.15 The chemical structures of the two kinds of POSS: (a) OA and (b) ONPS [74]...................................................................................... 16
Figure 1.16 Schematic of the two phase structure of POSS-benzyl$_7$(BF$_3$Li)$_3$/POSS-PEGs: (i) one phase is clustered phenyl groups with POSS-benzyl$_7$(BF$_3$)$^{3-}$ anions oriented outward; (ii) the other phase is POSS-PEGs with solvated Li$^+$. Inset shows the phase boundary. [135]........................................................................................................... 22

Figure 2.1 POSS molecules with different organic groups, in terms of length of hydrocarbons: (a) Methyl-, (b) Isobutyl-, (c) Isooctyl- [19]............................................................. 24

Figure 2.2 POSS model containing unit cell ......................................................................................... 26

Figure 2.3 Model PEO oligomer used in this study ............................................................................. 27

Figure 2.4 Unit cell filled with PEO chains and single POSS molecule in the middle ................................................................................................................................................................. 27

Figure 2.5 Five lowest energy values out of twenty-five results...................................................... 27

Figure 2.6 Methodology to calculate the interaction energy between PEO and POSS ................................................................................................................................................................. 28

Figure 2.7 Methodology to calculate the interaction energy between POSS and POSS ............................ 28

Figure 2.8 Polarized light microscope images of pure PEO films in different magnifications .......................................................... 31

Figure 2.9 Polarized optical light microscope images of Octamethyl POSS/PEO films
in different ratios and magnifications: (a)1%, (b)2.5%, (c)5% (d)7.5, (e)10% ...... 32

Figure 2.10 Polarized optical light microscope images of Octaisobutyl POSS/PEO films
in different ratios and magnifications: (a)1%, (b)2.5%, (c)5% (d)7.5, (e)10% 33

Figure 2.11 Polarized optical light microscope images of Isooctyl POSS/PEO films in
different ratios and magnifications: (a)1%, (b)2.5%, (c)5% (d)7.5, (e)10% .......... 34
Figure 2.12 PLM Images of 10% Octamethyl POSS containing PEO film............... 36
Figure 2.13 PLM Images of 10% Octaisobutyl POSS containing PEO film.......... 37
Figure 2.14 PLM Images of 10% Isooctyl POSS containing PEO film ............... 38
Figure 2.15 Longitudinal SEM view of %10 Octamethyl POSS containing PEO film and its EDS map for Silicon................................................................. 39
Figure 2.16 Longitudinal SEM view of %10 Octaisobutyl POSS containing PEO film and its EDS map for Silicon................................................................. 40
Figure 2.17 Longitudinal SEM view of %10 Isooctyl POSS containing PEO film and its EDS map for Silicon................................................................. 41
Figure 2.18 Cross sectional SEM view of %10 Octamethyl POSS containing PEO film and its EDS map for Silicon................................................................. 42
Figure 2.19 Cross sectional SEM view of %10 Octaisobutyl POSS containing PEO film and its EDS map for Silicon................................................................. 43
Figure 2.20 Cross sectional SEM view of %10 Isooctyl POSS containing PEO film and its EDS map for Silicon................................................................. 44
Figure 2.21 CLSM real images of PEO films (a) Pure, and with 10wt.% (b) Octamethyl POSS, (c) Octaisobutyl POSS (d) Isooctyl POSS ........................................ 46
Figure 2.22 CLSM height images of solvent-casted PEO films (a) Pure, and with 10wt.% (b) Octamethyl POSS, (c) Octaisobutyl POSS (d) Isooctyl POSS ............... 47
Figure 2.23 CLSM real (left) and height (right) images of solvent-casted PEO film with 10wt. % Octaisobutyl POSS (5 times higher magnification than Figure 2.21-c and Figure 2.22-c) .................................................................................. 48
Figure 2.24 CLSM height images of solvent-casted PEO films with 5wt. % (left) and 7.5wt. % (right) octaisobutyl POSS ................................................................. 49
Figure 2.25 CLSM height images of 10wt. % Octaisobutyl POSS/PEO films: 2wt. /v% PEO/CHCl₃ (left), 3wt. /v% PEO/CHCl₃ (right) ................................................................. 50
Figure 2.26 Synthesis of star-shaped fluorinated acrylate polymers [141] ............... 51
Figure 2.27 Dumbbell-shaped molecule of Wells-Dawson-type polyoxometalate (POM) anion (P₂W₁₅V₃O₆₂)⁹⁻ with its counterions: six tetrabutylammonium (TBA, Bu₄N⁺) surfactant cations and three protons (H⁺) and aminopropylisobutyl POSS [143] ......................................................................................................................... 51
Figure 2.28 TGA results for the different length hydrocarbon chains having POSS/PEO films ................................................................................................................. 54
Figure 2.29 Tensile Strength comparison of different length hydrocarbon chains having POSS / PEO films .......................................................................................... 55
Figure 3.1 Isobutyl POSS molecules used in this study: (a) Octaisobutyl-, (b) Aminopropyl isobutyl-, (c) Maleamic acid isobutyl-, (d) Allyl isobutyl- [19] .............. 59
Figure 3.2 POSS model containing unit cell ......................................................... 61
Figure 3.3 Model PEO oligomer used in this study .............................................. 61
Figure 3.4 Unit cell filled with PEO chains and single POSS molecule in the middle ......................................................................................................................... 61
Figure 3.5 Five lowest energy values out of 25 results ...................................... 62
Figure 3.6 Methodology to calculate the interaction energy between PEO and POSS ......................................................................................................................... 62
Figure 3.7 Methodology to calculate the interaction energy between POSS and POSS .............................................................................................................................................................................................. 63

Figure 3.8 Polarized light microscope images of pure PEO films in different magnifications .................................................................................................................................................................................................................. 65

Figure 3.9 PLM Image of 10% Octaisobutyl POSS containing PEO film .............. 66

Figure 3.10 PLM Image of 10% Aminopropyl isobutyl POSS containing PEO film. .................................................................................................................................................................................................................................................. 67

Figure 3.11 PLM Image of 10% Maleamic acid isobutyl POSS containing PEO film. .................................................................................................................................................................................................................................................. 68

Figure 3.12 PLM Image of 10% Allyl isobutyl POSS containing PEO film. ........ 69

Figure 3.13 Longitudinal SEM view of %10 Octaisobutyl POSS containing PEO film and its EDS map for Silicon............................................................................................................................................................................................................. 71

Figure 3.14 Longitudinal SEM view of %10 Aminopropyl Isobutyl POSS containing PEO film and its EDS map for Silicon............................................................................................................................................................................................................ 72

Figure 3.15 Longitudinal SEM view of %10 Maleamic acid Isobutyl POSS containing PEO film and its EDS map for Silicon............................................................................................................................................................................................................ 73

Figure 3.16 Longitudinal SEM view of %10 Allyl Isobutyl POSS containing PEO film and its EDS map for Silicon............................................................................................................................................................................................................ 74

Figure 3.17 SEM-EDS images comparison of Isobutyl-POSS-PEO series in longitudinal view: From first to fourth row: Octaisobutyl-, Aminopropyl isobutyl-, Maleamic acid isobutyl-, and Allyl isobutyl- .................................................................................................................................................................................................................. 75

Figure 3.18 Cross sectional SEM view of %10 Octaisobutyl POSS containing PEO film and its EDS map for Silicon. ............................................................................................................................................................................................................ 77
Figure 3.19 Cross sectional SEM view of %10 Aminopropyl Isobutyl POSS containing PEO film and its EDS map for Silicon................................................................. 78

Figure 3.20 Cross sectional SEM view of %10 Maleamic acid Isobutyl POSS containing PEO film and its EDS map for Silicon......................................................... 79

Figure 3.21 Cross sectional SEM view of %10 Allyl Isobutyl POSS containing PEO film and its EDS map for Silicon................................................................. 80

Figure 3.22 SEM-EDS images comparison of Isobutyl-POSS-PEO series in cross-sectional view: From first to fourth row: Octaisobutyl-, Aminopropyl isobutyl-, Maleamic acid isobutyl-, and Allyl isobutyl- .............................................................. 81

Figure 3.23 Confocal microscope images of solvent-cast PEO films containing 10% (a) octaisobutyl POSS, (b) aminopropyl isobutyl POSS, (c) maleamic acid isobutyl POSS, and (d) allyl isobutyl POSS (real color view)................................................................. 82

Figure 3.24 Confocal microscope images of solvent-casted PEO films containing 10% (a)Octaisobutyl POSS (b)Aminopropyl isobutyl POSS (c)Maleamic isobutyl POSS (d)Allyl isobutyl POSS. (Height view)........................................................................... 83

Figure 3.25 Comparison of octaisobutyl and allyl-isobutyl POSS molecules in terms of molecular connoly surfaces................................................................. 88

Figure 3.26 Illustrations of octaisobutyl POSS (left) and allylisobutyl POSS molecules according to their atomic Van der Waals volumes......................................... 89

Figure 3.27 Atomic charge comparison between isobutyl (left) and allyl groups (right) .............................................................................................................. 89

Figure 3.28 Atomic charge comparison between an octaisobutyl (left) and allyl isobutyl POSS (right) Si-O frameworks ................................................................. 90
Figure 3.29 Lowest energy structure for the self-interaction of octaisobutyl POSS 90
Figure 3.30 Lowest energy structure for the self-interaction of allyl-isobutyl POSS 91
Figure 3.31 Possible arrangement of allyl-isobutyl POSS molecules interacting by using allyl groups .............................................................................................................. 91
Figure 3.32 TGA results for the Isobutyl-POSS-PEO films. ................................. 92
Figure 3.33 Tensile strength comparison of the Isobutyl-POSS/PEO films. ........... 93
Figure 4.1 PLM images of solvent-casted 10wt% octaisobutyl POSS (left) and 10wt% allyl isobutyl POSS (right) in PMMA and CHCl₃ .............................................................. 95
Figure 4.2 PLM images of solvent-casted 10wt% octaisobutyl POSS (left) and 10wt% allyl isobutyl POSS (right) in PMMA and CHCl₃ .............................................................. 96
Figure 4.3 PLM images of pure allyl isobutyl POSS in CHCl₃ in different magnifications ................................................................................................................................. 97
Figure 4.4 PLM images of pure octaisobutyl POSS in CHCl₃ in different magnifications ................................................................................................................................. 98
Figure 4.5 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in CHCl₃ in low magnification ......................................................... 98
Figure 4.6 PLM images of pure allyl isobutyl POSS in THF in different magnifications ................................................................................................................................. 99
Figure 4.7 PLM images of pure octaisobutyl POSS in THF in different magnifications ................................................................................................................................. 99
Figure 4.8 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in THF in low magnification ......................................................... 99
Figure 4.9 PLM images of pure allyl isobutyl POSS in hexane in different magnifications .......................................................... 100
Figure 4.10 PLM images of pure octaisobutyl POSS in hexane in different magnifications .......................................................... 100
Figure 4.11 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in hexane in low magnification.......................................................... 101
Figure 4.12 PLM images of pure allyl isobutyl POSS in CH$_2$Cl$_2$ in different magnifications ........................................................................................................... 102
Figure 4.13 PLM images of pure octaisobutyl POSS in CH$_2$Cl$_2$ in different magnifications ........................................................................................................... 103
Figure 4.14 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in CH$_2$Cl$_2$ in low magnification.......................................................... 103
Figure 4.15 PLM images of pure allyl isobutyl POSS in CCl$_4$ in different magnifications ........................................................................................................... 104
Figure 4.16 PLM images of pure octaisobutyl POSS in CCl$_4$ in different magnifications ........................................................................................................... 104
Figure 4.17 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in CCl$_4$ in low magnification .......................................................... 105
Figure 4.18 Elemental analysis result for allyl isobutyl solvent-casted with chloroform. .......................................................................................................................... 105
Figure 4.19 Lowest energy state calculated with semi empirical method for allyl isobutyl POSS molecules around one chloroform molecule ........................................ 107
Figure 5.1 PLM images of pure PMMA film (10g 996k PMMA, 50ml Chloroform) .................................................................................................................. 112

Figure 5.2 PLM images of 10% Octaisobutyl POSS-PMMA film (10g 996k PMMA, 1g octaisobutyl POSS, 50ml Chloroform) .................................................................................................................. 113

Figure 5.3 Comparison of CLSM images of pure PMMA film (left) and 10% Octaisobutyl POSS-PMMA film (right) (10g 996k PMMA, 1g octaisobutyl POSS, 50ml Chloroform) .................................................................................................................. 113

Figure 5.4 Interacting sites of PMMA and octaisobutyl POSS ............................................. 114

Figure 5.5 Interacting sites of PMMA and PEO ..................................................................... 115

Figure 5.6 PLM images of PEO30.5-N samples ................................................................. 117

Figure 5.7 PLM images of PEO30.5-P samples .................................................................. 118

Figure 5.8 CLSM images of PEO30.5-N(left) and PEO30.5-P(right) samples........... 118

Figure 5.9 PLM images of PEO40-N samples ................................................................ 119

Figure 5.10 PLM images of PEO40-P samples ................................................................ 119

Figure 5.11 CLSM images of PEO40-N(left) and PEO40-P(right) samples............. 120

Figure 5.12 PLM images of PEO50-N samples ................................................................ 120

Figure 5.13 PLM images of PEO50-P samples ................................................................ 121

Figure 5.14 Comparison of CLSM images of PEO50-N (left column) and PEO50-P (right column) samples. First row is for real color, second row shows height difference. .................................................................................................................. 122

Figure 5.15 CLSM images of PEO50-P after staying for 24h in DI water ............... 123

Figure 5.16 SEM image of PEO50-P under CBS detector ............................................. 124

Figure 5.17 SEM-EDS image(left) and silicon map (right) of PEO50-P film......... 124
Figure 5.18 PLM images of PEO70-N samples .......................................................... 125
Figure 5.19 PLM images of PEO70-P samples .......................................................... 125
Figure 5.20 Comparison of CLSM images of PEO70-N (left) and PEO70-P (right) samples ........................................................................................................................................ 126
Figure 5.21 PLM images of PEO100-N samples ........................................................... 126
Figure 5.22 PLM images of PEO100-P samples ........................................................... 126
Figure 5.23 Comparison of CLSM images of PEO100-N (left) and PEO100-P (right) samples ........................................................................................................................................ 127
Figure 5.24 Modulus vs. PEOwt% plots for both w/ and w/o POSS series ............... 127
Figure 5.25 Tensile Strength vs. PEOwt% plots for both w/ and w/o POSS series. 129
Figure 5.26 Breaking strain% vs. PEOwt% plots for both w/ and w/o POSS series. ........................................................................................................................................ 130
Chapter 1  Introduction

1.1  Background

Polyhedral oligomeric silsesquioxanes (POSS) are three-dimensional nano-sized cage-like inorganic-organic hybrid building blocks. [1–5] (See Figure 1.1) While describing POSS, it is better to start with silsesquioxanes, which are actually a class of materials on their own. [6,7] Silsesquioxanes are a unique inorganic-organic hybrid material family with the general formula (RSiO\textsubscript{1.5})\textsubscript{n}. [6–8] With this formula, silsesquioxanes stay between silica (SiO\textsubscript{2}) and the silicones (R\textsubscript{2}SiO)\textsubscript{n} in terms of silicon content. [8,9] From this point of view, they are between ceramics and polymers in the world of materials. [4] The name silsesquioxane can be divided into four sections. While sil- refers to silicon in the formula, sesqui- is the Latin prefix meaning one and a half. [7,8] When we divide oxane into two parts, ox- is clearly for oxygen and -ane means the silicon atom has a covalent bond with a hydrocarbon. [4,8] This organic bond makes the silsesquioxane family unique and a hybrid molecule. [6] Silsesquioxanes were first isolated in 1946 by Scott using branched-chain methylpolysiloxanes. [10] The organic R groups attached to silsesquioxanes are limited only by the imagination of chemists. They can be small hydrocarbons, amines, alcohols, acids, etc., and even polymers. [1,3,4] These different R groups can vastly affect the structural behavior of POSS and/or their mechanical, thermal, and rheological properties of their composites, providing POSS its unique versatility for nearly endless applications. [11–13]
Figure 1.1 General structure of POSS [3]

Silsesquioxanes exists generally in four different molecular architecture, *i.e.*, random, ladder, partial cage or cage. [1,3,7](See Figure 1.2)

![Polyhedral Oligomeric Silsesquioxanes (POSS)](image)

![Open Cage](image)

![Ladder Structure](image)

![Random Structure](image)

![Spherosilicate](image)

Figure 1.2 Types of silsesquioxanes and difference between T₈ and Q₈ [7]

Considering the name of POSS, “polyhedral” means multi-face. Thus, cage structure having silsesquioxanes are classified as POSS. (See Figure 1.2) However not
every cage-like silica structure can be named as POSS. Since POSS is a type of silsesquioxane, every silicon atom of the cage has to have covalent bonds with three oxygen. In Figure 1.2 we observe spherosilicate structure which is not a silsesquioxane as each silicon atom has covalent bonds with four oxygen. [7,8] According to the General Electric’s practical nomenclature for silicon containing molecules, if each silicon atom has covalent bonds with three different oxygen atoms, that silsesquioxane can be simply named with T “number of silicon atoms”. [7,8] If there are four oxygen bonds per silicon then we name it with Q “number of silicon atoms”, thus in Figure 1.2 POSS compound is a T₈, but spherosilicate is a Q₈. [7]

Lastly, “oligomeric” refers to the limited number of \((\text{SiO}_{1.5})\) units of POSS molecules. With General Electric’s nomenclature, POSS molecules are named simply as T₆, T₈, T₁₀, (See Figure 1.3), T₁₂, T₁₄ … [2,3,7]

![Figure 1.3 Different cage structures of POSS based on number of silicon atoms. [7]](image)

POSS, different from random and ladder silsesquioxanes, have very well defined three dimensional molecular structures and silica cage. [1,4,7] Considering T₈, which is also called as cubic-POSS [14], the size of its inorganic cage is around 0.5 nm, while the
R to R distance is around 1-3 nm. [2–4,8] Though T₈ is called as cubic POSS, of course it is not in perfect cubic shape since the O-Si-O bond angles are not 90°. [8,15]

POSSes, though often referred to as particles, they are actually molecules that, depending on their organic groups, can be dissolved in many common organic solvents. [1,2] They are not only nano-fillers. [16] When covalently bonded to a matrix polymer, according to the number of reacted sites and their positions along the polymer backbone, POSS can be either grafted, copolymerized or crosslinked. [17,18] If there are no reactive groups, POSS can be called molecular silica [19], while with one reactive group or more multifunctional groups they are called, respectively, mono- and multi-functional POSSes. [20] Even the simplest POSS molecules can be dissolved in either hexane, THF, or chloroform. [19] POSS can be recrystallized either from melt or solution. [2,3,14] It can be fully characterized using solution NMR and some POSS types (i.e. isooctyl POSS) are liquid even when they are pure, while particles cannot be liquid even when they are pure. [16]

With these unique features, they are a favorite option in many types of nanocomposites, which are produced in order to improve the thermal stability, glass transition temperature, tensile strength, abrasion resistance, and dielectric properties of matrix polymers. [3,17,21,22]

1.2 History of POSS

The first silsesquioxane synthesis was reported in 1946 by Scott of the General Electric Research Laboratories. [10] In 1955, Sprung and Guenther achieved to isolate the structures [23] Many research groups worked to increase the product yield and by the
1990’s many publications and patents had been published [6] (See Figure 1.4). No research group was able to mass produce POSS. [24]

![Figure 1.4 The number of patents and publications about silsesquioxanes before foundation of Hybrid Plastics [6]](image)

In the early 1990’s, Dr. Joe Lichtenhan got a project to make aerospace composites from POSS. [24] He began to work at Edwards Air Force Base in Palmdale, CA. [24] In 1996, his group received a basic research award from the US Air Force, and the 1997 Future Technology Award. [25] Finally, in 1998, Dr. Lichtenhan and Dr. Schwab got funding from Advanced Technology program in NIST to start Hybrid Plastics, Inc., which is currently the commercial producer of POSS. [24–26]

1.3 Production of POSS

Invention of the silsesquioxide family is the result of trifunctional organosilanes’ synthesis (RSiX₃) [8,20]. Hydrolytic condensation is the common reaction to produce silsesquioxanes. [8,23] (See Figure 1.5) [8]. It involves many interrelated parameters such as: solvent type, type and concentration of monomer, chemical characteristics of R (non-
reactive organic groups) and X (reactive groups), chemistry of the catalyst, reaction
temperature, and water content. [8]

![Figure 1.5 Hydrolytic condensation of trifunctional organosilanes resulting with POSS formation](image)

1.4 Hydrosilylation

After producing POSS by hydrolytic condensation, organic groups can be substituted
on the cage with hydrosilylation reactions. [8,27] Hydrosilylation is a general reaction to
synthesize organosilicons. [8,27] There are two possible outcomes for this reaction: α- and
β- additions (See Figure 1.6) [8]

![Figure 1.6 Possible outcomes of hydrosilylation reaction: α- and β- additions](image)

In Figure 1.7, three different routes to produce monosubstituted POSS can be seen.
Route 1, which is the general technique to produce silsesquioxanes (hydrolytic
condensation), ends up with a mix of both hetero- and monosubstituted POSS structures.
Route 2 is also applicable but it can substitute all groups as well. Route 3 can, of course,
produce only monosubstituted POSSes, however it can be used only with large organic groups. [28]

Figure 1.7 Three different ways to synthesize mono-substituted POSS molecules. [8]

1.5 Metallasilsesquioxanes

POSS is a hybrid molecule which fuses the ceramic and polymer worlds. However, metals like Li, Mg, Ti, Zr, Hf, V, Mo, Fe, Zn, Sn and Al can also be incorporated, as well in incompletely condensed POSSes. These unique structures serve as catalysts and can show even better efficiencies than classic heterogeneous silica-catalysts [29–35].
Figure 1.8 Synthesis of the titanasilsesquioxanes \[29,36\]

Figure 1.8 describes the synthesis of titanasilsesquioxanes, which is a typical metallasilsesquioxane example in terms of molecular architecture. [29,31,36]
Another important property of POSS is that it can mimic the silanol groups in a silica surface (See Figure 1.9).

1.6 POSS in Polymers

POSS molecules can be integrated into polymers either by covalently bonding or by physical mixing. Short chain hydrocarbon functionalized POSS molecules can be dissolved at room temperature in either tetrahydrofuran (THF), hexane, or chloroform. Depending on different functional groups, it can be dissolved in many other solvents. Thus, solvent mixing is an easy choice for making POSS-Polymer nanocomposites. POSS molecules can be either solid powder, oily liquid, or pale yellow/orange semi-solid. Commercially available POSS densities vary from 1.82 g/cm$^3$ (octahydrido) to 0.97 g/cm$^3$ (isooctyl). Depending on their organic groups, melting temperatures are varying widely. For instance, while functionalized POSS with just one
PEG leg melts at 65°C, POSSes with short chain hydrocarbons (*i.e* isobutyl) show average melting at 260°C, which may degrade some functional groups. This is the reason that melt-mixing of POSS with polymers depends on the matching of melting temperatures of both POSS type and the polymer. When used as monomer, POSS molecules can be incorporated into polymer chain in several different ways (See Figure 1.10)

![POSS-Polymer configurations](image)

**Figure 1.10 POSS-Polymer configurations [21]**

1.7 Applications of POSS with Polymers

Polymers are the building blocks of all life on Earth. Natural polymers such as deoxyribonucleic acids (DNA), ribonucleic acids (RNA), and proteins are essential to the lives of animals and plants. For a long time, industries and businesses have utilized
polymers to create the products that are in use today, including plastics, rubbers, and clothing. In past decades, there has been a considerable amount of interest in improving the properties of industrial products made from polymers. These enhancements involve the mixing in nano-fillers to form so-called nanocomposites. POSS is a cage like molecule (RSiO$_{1.5}$)$_n$ with a robust silicon/oxygen polyhedral framework. The functionality, solubility and reactivity of POSS can be changed by modifying the R groups with other organic substituents. Therefore, unlike most other fillers, POSS can be made compatible or miscible with many polymers. POSSes’ wide variety of functional organic groups covalently linked on their Si corners affect the nucleation ability, crystal size, phase separation behavior and overall performance of the polymer matrix.

Although the proposed enhancements of POSS prove very beneficial in commercial and industrial products, there is a concentration limit for POSS performance in polymer mixtures. Several studies have shown that above a concentration of 7-9% POSS in a polymer mixture, the properties of the composite begin to decrease significantly below their maximum enhancement amount. Ideally, the POSS reagents, once incorporated into the polymer matrix, modify the local morphological structure and chain mobility, resulting in an increase in the properties of the matrix. However, when it is added to a polymer matrix beyond that wt.% limit, POSS, with its inorganic core cage structure, has phase separation and agglomeration problems. This causes a limit to the desired increase in properties of polymer composite materials that can be obtained when processing POSS into polymer melts or solutions.
POSS-polymer nanocomposites are generally produced to improve thermal resistance, mechanical properties, oxidation resistance, and surface hardening. Besides these general property improvements, there are several case-specific applications.

![Molecular structure of Ts POSS, list of important properties and applications](image)

**Figure 1.11 Molecular structure of Ts POSS, list of important properties and applications [14]**

### 1.7.1 Electronics and Energy Applications

Silsesquioxanes were first synthesized in the General Electric Research Laboratories[10] and it is not a big surprise that the POSS family has many applications in electronics such as liquid crystals [40–45], electroluminescent (EL) materials in light-emitting devices [46–49], sensor systems [50–56], fuel cell membranes [57–64], battery electrolytes, lubricants, coatings and adhesives in space photovoltaic solar cells.
Electroluminescent (EL) polymers, covalently bonded with POSS either as dumbbell or pendant group can be seen in Figure 1.13 and Figure 1.14, respectively. [46,47] These approaches resulted in higher thermal stability, better solubility of polymers in organic solvents, higher brightness and higher external quantum efficiency.
Figure 1.14 Synthesis route of POSS-functionalized polyfluorene [47]

1.7.2 Space Applications

As mentioned in the POSS history (Section 1.2), POSS was first mass produced in the Air Force Laboratories. Thus it has wide variety of applications especially in satellites. Most of the satellites orbit in the Low Earth orbit (LEO) (160-2000 km from Earth surface). [12,65] In this region, ultraviolet light breaks down molecular oxygen into atomic oxygen (AO), which is very reactive and concentrated. As C-C bonds are easily broken by these reactive oxygen atoms, there needs to be a layer to protect the polymeric material of satellites especially the solar panels. Silicones can be used, but will turn to silica (SiO₂) in the long term at the surface. [66] When polydimethylsiloxane (PDMS) was used, as methyl groups reacted with oxygen, cracks formed and eventually the whole system was exposed to atomic oxygen. However, when POSS molecules are used, they do not permit cracking as they have 1.5 oxygens per silicon atom and not 1, unlike silicones. [67] Also, as the metallasilsesquioxane derivative cerium-POSS can be produced, it can be used to absorb the UV-light and protects the satellite. [12]

1.7.3 Biomaterial Applications

Though use as a biomaterial was not the first aim of the POSS inventors, the POSS family found large application area as biomaterial. POSS-polymer nanocomposites are used either in drug delivery[68], biosensors[53], breast implants[69], dental
POSS improves the degradative resistance and mechanical properties of their polymer composites which is expected especially for long term used devices such as heart valves. It has better cell adhesion efficiency compared with other silicone polymers. [73]

1.8 Fiber Applications with POSS

This review aims to summarize the different fiber applications of POSS and generally silsesquioxane molecules either copolymerized with, as a physical mixture, or as a surface application. [22,74–111] Since the R groups of the POSS molecules provide unlimited options (See Figure 1), many publications compare the effects of different R groups on fibrous structures.

Butola et al. (2010) produced polypropylene fibers by melt blending either octamethyl- or octaphenyl-POSSes, which acted as a lubricant due to their spherical shape below a certain concentration level, thus make drawing easier. Although they did not make any significant changes on the melting temperature of the resulting fibers, decomposition temperatures were highly affected with both of the POSS types, and above certain concentrations, both of the POSS structures tended to aggregate and crystallize. [89]

Chitosan is a copolymer with 2 different repeat units β-(1–4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit), which are called deacetylated and acetylated units, respectively. [74]. Chen, Loo, Wang (2011) compared the mechanical effects of single walled carbon nanotubes (SWNT) and POSS structures (Octaammonium (OA) and octa- nitro phenyl silsesquioxane (ONPS)) on chitosan fibers (See Figure 1.15). The fibers were wet-spun and the polymer and POSS or SWNT were mixed in the same solution. [74]
Chew et al. (2011) also produced chitosan microfibers by a wet-spinning process, which were reinforced with aminopropylphenyl POSS. The resulting microfibers with various POSS contents (1-9 w/w%) showed improved maximum stress, elastic energy storage, and fracture toughness up to 7 w/w% POSS content. [112] Beyond this value, there was a decrease in these properties, which was assumed due to clustering of POSS molecules produced by increased VDW forces in the system as the number of POSS molecules increases. [112] A disadvantage of this study was to use only acetic acid as a solvent to completely dissolve both chitosan and POSS, which is not suitable for the latter. This might have caused further phase separation and clustering of POSS in the system.

Cozza et al. (2010) produced both solvent-cast films and electrospun fibers from mixtures of cellulose acetate (CA) and epoxycyclohexylisobutyl POSS in the solvent system of dimethylacetamide and acetone. [113] The same group used the same type of POSS with poly (vinylidene fluoride) (PVDF) to produce electrospun fibers and solvent cast films. With 3 wt% load of POSS in the solution, both modulus and tensile stress at yield increased 100% compared with the as received PVDF fibers. [75] Finally, they produced poly (butylene terephthalate) (PBT) fibers with the epoxy functionalized POSS molecules that were melt-mixed with PBT for various amounts of time and then melt-spun.
into fibers. Because the resulting fibers had lower mechanical properties and showed phase separation, additionally in-situ polymerization between POSS and PBT was performed. The product of the in-situ polymerization had lower melting and crystallization temperatures, while having higher modulus and lower strain values. [114]

Similarly, PET fibers were produced both by melt mixing of two types of non-crystalline POSS and in-situ polymerization of diol functionalized crystalline POSS. [76] All three types of POSS increased tensile modulus and compressive strength while decreasing strain values compared with pure PET. The in-situ polymerized sample showed the highest crystallization and melting temperatures and all the approaches increased the decomposition temperature of PET.

Two types of amine functionalized POSS (isobutyl and isoctyl) were added into the PET matrix also via in-situ polymerization and melt-spun into fibers. [115] Although isoctyl amine POSS is non-crystalline at room temperature, as a result of condensation between PET and isoctyl amine POSS, phase separation of POSS crystals occurred. While 1% of either POSS molecules increased mechanical properties, beyond this POSS loading mechanical properties and glass transition temperatures of the composites decreased. A common aspect of these similar PET-POSS studies [76,114,115] was the increase of PET decomposition temperature. They also demonstrated that POSS increases the modulus of PET, much better than self-nucleated PET. [116]

For use on space shuttles under low earth orbit (LEO) conditions, carbon fiber composites are produced with two different types of siloxane copolymer resins: Polyimide-siloxane(PISX) and POSS-siloxane. [66] Under simulated LEO conditions POSS-Siloxane showed better performance. Carbon fibers (CFs) and POSS have been used in further
studies to improve interfacial properties of the composites. [77–85,117–120] Methacrylisobutyl- or trisilanophenyl-POSS coated CFs were treated with polyarylacetylene (PAA) to produce composites. It is found that both POSS coatings improved interlaminar and interfacial shear strength and impact properties. [77]

The same group investigated structural differences of methacryl functionalized POSS molecules which vary from T5 to T12. Interfacial properties of CF-PAA composites were best with T8. [117] In order to improve the interfacial properties between carbon fibers and POSS coatings and polymer matrix, air plasma was applied to the carbon fibers. [118] Activated and non-activated carbon fibers were coated with three different silsesquioxane (SSO) and two different POSS molecules before composite formation. Interfacial, impact, and heat resistant properties of the composites were compared. While all coatings improved the above-mentioned properties of the composites, best results belonged to the ones coated with POSS rather than SSOs [118].

Besides coating as a physical mixture, grafting of POSS on the carbon fibers was also done [78,82,83]. PAN-based carbon fiber surfaces were amine-functionalized with three types of reactions [78]. The amine groups were reacted with octa-glycidyl functionalized POSS, which is also used to improve the interfacial properties with epoxy matrix. As a result of this reaction, surface roughness, surface energy, interlaminar shear strength (ILSS), and impact toughness were significantly increased [78]. This composite was further analyzed in terms of interfacial shear strength, elastic modulus, glass transition temperature, and wettability, and all were also improved [82]. As a further approach, carbon nanotubes (CNTs) were grafted on to the POSS which was linked to the carbon fiber surface (CF-POSS-CNT structure). CNTs improved mechanical interlocking at the
interphase of the composite, and can transfer stress better with improved impact resistance and ILLS results [83].

POSS grafted carbon fibers were also used to improve interfacial strength of unsaturated polyester composites [79,81,85,120]. As the first approach, methacryl POSS molecules were affixed onto carbon fibers with epoxy as a binder [120]. Further, methacryl POSS was linked to the CF surface with covalent bonds, and, in order to investigate the effect of the methacryl groups, two different types of POSS (methacryl and methacryloIsobutyl) were grafted on carbon fiber [81].

Table 1.1 Properties of carbon fibers used in unsaturated polyester composites [79,81,84,85,120]

<table>
<thead>
<tr>
<th>Surface Energy (MJ/m)</th>
<th>Surface Roughness (nm)</th>
<th>ILSS (MPa)</th>
<th>IFSS (MPa)</th>
<th>Impact Toughness (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>34.46</td>
<td>56.8</td>
<td>47.1</td>
<td>46</td>
</tr>
<tr>
<td>Methacryl-POSS coated CF</td>
<td>39.05</td>
<td>75.1</td>
<td>50.34</td>
<td>N/A</td>
</tr>
<tr>
<td>E-51 coated CF</td>
<td>42.63</td>
<td>82.1</td>
<td>52.66</td>
<td>N/A</td>
</tr>
<tr>
<td>E-51+methacryl POSS coated CF</td>
<td>48.48</td>
<td>121.1</td>
<td>60.33</td>
<td>N/A</td>
</tr>
<tr>
<td>CF-SPDPC grafted</td>
<td>64.86</td>
<td>79.1</td>
<td>52</td>
<td>62</td>
</tr>
<tr>
<td>CF-SPDPC-aminopropyl phenyl POSS grafted</td>
<td>58.42</td>
<td>112.6</td>
<td>61</td>
<td>87</td>
</tr>
<tr>
<td>CF-MethacryloIsobutyl POSS grafted</td>
<td>43.08</td>
<td>129.6</td>
<td>62</td>
<td>87</td>
</tr>
<tr>
<td>CF-Methacryl POSS grafted</td>
<td>44.09</td>
<td>131.6</td>
<td>67</td>
<td>93</td>
</tr>
<tr>
<td>CF-TrisilanollIsobutyl POSS grafted</td>
<td>64.76</td>
<td>108.4</td>
<td>61</td>
<td>88</td>
</tr>
</tbody>
</table>
While surface roughness and surface energy values were almost the same for these structures, methacryl POSS grafted carbon fibers had higher ILSS and interfacial shear strength (IFSS) results compared with the methacryloIsobutyl POSS containing fibers. Both were better than as-received carbon fiber in terms of the above mentioned properties [81]. Besides methacryl functionalized POSSes, phenyl POSS (aminopropyl phenyl POSS), and trisilanollsobutyl POSS were also grafted on to the CF surface [79,85]. These grafting’s effects are summarized in Table 1.1.

1.9 POSS in PEO

POSS and poly ethylene glycol (PEG) have been used together either as physical blends or as tadpole-structure, dumbbell-shaped [121,122], or star molecules [9,123–125] in a wide variety of applications such as electrolytes in lithium batteries [126], and dielectric insulators [9]. Markovic et al. [124,125] investigated the effect of PEG molecular weight (Mw) on thermal and crystallization behaviors of star-shaped PEG-POSS.

In 2004, 8-arms PEG-POSS star molecules were synthesized and cyclodextrin (CD) inclusion complexes (IC) were formed on the PEG legs by using α-, and γ- CDs. It was observed that they formed IC with the parts of PEG far from the POSS core channel structure, which was supported by molecular dynamics results. [127] Similarly, POSS-cored star molecule was produced with PCL legs, and CD-ICs formed again with α-, and γ- CDs as columnar crystalline structure, while β-CD did not. [128] For biomedical applications, POSS is used as a co-crosslinker with PEG and PDMS, resulting in an amphiphilic membrane due to the hydrophilic nature of PEG and hydrophobic structure of PDMS. [129] Water responsive shape memory polymer is produced with polyurethane (PU), PEG, and POSS. Hard and hydrophobic segments of the block copolymer are made
of PU and POSS, while PEG and PU make the hydrophilic and soft parts. As the POSS content increases, phase separation occurs and %crystallinity increases. Final products can recover up to 70%. [130] Kim and Mather synthesized amphiphilic POSS-PEG-POSS dumbbell molecules with several Mw of PEGs varying from 1k to 10k [121,131]. It is observed that those urethane-linked dumbbells are amorphous until their POSS% gets lower than 50%. Another important finding was that the intrinsic viscosity value drops around 37% for 8 and 10K PEGs after they form dumbbell structures with POSS.

Amphiphilic telechelics are produced by using isocyanate functionalized POSS and PEO with different Mws. When we look at the literature of POSS usage with poly(ethylene oxide)(PEO) or with poly(ethylene glycol) (PEG), the main motivation is the battery applications especially for use as electrolytes. This is because that PEO can solvate lithium ions. Maitra and Wunder [132,133] did this by synthesizing PEO-POSS star molecules with different numbers of PEO repeating units and systematically changed the lithium salt content, making thermal and conductivity analyses to check the availability as electrolyte in lithium-ion batteries. [133,134] The same research group added star PEO-POSS molecules with four repeat units into PEO matrix (600k g/mol) and again checked its electrolyte performance at different temperatures and with different lithium salt concentrations. It was seen that the system works well for this application below the melting temperature of PEO but not above. [126] An interesting further study mixed two different POSS molecules, one POSS-benzyl\(\text{BF}_3\text{Li})_3\) and other one PEG-POSS (PG1190) molecule from Hybrid Plastics, to form an electrolyte system. As shown in Figure 1.16, while phenyl groups crystallize and form the structural phase, liquid PEG-POSS works in the conductive side. [135] This interesting design both increased conductivity compared to
previous studies and also the glass transition temperature. [135] When high molecular weight PEO(600k g/mol) was used instead of PEG-POSS, still high efficiency is achieved with POSS-phenyl\textsubscript{7}B\textsubscript{F\textsubscript{3}}Li\textsubscript{3} as electrolyte. [136,137] PEG-POSS was also mixed with methylcellulose (MC) in the same fashion as PEO(600k g/mol) to produce solid films as electrolyte. Several films with different mechanical properties were produced and each of them characterized to engineer the best performance. Under TEM, microphase separation is observed between PEG-POSS and MC. [138] Recently, this blend was further analyzed. [139]

![Figure 1.16 Schematic of the two phase structure of POSS-benzyl\textsubscript{7}B\textsubscript{F\textsubscript{3}}Li\textsubscript{3}/POSS-PEG\textsubscript{8}: (i) one phase is clustered phenyl groups with POSSbenzyl\textsubscript{7}B\textsubscript{F\textsubscript{3}}Li\textsubscript{3} anions oriented outward; (ii) the other phase is POSS-PEG\textsubscript{8} with solvated Li\textsuperscript{+}. Inset shows the phase boundary. [135]
Chapter 2 Investigation of POSS molecules with different hydrocarbon side chains

In this study, we systematically investigate the effect of non-functional hydrocarbon chain length as POSS molecules’ organic groups on their miscibility, crystallinity and distribution in a polymer matrix. We use POSS molecules having as organic groups either methyl, isobutyl, or isooctyl side chains. Each organic group leg has one, four or seven carbons, respectively, producing a systematic increase in the side group lengths.

We aim to obtain a basic understanding of how organic group chain length affects the non-functional POSS molecules’ behavior in a semi-crystalline polymer film in terms of topographic changes and mechanical and thermal properties. It is especially important not to have any functional groups in the POSS molecules, so we can investigate only the length parameter.

Each of these POSS molecules are soluble in chloroform. As matrix polymer, we used polyethylene oxide (PEO), which is also chloroform-soluble. After dissolving each of these POSS molecules with PEO, we produced films by solvent-casting. Both glass and Teflon substrates were used for film casting. The samples cast on glass were investigated by microscope analyses, while films cast on Teflon were used on mechanical and thermal analyses.

In addition, we also made computer-based calculations and simulations. By calculating, the interaction energy values of PEO-POSS, POSS-POSS, and PEO-PEO pairs, we aim to have interchange energy of each POSS-polymer nanocomposite. By dividing that value to ideal gas constant (R) and temperature (T), we can have a normalized
molecular interaction parameter, which may guide us in terms of phase behavior characteristics of each POSS type in PEO matrix.

2.1 Materials and Methods

As matrix polymer poly (ethylene oxide) (PEO) with Mw 900,000 g/mol (Sigma Aldrich, St. Louis, MO) was used. POSS molecules in this study were Octamethyl (MS0830), Octaisobutyl (MS0825), and Isooctyl (MS0805). (See Figure 3.1) All of them were purchased from Hybrid Plastics Inc. (Hattiesburg, MS). As solvent, only chloroform was used and purchased from Alfa Aesar (Ward Hill, MA). Glass slides are Corning 2947-75x25 (Corning, NY) plain micro slides, which are generally used on optical microscopes as sample holders.

Figure 2.1 POSS molecules with different organic groups, in terms of length of hydrocarbons: (a) Methyl-, (b) Isobutyl-, (c) Isooctyl- [19]

POSS-PEO nanocomposite films were produced by solvent-casting method. Both of these components can be fully dissolved in chloroform. For all solutions PEO/chloroform (wt. /v %) ratio is constant at 2%. All solutions were prepared in Teflon
beakers to avoid any loss in POSS concentration, while casting the solution due to possible adhesion between glass and POSS molecules. An octamethyl, octaisobutyl, and isoctyl POSS comparison series with POSS/PEO ratio (wt./wt.% ) of 1, 2.5, 5, 7.5, and 10% was observed.

Films, cast on glass, were analyzed under polarized optical light (PLM), confocal laser-scanning (CLSM), and scanning electron (SEM) microscopes in both longitudinal and cross-sectional directions, including energy dispersive X-ray spectroscopy (EDS) maps for silicon atoms. The films cast on Teflon were analyzed with thermogravimetric analysis (TGA), and tensile tests.

2.1.1 Polarized optical light microscopy
PLM images were taken by using Nikon Eclipse 50i POL compound light microscope and Nikon DSFi1 camera was used to take the observed images.

2.1.2 Confocal Laser-Scanning Microscopy
CLSM images were obtained with Olympus LEXT 3D measuring laser microscope (OLS 4000) and were recorded both in height and real color options either in 3D in 2D modes, under the display color option Primary-1.

2.1.3 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDS)
SEM images were taken with FEI Verios 460L SEM. It is equipped with a concentric backscattered electron detector (CBS) that is a traditional, high energy electron detector used to sense back-scattered electrons. The EDS system is an Oxford AZTec with a 50 mm² silicon drift detector. On EDS maps, red areas are represent silicon.
2.1.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analyses (TGA) was performed using a Perkin Elmer Thermogravimetric analyzer. Air was used as purging gas. Samples were heated from 20 to 600° C at a rate of 20° C/min and Pyris software was used to analyze the data.

2.1.5 Mechanical Testing

Uniaxial tensile testing was conducted on a MTS-30G load frame with a testing speed of 10 mm min⁻¹ and the gage length was 20 mm. All samples were cut in rectangular of 10mm in width and 50mm in length.

Besides these experimental methods, computational calculations were done in the following systematics:

2.1.6 Methodology of Computational Calculations

We prepared a cell, which has in the center either an octamethyl-, octaisobutyl-, or isooctyl POSS molecule. Cell volume is 30x30x30Å³ (See Figure 2.2)

![POSS model containing unit cell](image)

**Figure 2.2 POSS model containing unit cell**

We model a PEO oligomer. (See Figure 2.3)
Figure 2.3 Model PEO oligomer used in this study

We added PEO oligomers to the cell until the density reached 1.21 g/ml, which is the average density of PEO at room temperature. The model builds PEO molecules into the POSS cell in a Monte Carlo fashion, by minimizing close contacts between atoms, while ensuring a realistic distribution of torsion angles for any given forcefield. (See Figure 2.4)

Figure 2.4 Unit cell filled with PEO chains and single POSS molecule in the middle

We repeated this process 25 times and chose the 5 cells of lowest energy. (See Figure 2.5)

Figure 2.5 Five lowest energy values out of twenty-five results

For these 5 lowest energy cells, we calculated the interaction energy of PEO oligomers with the central POSS molecule.
Interaction energies were given for each POSS type. Average of interaction energies for 5 different cell of the different POSS-PEO interactions were calculated. (See Figure 2.6) The same methodology was applied to calculate the average PEO-PEO interaction energy by just replacing POSS molecule in Figure 2.6 with the model PEO oligomer shown in Figure 2.3 as center molecule.

Procedure shown in Figure 2.7 was followed to calculate POSS-POSS self-interaction energy for each type of POSS. While calculating POSS-POSS interaction energy values, we added POSS molecules to the cell until the density reaches the average density of each
particular POSS type. Density values of each POSS type were taken from Hybrid Plastics. In the spirit of quasichemical theory, we define $\alpha$ as

$$\left[<E_{\text{POSS/PEO}}>-\frac{1}{2}(<E_{\text{POSS/POSS}}>+<E_{\text{PEO/PEO}}>)\right]/RT = \Delta \overline{E}/RT$$ [140] which is a normalized molecular interaction parameter. This value may guide us in terms of phase behavior characteristics of each POSS type in PEO matrix.

2.2 Results and Discussion

When we observe polarized light, confocal laser scanning, and scanning electron microscope images with energy dispersive x-ray spectroscopy (EDS) maps both in longitudinal and cross-sectional directions, it is easier to understand the different structural effects of POSS molecules with varying lengths of their hydrocarbon legs (methyl-, isobutyl-, and isooctyl-).

2.2.1 Polarized Optical Light Microscopy

Figure 2.8 shows the PLM images of pure PEO film in different magnifications. Non-crystalline regions are obvious on the red-pink sides which is the color of the red plate of the microscope. We took images of 1, 2.5, 5, 7.5, and 10% POSS containing PEO films for methyl-, isobutyl- and isooctyl- POSS samples.

Figure 2.9 describes the change in crystal structure of the octamethyl POSS/PEO composites from 1 to 10% POSS. It is clear that 1% POSS did not make a big difference compared with pure PEO. However starting at 2.5%, methyl-POSS domains get larger and PEO crystals lose their shape and size. In Figure 2.9, Figure 2.10, and Figure 2.11 right column images are four times more magnified than left ones.

Figure 2.10 shows the same results for octaisobutyl POSS/PEO composites. Starting from 5% POSS, POSS domains can be seen easily. We should note the difference
in domain size between octamethyl- and octaisobutyl POSS. However these domains’ special structure will be understood more clearly from CLSM and SEM-EDS images.

Isooctyl POSS/PEO composite series are shown in Figure 2.11. As isooctyl POSS is liquid at room temperature, it cannot form solid phase domains unlike octamethyl- and octaisobutyl POSS. The 10% isooctyl POSS/PEO composite seems homogeneous in terms of crystal structure.
Figure 2.8 Polarized light microscope images of pure PEO films in different magnifications
Figure 2.9 Polarized optical light microscope images of Octamethyl POSS/PEO films in different ratios and magnifications: (a)1%, (b)2.5%, (c)5% (d)7.5, (e)10%
Figure 2.10 Polarized optical light microscope images of Octaisobutyl POSS/PEO films in different ratios and magnifications: (a) 1%, (b) 2.5%, (c) 5%, (d) 7.5%, (e) 10%
Figure 2.11 Polarized optical light microscope images of Isooctyl POSS/PEO films in different ratios and magnifications: (a)1%, (b)2.5%, (c)5% (d)7.5, (e)10%
In Figure 2.12, Figure 2.13, and Figure 2.14, we observe PLM images of 10wt.% octamethyl-, octaisobutyl-, and isooctyl POSS containing PEO films, respectively. In octamethyl- and octaisobutyl POSS films not only the POSS phase domains but also the change in the crystal structure of PEO is very visible. Isooctyl POSS-PEO film has tight non-crystalline regions; however, they are very homogenously distributed and smaller compared with the pure PEO film. There is no clear macro-phase separation with isooctyl POSS. Now, we are going to investigate the molecular-level distribution of each POSS type under SEM with EDS maps for silicon element.

2.2.2 Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) Map

From Figure 2.15 to Figure 2.17, longitudinal SEM images of three different POSS containing PEO films with EDS maps for silicon can be seen. On EDS maps, silicon signal is depicted with red dots.

In Figure 2.15, cubic shaped octamethyl POSS cluster is visible. However, a large one on the left side is mostly covered by PEO matrix, thus silicon signals cannot be detected well. This is proven with Figure 2.18, which shows the cross-sectional view of the same sample. Cubic shape of the POSS crystals are more visible and their PEO cover is shown.

Figure 2.16 shows one of the most interesting POSS phase domains of this study. There is hexagonal agglomeration of POSS. This honeycomb-like formation might be due to several reasons. We are going to keep searching the underlying reasons behind this special phase-domain. In Figure 2.19, the cross-section of this film can be seen. Important case is that these hexagonal formations are mostly clustered at the upper side of the film and did not agglomerate in the film as much. Both of these figures prove with the EDS map that these special phase domains are made of POSS molecules.
Figure 2.12 PLM Images of 10% Octamethyl POSS containing PEO film
Figure 2.13 PLM Images of 10% Octaisobutyl POSS containing PEO film
Figure 2.14 PLM Images of 10% Isooctyl POSS containing PEO film
Figure 2.15 Longitudinal SEM view of %10 Octamethyl POSS containing PEO film and its EDS map for Silicon.
Figure 2.16 Longitudinal SEM view of %10 Octaisobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 2.17 Longitudinal SEM view of %10 Isooctyl POSS containing PEO film and its EDS map for Silicon.
Figure 2.18 Cross sectional SEM view of % 10 Octamethyl POSS containing PEO film and its EDS map for Silicon.
Figure 2.19 Cross sectional SEM view of %10 Octaisobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 2.20 Cross sectional SEM view of %10 Isooctyl POSS containing PEO film and its EDS map for Silicon.
Last, isoctyl POSS-PEO film is shown in Figure 2.17 and Figure 2.20. Previously, we observed the homogeneous crystal structure of this sample under PLM. With SEM-EDS, we prove that there is also perfect miscibility of isoctyl POSS in PEO matrix both in longitudinal and cross-sectional directions. This is especially important for the computational calculations and comparisons as an example of fully miscible POSS.

2.2.3 Confocal-Laser Scanning Microscopy (CLSM)

Visual analyses of this study ends with confocal-laser scanning microscopy analyses. We investigate topographic differences between PEO films both as real and height settings. Benefit of CLSM images below (Figure 2.21 and Figure 2.22) is that each one shows ≈410,000-µm² surface area. This amount of area is large enough to show the entire surface characteristics of each film.

In Figure 2.21 and Figure 2.22, we can observe amorphous regions of PEO especially on pure PEO film. Iceberg-like domains of octamethyl POSS and smooth surface of isoctyl POSS containing film are obvious. On octaisobutyl POSS-PEO film surface there is a pattern with hexagonal POSS domains, which is mixed with some amorphous regions. This way, we can prove that this honeycomb-like domain (See Figure 2.16) is not a local feature but a general surface characteristic for this film.

Figure 2.23 shows 5 times more magnified octaisobutyl POSS-PEO film surface compared with Figure 2.21-c and Figure 2.22-c. Honeycomb-like POSS domains are visible.
Figure 2.21 CLSM real images of PEO films (a) Pure, and with 10wt.% (b) Octamethyl POSS, (c) Octaisobutyl POSS, (d) Isooctyl POSS
Figure 2.22 CLSM height images of solvent-casted PEO films (a) Pure, and with 10wt.% (b) Octamethyl POSS, (c) Octaisobutyl POSS (d) Isooctyl POSS
Figure 2.23 CLSM real (left) and height (right) images of solvent-casted PEO film with 10wt. % Octaisobutyl POSS (5 times higher magnification than Figure 2.21-c and Figure 2.22-c)

As mentioned before, in terms of SEM-EDS and CLSM analyses, we compared only 10wt. % POSS containing PEO films. However, we would like to understand the underlying reason for this honeycomb-like phase domain formation caused by POSS molecules. As starting point, we investigate the effect of POSS wt. % on the formation of these domains. We can see 5 and 7.5 wt. % octaisobutyl POSS containing PEO films in Figure 2.24.

It is obvious that 7.5 wt. % octaisobutyl POSS having PEO film has hexagonal POSS domains as well. However, 5 wt. % film did not form them. There is macro phase separation and again a round-like agglomeration tendency, but no continuous phase domains are formed. With this analysis, we prove the wt. % of POSS dependence of this special morphology.
After understanding the effect of POSS wt. % on phase domain formation, we would like to check the PEO molecular weight effect on this formation. Since molecular weight affects entropy of the polymer chains and phase separation behavior, the shapes of the phase domains might be heavily affected upon changing the molecular weight of the matrix polymer.

For this purpose, we used 400,000 g/mol PEO (Sigma-Aldrich) instead of 900,000 g/mol. Polymer weight in the solution (1g), octaisobutyl POSS amount (0.1g), and chloroform volume (50ml) were kept the same as with previous solutions, while using this time PEO with ~1/2 the Mw. The resulting film surface is displayed in Figure 2.25 on the left side. As seen, honeycomb-like POSS domains did not form under these conditions. As the polymer matrix is chemically the same, polymer-POSS interaction energy should be the same, so we became suspicious about the solution viscosity effect on the formation of such a special morphology. In order to check the viscosity effect, we used 1g PEO, 0.1g octaisobutyl POSS, and 33.3 ml chloroform. PEO and POSS amounts were not changed,
as we do not know yet the exact mechanism of this formation. With a 3 wt./v% polymer/chloroform ratio we obtain the film shown in Figure 2.25 on the left. With this experiment, we understand viscosity might be an important parameter for the formation of the honeycomb-like morphology.

Figure 2.25 CLSM height images of 10wt. % Octaisobutyl POSS/PEO films: 2wt. /v% PEO/CHCl₃ (left), 3wt. /v% PEO/CHCl₃ (right)

Though we understand some of the conditional parameter requirements, currently we cannot explain this behavior’s exact reason. However, in the literature, there are a few hexagonally packed POSS structures, which were published between 2014 and 2016 [141–143]. Nevertheless, as they can be seen below in Figure 2.26 and Figure 2.27, they are either star-shaped fluorinated acrylate polymers or dumbbell-shaped polyoxometalate (POM)-POSS molecule. Thus, to the best of our knowledge, we can report that our structure is seen for the first time with only a physical mixture of POSS and a polymer (See Figure 2.16)
Figure 2.26 Synthesis of star-shaped fluorinated acrylate polymers [141]

Figure 2.27 Dumbbell-shaped molecule of Wells-Dawson-type polyoxometalate (POM) anion ($P_2W_{15}V_3O_{62})^9-$ with its counterions: six tetrabutylammonium (TBA, $Bu_4N^+$) surfactant cations and three protons ($H^+$) and aminopropylisobutyl POSS [143]

After our visual evaluations, we will compare them with computational calculations and try to develop correlations, if there are any, for future studies.
2.2.4 Computational Calculations

As described under the title Methodology of Computational Calculations (See 2.1.6), we obtained 5 lowest energy values for each POSS type-PEO interaction. Their average value and standard error are given in Table 2.1. Likewise, POSS-POSS interaction energies were also calculated and listed in Table 2.2. PEO-PEO interaction energy and its standard deviation were calculated as 130.1±7.9 kcal/mol and both average POSS-POSS interaction energies and POSS-PEO interaction energies are listed in Table 2.1.

Table 2.1 List of interaction energies between PEO and POSS samples

<table>
<thead>
<tr>
<th></th>
<th>ENERGY MethylPOSS-PEO</th>
<th>ENERGY PEO</th>
<th>ENERGY MethylPOSS-center</th>
<th>ENERGY Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2533.07</td>
<td>-1479.16</td>
<td>-990.19</td>
<td>-63.72</td>
</tr>
<tr>
<td>2</td>
<td>-2501.99</td>
<td>-1448.20</td>
<td>-988.59</td>
<td>-65.20</td>
</tr>
<tr>
<td>3</td>
<td>-2483.21</td>
<td>-1421.98</td>
<td>-993.17</td>
<td>-68.06</td>
</tr>
<tr>
<td>4</td>
<td>-2456.02</td>
<td>-1403.80</td>
<td>-989.39</td>
<td>-62.83</td>
</tr>
<tr>
<td>5</td>
<td>-2439.43</td>
<td>-1388.69</td>
<td>-989.28</td>
<td>-61.46</td>
</tr>
<tr>
<td>Average±SE</td>
<td></td>
<td></td>
<td></td>
<td>-64.3±1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>ENERGY IsobutylPOSS-PEO</th>
<th>ENERGY PEO</th>
<th>ENERGY IsobutylPOSS-center</th>
<th>ENERGY Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2487.81</td>
<td>-1340.86</td>
<td>-1034.58</td>
<td>-112.36</td>
</tr>
<tr>
<td>2</td>
<td>-2515.15</td>
<td>-1362.11</td>
<td>-1035.68</td>
<td>-117.35</td>
</tr>
<tr>
<td>3</td>
<td>-2531.88</td>
<td>-1391.30</td>
<td>-1033.28</td>
<td>-107.31</td>
</tr>
<tr>
<td>4</td>
<td>-2491.22</td>
<td>-1352.12</td>
<td>-1034.11</td>
<td>-104.99</td>
</tr>
<tr>
<td>5</td>
<td>-2515.39</td>
<td>-1372.39</td>
<td>-1036.18</td>
<td>-106.81</td>
</tr>
<tr>
<td>Average±SE</td>
<td></td>
<td></td>
<td></td>
<td>-109.8±2.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>ENERGY IsooctylPOSS-PEO</th>
<th>ENERGY PEO</th>
<th>ENERGY IsooctylPOSS-center</th>
<th>ENERGY Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2599.31</td>
<td>-1275.17</td>
<td>-1160.86</td>
<td>-163.28</td>
</tr>
<tr>
<td>2</td>
<td>-2615.74</td>
<td>-1277.91</td>
<td>-1160.71</td>
<td>-177.12</td>
</tr>
<tr>
<td>3</td>
<td>-2606.45</td>
<td>-1280.42</td>
<td>-1158.21</td>
<td>-167.82</td>
</tr>
<tr>
<td>4</td>
<td>-2622.91</td>
<td>-1283.25</td>
<td>-1164.12</td>
<td>-175.54</td>
</tr>
<tr>
<td>5</td>
<td>-2611.55</td>
<td>-1275.51</td>
<td>-1157.20</td>
<td>-178.85</td>
</tr>
<tr>
<td>Average±SE</td>
<td></td>
<td></td>
<td></td>
<td>-172.5±3.0</td>
</tr>
</tbody>
</table>

(These are the best estimates of interaction energies as of the filing time of this dissertation)
Table 2.2 List of interaction energies between POSS and POSS samples

<table>
<thead>
<tr>
<th></th>
<th>ENERGY Methylposs-Methylposs Center</th>
<th>ENERGY Methylposs</th>
<th>ENERGY Methylposs Center</th>
<th>ENERGY Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-44895.50</td>
<td>-43818.10</td>
<td>-971.96</td>
<td>-105.43</td>
</tr>
<tr>
<td>2</td>
<td>-45104.21</td>
<td>-44029.59</td>
<td>-971.01</td>
<td>-103.62</td>
</tr>
<tr>
<td>3</td>
<td>-44997.29</td>
<td>-43928.99</td>
<td>-971.00</td>
<td>-97.29</td>
</tr>
<tr>
<td>4</td>
<td>-45050.44</td>
<td>-43986.71</td>
<td>-971.23</td>
<td>-92.50</td>
</tr>
<tr>
<td>5</td>
<td>-45083.97</td>
<td>-44012.04</td>
<td>-971.58</td>
<td>-100.35</td>
</tr>
<tr>
<td>Average±SE</td>
<td></td>
<td></td>
<td></td>
<td>-99.84±2.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>ENERGY Isobutylposs-Isobutylposs Center</th>
<th>ENERGY Isobutylposs</th>
<th>ENERGY Isobutylposs Center</th>
<th>ENERGY Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-22381.52</td>
<td>-21267.22</td>
<td>-1031.74</td>
<td>-82.56</td>
</tr>
<tr>
<td>2</td>
<td>-22295.74</td>
<td>-21190.81</td>
<td>-1024.86</td>
<td>-80.07</td>
</tr>
<tr>
<td>3</td>
<td>-22328.14</td>
<td>-21216.04</td>
<td>-1024.71</td>
<td>-87.38</td>
</tr>
<tr>
<td>4</td>
<td>-22342.19</td>
<td>-21237.98</td>
<td>-1022.22</td>
<td>-81.98</td>
</tr>
<tr>
<td>5</td>
<td>-22354.92</td>
<td>-21255.87</td>
<td>-1027.89</td>
<td>-71.17</td>
</tr>
<tr>
<td>Average±SE</td>
<td></td>
<td></td>
<td></td>
<td>-80.63±2.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>ENERGY Isooctylposs-IsooctylpossCenter</th>
<th>ENERGY Isooctylposs</th>
<th>ENERGY Isooctylposs Center</th>
<th>ENERGY Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-14564.54</td>
<td>-13324.91</td>
<td>-1166.59</td>
<td>-73.04</td>
</tr>
<tr>
<td>2</td>
<td>-14548.72</td>
<td>-13318.01</td>
<td>-1155.78</td>
<td>-74.92</td>
</tr>
<tr>
<td>3</td>
<td>-14650.90</td>
<td>-13402.72</td>
<td>-1167.72</td>
<td>-80.46</td>
</tr>
<tr>
<td>4</td>
<td>-14593.20</td>
<td>-13358.30</td>
<td>-1166.06</td>
<td>-68.85</td>
</tr>
<tr>
<td>5</td>
<td>-14562.64</td>
<td>-13336.27</td>
<td>-1162.94</td>
<td>-63.43</td>
</tr>
<tr>
<td>Average±SE</td>
<td></td>
<td></td>
<td></td>
<td>-72.14±2.9</td>
</tr>
</tbody>
</table>

(These are the best estimates of interaction energies as of the filing time of this dissertation)
Table 2.3 Summary of interaction energies* including the $\Delta E/RT$ normalized interaction parameter

<table>
<thead>
<tr>
<th>POSS type</th>
<th>$E_{POSS-PEO}$ Interaction (kcal/mol)</th>
<th>$E_{POSS-POSS}$ Interaction (kcal/mol)</th>
<th>$E_{PEO-PEO}$ Interaction (kcal/mol)</th>
<th>$\Delta E/RT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octamethyl</td>
<td>-64.3±1.1</td>
<td>-99.8±2.3</td>
<td>-130.1±7.9</td>
<td>85.1±10.4</td>
</tr>
<tr>
<td>Octaisobutyl</td>
<td>-109.8±2.3</td>
<td>-80.6±2.7</td>
<td>-130.1±7.9</td>
<td>-7.6±12.7</td>
</tr>
<tr>
<td>Isooctyl</td>
<td>-172.5±3.0</td>
<td>-72.1±2.9</td>
<td>-130.1±7.9</td>
<td>-119.81±14.2</td>
</tr>
</tbody>
</table>

(* These are the best estimates of interaction energies as of the filing time of this dissertation)

2.2.5 Thermogravimetric Analysis

![TGA graph]

Figure 2.28 TGA results for the different length hydrocarbon chains having POSS/PEO films
In Figure 2.28, we can clearly see that methyl- and isobutyl- POSS molecules decrease the thermal stability of PEO by decreasing the onset temperature for degradation. Though isooctyl POSS is an oily liquid material, it does not harm the thermal stability of PEO. It might be due to its better interaction with PEO compared with methyl- and isobutyl- POSS.

We should note that these results belong to only 10wt.% POSS containing samples. Thus, we cannot guess directly how the results would be affected with different weight fractions.

### 2.2.6 Mechanical Analyses

As data from mechanical analysis, we are sharing only the tensile strengths. The reason is that the other results showed large standard error, and prevented us from making clear judgment from them. We will test more samples for each composite film in order to lower the experimental deviations in the results.

![Tensile Strength comparison of different length hydrocarbon chains having POSS / PEO films](image)

*Figure 2.29 Tensile Strength comparison of different length hydrocarbon chains having POSS / PEO films*
When we examine the tensile strength values for PEO films with POSSes of different length hydrocarbon chains, we can see that all of them have lower values than pure PEO (See Figure 2.29). Though isoctyl POSS was very well mixed in PEO, its tensile strength results are the worst. The reason might be that it is liquid at room temperature.

2.3 Conclusion

In this chapter, we investigated the POSS molecules having non-functional hydrocarbon groups with systematically different length. According to three different microscopy techniques, interesting surface topographies and phase domain formations were explored. Especially, octaisobutyl domains on PEO film are forming hexagonal structures above certain weight % of POSS. Besides weight % also solution viscosity plays a critical role in this formation. From this point of view, we can assume the importance of viscosity in the surface properties of non-covalently bonded POSS-polymer nanocomposites. Computational calculations and
Chapter 3  Investigation of Isobutyl POSS molecules with mono-substituted functional groups

In this study, we systematically investigate the effect of mono-substituted functional group as POSS molecules’ organic group, on their miscibility, crystallinity and distribution in a polymer matrix. In the previous chapter, we used POSS molecules having as organic groups either methyl, isobutyl, or isooctyl. Among those, especially octaisobutyl POSS showed very intriguing results. Thus, we would like to make further investigations on that molecule. In this chapter, we will keep using octaisobutyl POSS but this time we will compare its behavior with three different mono-substituted isobutyl POSS molecules. These three molecules are aminopropyl isobutyl POSS, maleamic acid isobutyl POSS, and allyl isobutyl POSS. They all are T8 type POSS molecules and out of their eight organic groups, there are seven isobutyl groups, while the different ones give them their names.

By doing this study, we aim to have a basic understanding about how mono-substitution of POSS results in terms of crystal size, distribution, miscibility, topography, phase behavior and mechanical properties. It is also worth to note that how the honeycomb-like phase domains will be affected from that change in one functional group. In the last chapter, for each POSS type we prepared five different solutions with varying POSS%. This time, we are using for each POSS type only one POSS concentration, which is 10%. The reason behind that is to compare them at the concentration that octaisobutyl forms honeycomb-like phase-domains in the PEO film.

Likewise, each of these POSS molecules are soluble in chloroform. As matrix polymer, we used again polyethylene oxide (PEO) and produced films by solvent-casting. Both glass and Teflon substrates were used on casting. The samples casted on glass were
investigated under microscope analyses, while Teflon-casted films were used on mechanical and thermal analyses.

Besides these experimental studies, we also made computer-based calculations and simulations. By doing this, a numerical correlation was aimed to set between POSS miscibility with the polymer matrix and POSS-Polymer interaction ratio.

### 3.1 Materials and Methods

As matrix polymer poly (ethylene oxide) (PEO) with Mw 900,000 g/mol (Sigma Aldrich) was used. POSS molecules of this study were Octaisobutyl (MS0825), Aminopropyl isobutyl (AM0265), Maleamic acid isobutyl POSS (CA0296), and Allyl isobutyl (OL1118). (See Figure 3.1) All of them were purchased from Hybrid Plastics Inc. (Hattiesburg, MS). As solvent, only chloroform was used and purchased from Alfa Aesar. Glass slides are Corning 2947-75x25 plain micro slides, which are generally used on optical microscopes as sample holder.
POSS-PEO nanocomposite films were produced by solvent casting. Both of these components can be fully dissolved in chloroform. For all solutions PEO/chloroform (wt./v %) ratio is constant and 2%. All solutions are prepared in Teflon beakers and not glass to avoid any loss in POSS concentration while casting the solution due to possible adhesion between glass and POSS molecules. Octaisobutyl, aminopropyl isobutyl, maleamic acid isobutyl POSS, and allyl isobutyl comparison series POSS/PEO ratio (wt./wt.%) was 10%.

Films, casted on glass, were analyzed under polarized optical light microscope (PLM), confocal laser-scanning microscope (CLSM), scanning electron microscope (SEM) in both longitudinal and cross-sectional directions including energy dispersive X-ray spectroscopy (EDS) maps for silicon atoms. The films, cast on to Teflon, were analyzed
with thermogravimetric analysis (TGA), and tensile tests. They will be analyzed with differential scanning calorimetry (DSC) as well.

3.1.1 Polarized optical light microscope
PLM images were taken by using Nikon Eclipse 50i POL compound light microscope and Nikon DSFi1 camera was used to take images.

3.1.2 Confocal Laser-Scanning Microscope
CLSM images were obtained with Olympus LEXT 3D measuring laser microscope (OLS 4000) and were recorded both in height and color options either in 3D in 2D modes, under the color option Primary-1.

3.1.3 Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDS)
SEM images were taken with FEI Verios 460L SEM. It is equipped with a concentric backscattered electron detector (CBS) that is a traditional, high energy electron detector used to sense back scattered electrons. The EDS system is an Oxford AZTec with a 50 mm² silicon drift detector. On EDS maps, red points are representing silicon.

3.1.4 Thermogravimetric Analysis
Thermogravimetric analysis (TGA) was performed using a Perkin Elmer Thermogravimetric analyzer. Air was used as purging gas. Samples were heated from 20 to 600°C at a rate of 20°C/min and Pyris software was used to analyze the data.

3.1.5 Mechanical Tests
Uniaxial tensile testing was conducted on a MTS-30G load frame with testing speed of 10 mm min⁻¹ and the gage length is 20mm. All samples were cut in rectangular of 10mm in width and 50mm in length. Besides these experiments, molecular dynamics (MD) simulations were done in the following systematics:
3.1.6 Methodology of Computational Calculations

We prepared a cell, which has in the center either an octamethyl-, octaisobutyl-, or isooctyl POSS molecule. Cell volume is 30x30x30 Å₃ (See Figure 3.2)

![Figure 3.2 POSS model containing unit cell](image)

We model a PEO oligomer. (See Figure 3.3)

![Figure 3.3 Model PEO oligomer used in this study](image)

We added PEO oligomer to the cell until cell density reach 1.21 g/ml, which is the average density of PEO at room temperature. The model builds PEO molecules into the POSS cell in a Monte Carlo fashion, by minimizing close contacts between atoms, while ensuring a realistic distribution of torsion angles for any given forcefield. (See Figure 3.4)

![Figure 3.4 Unit cell filled with PEO chains and single POSS molecule in the middle](image)
We repeated this process 25 times and chose lowest 5 cells. (See Figure 3.5)

**Figure 3.5 Five lowest energy values out of 25 results**

For these 5 lowest energy cells, we calculated interaction energy of PEO oligomers with the POSS center molecule.

**Figure 3.6 Methodology to calculate the interaction energy between PEO and POSS**

Interaction energies were given for each POSS type. Average of interaction energies for 5 different cell of different POSS type-PEO interactions were calculated.
The same methodology was applied to calculate the average PEO-PEO interaction energy by just replacing POSS molecule in Figure 3.6 with the model PEO oligomer shown in Figure 3.3 as center molecule.

Figure 3.7 Methodology to calculate the interaction energy between POSS and POSS

Procedure shown in Figure 3.7 was followed to calculate POSS-POSS self-interaction energy for each type of POSS. While calculating POSS-POSS interaction energy values, we added POSS molecules to the cell until the density reaches the average density of each particular POSS type. Density values of each POSS type were taken from Hybrid Plastics.

In the spirit of quasichemical theory, we define $\alpha$ as

$$[<E_{\text{POSS/PEO}}>-\frac{1}{2}(<E_{\text{POSS/POSS}}>+<E_{\text{PEO/PEO}}>)/RT]=\Delta E/RT$$

[140] which is a normalized molecular interaction parameter. This value may guide us in terms of phase behavior characteristics of each POSS type in PEO matrix.

3.2 Results and Discussion

When we observe polarized light microscope, confocal laser scanning microscope, and scanning electron microscope images with energy dispersive x-ray spectroscopy (EDS) maps both in longitudinal and crosssectional directions, it is easier to understand the
different structural effects of POSS molecules varying functional groups (isobutyl-, aminopropyl-, maleamic acid-, and allyl).

3.2.1 Polarized Optical Light Microscope

Figure 3.8 shows the PLM images of pure PEO film both in different magnifications. Non-crystalline regions are obvious on the red-pink sides which is the color of the red plate of the microscope. We took images of 10% POSS containing PEO films for octaisobutyl, aminopropyl isobutyl-, maleamic acid isobutyl-, and allyl isobutyl POSS samples.

Figure 3.9 describes the change in crystal structure of the octaisobutyl POSS/PEO composites at 10%. We know its behavior from the previous chapter. Figure 3.10 and Figure 3.11 show the aminopropyl isobutyl and maleamic acid isobutyl POSS-PEO nanocomposites’ PLM images, respectively. Both of them have homogeneous crystal structure. Maleamic acid isobutyl POSS containing nanocomposite has larger crystal size but neither of them seem to have macro-phase separation at these images.

Probably the most interesting image of this study is Figure 3.12. Considering pure PEO’s PLM images, it is very weird to have such a crystal structure. Not only crystal size but also topography of this film is intriguing. We will try to explore this behavior.
Figure 3.8 Polarized light microscope images of pure PEO films in different magnifications
Figure 3.9 PLM Image of 10% Octaisobutyl POSS containing PEO film
Figure 3.10 PLM Image of 10% Aminopropyl isobutyl POSS containing PEO film.
Figure 3.11 PLM Image of 10% Maleamic acid isobutyl POSS containing PEO film.
Figure 3.12 PLM Image of 10% Allyl isobutyl POSS containing PEO film.
Now, we are going to investigate the molecular-level distribution of each POSS type under SEM with EDS maps for silicon element.

### 3.2.2 Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) Map

From Figure 3.13 to Figure 3.16, longitudinal SEM images of four different POSS containing PEO films with EDS maps for silicon can be seen. On EDS maps, each silicon atom signal is depicted with a red dot.

In Figure 3.13, honeycomb-like POSS domain is visible. We already discussed about it in detail in the previous chapter. Figure 3.14 shows aminopropyl isobutyl POSS-PEO film, while PLM (Figure 3.10) images were showing pretty nice and homogeneous distributions, SEM-EDS images showed the deep inside of its behavior. As it can be seen in the longitudinal view (Figure 3.14) pretty heterogeneously distributed POSS clusters and in the cross-sectional view (Figure 3.19) POSS molecules are making long clusters in the film, and not much on the surface unlike allyl-isobutyl and octaisobutyl POSS molecules do it rather on the surface. It is assumed that this behavior is due to higher surface energy of aminopropyl isobutyl POSS compared to octaisobutyl and allyl-isobutyl ones due to its amine group.

Maleamic acid isobutyl POSS showed in all images best homogeneity. It might be expected to have fine distribution due to its carboxylic acid function following an amide group in the same leg however thinking aminopropyl isobutyl POSS’ heterogeneous locations, it is an important property. This difference will be further discussed with computational calculations (Section 3.2.4).
Figure 3.13 Longitudinal SEM view of %10 Octaisobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 3.14 Longitudinal SEM view of %10 Aminopropyl Isobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 3.15 Longitudinal SEM view of %10 Maleamic acid Isobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 3.16 Longitudinal SEM view of %10 Allyl Isobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 3.17 SEM-EDS images comparison of Isobutyl-POSS-PEO series in longitudinal view: From first to fourth row: Octaisobutyl-, Aminopropyl isobutyl-, Maleamic acid isobutyl-, and Allyl isobutyl-
Ally-isobutyl POSS/PEO film is the most mysterious one for now. All of its images show very interesting morphologic properties about it. Firstly, we need to mention that this film crystallized in more than 4 hours after solvent-casting only a few ml chloroform dissolved solution, while all other film types finalized their crystallizations in 10-15 minutes. Although its chloroform was evaporated at room temperature, it stayed for long time amorphous and began to crystallize very slowly after around 3 hours and completed that after one more hour. This behavior will be further analyzed. Looking its PLM image especially at lower magnifications (Figure 3.12), it can be seen fingerprint like regions. CLSM images shows broken plaque like structures, which is completely different compared with other POSS-PEO film surfaces in this study. This observation is supported with SEM-EDS images especially with cross-sectional one (Figure 3.21), which shows the POSS plaques are forming at the surface.
Figure 3.18 Cross sectional SEM view of %10 Octaisobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 3.19 Cross sectional SEM view of %10 Aminopropyl Isobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 3.20 Cross sectional SEM view of %10 Maleamic acid Isobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 3.21 Cross sectional SEM view of %10 Ally Isobutyl POSS containing PEO film and its EDS map for Silicon.
Figure 3.22 SEM-EDS images comparison of Isobutyl-POSS-PEO series in cross-sectional view: From first to fourth row: Octaisobutyl-, Aminopropyl isobutyl-, Maleamic acid isobutyl-, and Allyl isobutyl-
3.2.3 Confocal-Laser Scanning Microscope (CLSM)

Visual analyses of this study ends with confocal-laser scanning microscope analysis. We investigate topographic differences between PEO films both as real and height settings.

Figure 3.23 Confocal microscope images of solvent-cast PEO films containing 10% (a) octaisobutyl POSS, (b) aminopropyl isobutyl POSS, (c) maleamic acid isobutyl POSS, and (d) allyl isobutyl POSS (real color view)

In Figure 3.23 and Figure 3.24, we can observe four different isobutyl POSS molecules containing PEO film surfaces. While aminopropyl isobutyl and maleamic acid isobutyl POSS does not have any POSS agglomeration on the film surface, octaisobutyl POSS
forms hexagonal structures. Nevertheless, as we observed on SEM-EDS images, allyl isobutyl POSS forms plaque-like structures at the surface and with CLSM images it can be much better observed. This phenomenon needs to be better understood in order to be able to predict POSS behavior generally and engineer better materials.

![Image](image_url)

**Figure 3.24** Confocal microscope images of solvent-casted PEO films containing 10% (a)Octaisobutyl POSS (b)Aminopropyl isobutyl POSS (c)Maleamic isobutyl POSS (d)Allyl isobutyl POSS. (Height view)

For this purpose, after our visual evaluations, we will compare them with computational calculations and try to have correlations for future studies, if there is any.
3.2.4 Computational Calculations

As described under the title Methodology of Computational Calculations (See 3.1.6), we got 5 lowest energy values for each POSS type-PEO interaction. Their average value and standard error were given in Table 3.1. Likewise, POSS-POSS interaction energies were also calculated by using same technique and both average POSS-POSS interaction energies and POSS-PEO interaction energies were listed in Table 3.2.
### Table 3.1 List of interaction energies between PEO and POSS samples

<table>
<thead>
<tr>
<th></th>
<th>Isobutylposs-peo</th>
<th>PEO</th>
<th>Isobutylposs-center</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong></td>
<td>-2487.81</td>
<td>-1340.86</td>
<td>-1034.58</td>
<td>-112.36</td>
</tr>
<tr>
<td><strong>2</strong></td>
<td>-2515.15</td>
<td>-1362.11</td>
<td>-1035.68</td>
<td>-117.35</td>
</tr>
<tr>
<td><strong>3</strong></td>
<td>-2531.88</td>
<td>-1391.30</td>
<td>-1033.28</td>
<td>-107.31</td>
</tr>
<tr>
<td><strong>4</strong></td>
<td>-2491.22</td>
<td>-1352.12</td>
<td>-1034.11</td>
<td>-104.99</td>
</tr>
<tr>
<td><strong>5</strong></td>
<td>-2515.39</td>
<td>-1372.39</td>
<td>-1036.18</td>
<td>-106.81</td>
</tr>
<tr>
<td><strong>Average±SE</strong></td>
<td></td>
<td></td>
<td></td>
<td>-109.8±2.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Aminopropyl isobutyl poss-PEO</th>
<th>PEO</th>
<th>Aminopropyl isobutyl poss-center</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong></td>
<td>-2518.15</td>
<td>-1377.46</td>
<td>-1019.56</td>
<td>-121.13</td>
</tr>
<tr>
<td><strong>2</strong></td>
<td>-2472.07</td>
<td>-1332.70</td>
<td>-1024.28</td>
<td>-115.10</td>
</tr>
<tr>
<td><strong>3</strong></td>
<td>-2525.18</td>
<td>-1383.74</td>
<td>-1022.57</td>
<td>-118.87</td>
</tr>
<tr>
<td><strong>4</strong></td>
<td>-2483.92</td>
<td>-1345.60</td>
<td>-1026.78</td>
<td>-111.54</td>
</tr>
<tr>
<td><strong>5</strong></td>
<td>-2470.37</td>
<td>-1322.54</td>
<td>-1021.99</td>
<td>-125.85</td>
</tr>
<tr>
<td><strong>Average±SE</strong></td>
<td></td>
<td></td>
<td></td>
<td>-118.5±2.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Maleamic acid isobutyl poss-PEO</th>
<th>PEO</th>
<th>Maleamic acid isobutyl poss-center</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong></td>
<td>-2673.84</td>
<td>-1361.24</td>
<td>-1177.78</td>
<td>-134.82</td>
</tr>
<tr>
<td><strong>2</strong></td>
<td>-2657.81</td>
<td>-1338.80</td>
<td>-1177.32</td>
<td>-141.69</td>
</tr>
<tr>
<td><strong>3</strong></td>
<td>-2708.48</td>
<td>-1378.19</td>
<td>-1185.79</td>
<td>-144.50</td>
</tr>
<tr>
<td><strong>4</strong></td>
<td>-2642.47</td>
<td>-1317.32</td>
<td>-1189.49</td>
<td>-135.66</td>
</tr>
<tr>
<td><strong>5</strong></td>
<td>-2684.05</td>
<td>-1360.57</td>
<td>-1188.96</td>
<td>-134.53</td>
</tr>
<tr>
<td><strong>Average±SE</strong></td>
<td></td>
<td></td>
<td></td>
<td>-138.2±2.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ally isobutyl poss-PEO</th>
<th>PEO</th>
<th>Ally isobutylposs-center</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1</strong></td>
<td>-2497.44</td>
<td>-1367.35</td>
<td>-1013.70</td>
<td>-116.39</td>
</tr>
<tr>
<td><strong>2</strong></td>
<td>-2503.65</td>
<td>-1379.62</td>
<td>-1013.00</td>
<td>-111.03</td>
</tr>
<tr>
<td><strong>3</strong></td>
<td>-2475.26</td>
<td>-1346.98</td>
<td>-1013.03</td>
<td>-115.25</td>
</tr>
<tr>
<td><strong>4</strong></td>
<td>-2471.54</td>
<td>-1344.23</td>
<td>-1012.38</td>
<td>-114.93</td>
</tr>
<tr>
<td><strong>5</strong></td>
<td>-2459.15</td>
<td>-1334.77</td>
<td>-1013.09</td>
<td>-111.29</td>
</tr>
<tr>
<td><strong>Average±SE</strong></td>
<td></td>
<td></td>
<td></td>
<td>-113.8±1.1</td>
</tr>
</tbody>
</table>

(These are the best estimates of interaction energies as of the filing time of this dissertation)
Table 3.2 List of interaction energies between POSS and POSS samples

<table>
<thead>
<tr>
<th></th>
<th>Isobutylposs+ Isobutyl poss center (kcal/mol)</th>
<th>Isobutyl POSS (kcal/mol)</th>
<th>Isobutylposs-center</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-22381.52</td>
<td>-21267.22</td>
<td>-1034.74</td>
<td>-82.56</td>
</tr>
<tr>
<td>2</td>
<td>-22295.74</td>
<td>-21190.81</td>
<td>-1024.86</td>
<td>-80.07</td>
</tr>
<tr>
<td>3</td>
<td>-22328.14</td>
<td>-21216.04</td>
<td>-1024.71</td>
<td>-87.38</td>
</tr>
<tr>
<td>4</td>
<td>-22342.19</td>
<td>-21237.98</td>
<td>-1022.22</td>
<td>-81.98</td>
</tr>
<tr>
<td>5</td>
<td>-22354.93</td>
<td>-21255.87</td>
<td>-1027.89</td>
<td>-71.17</td>
</tr>
</tbody>
</table>

Average±SE -80.63±2.66

<table>
<thead>
<tr>
<th></th>
<th>Aminopropyl isobutyl poss-POSScenter</th>
<th>Aminopropyl isobutyl POSS</th>
<th>Aminopropyl isobutyl poss-center</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-23132.35</td>
<td>-22019.87</td>
<td>-1023.24</td>
<td>-89.25</td>
</tr>
<tr>
<td>2</td>
<td>-23172.59</td>
<td>-22058.95</td>
<td>-1017.55</td>
<td>-96.09</td>
</tr>
<tr>
<td>3</td>
<td>-23103.60</td>
<td>-21993.62</td>
<td>-1022.73</td>
<td>-87.25</td>
</tr>
<tr>
<td>4</td>
<td>-23114.90</td>
<td>-22005.79</td>
<td>-1012.98</td>
<td>-96.13</td>
</tr>
<tr>
<td>5</td>
<td>-23112.09</td>
<td>-22014.40</td>
<td>-1006.71</td>
<td>-90.98</td>
</tr>
</tbody>
</table>

Average±SE -91.94±1.80

<table>
<thead>
<tr>
<th></th>
<th>Maleamic acid isobutyl poss-PEO</th>
<th>Maleamic acid isobutyl POSS</th>
<th>Maleamic acid isobutyl poss-center</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-24410.82</td>
<td>-23148.31</td>
<td>-1175.35</td>
<td>-87.17</td>
</tr>
<tr>
<td>2</td>
<td>-24403.50</td>
<td>-23134.20</td>
<td>-1175.37</td>
<td>-93.94</td>
</tr>
<tr>
<td>3</td>
<td>-24451.00</td>
<td>-23191.92</td>
<td>-1176.96</td>
<td>-82.13</td>
</tr>
<tr>
<td>4</td>
<td>-24420.70</td>
<td>-23166.48</td>
<td>-1171.74</td>
<td>-82.48</td>
</tr>
<tr>
<td>5</td>
<td>-24490.85</td>
<td>-23220.96</td>
<td>-1177.57</td>
<td>-92.32</td>
</tr>
</tbody>
</table>

Average±SE -87.61±2.44

<table>
<thead>
<tr>
<th></th>
<th>Ally isobutyl poss-PEO</th>
<th>PEO</th>
<th>Ally isobutylposs-center</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-22959.81</td>
<td>-21868.77</td>
<td>-1001.49</td>
<td>-89.55</td>
</tr>
<tr>
<td>2</td>
<td>-22962.21</td>
<td>-21873.38</td>
<td>-1000.87</td>
<td>-87.96</td>
</tr>
<tr>
<td>3</td>
<td>-22985.12</td>
<td>-21895.17</td>
<td>-1010.76</td>
<td>-79.20</td>
</tr>
<tr>
<td>4</td>
<td>-22930.05</td>
<td>-21834.27</td>
<td>-1015.39</td>
<td>-80.38</td>
</tr>
<tr>
<td>5</td>
<td>-22938.62</td>
<td>-21846.25</td>
<td>-1009.82</td>
<td>-82.56</td>
</tr>
</tbody>
</table>

Average±SE -83.93±2.06

(These are the best estimates of interaction energies as of the filing time of this dissertation)
Table 3.3 Summary of interaction energies* including the $\Delta E/RT$ normalized interaction parameter

<table>
<thead>
<tr>
<th>POSS type</th>
<th>$E_{POSS-PEO}$ Interaction (kcal/mol)</th>
<th>$E_{POSS-POSS}$ Interaction (kcal/mol)</th>
<th>$E_{PEO-PEO}$ Interaction (kcal/mol)</th>
<th>$\Delta E$ (kcal/mol)</th>
<th>$\Delta E/RT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octaisobutyl</td>
<td>-109.8±2.3</td>
<td>-80.6±2.7</td>
<td>-130.1±7.9</td>
<td>-4.5±7.6</td>
<td>-7.6±12.7</td>
</tr>
<tr>
<td>Aminopropyl isobutyl</td>
<td>-118.5±2.5</td>
<td>-91.9±1.8</td>
<td>-130.1±7.9</td>
<td>-7.5±7.4</td>
<td>-12.6±12.4</td>
</tr>
<tr>
<td>Maleamic acid isobutyl</td>
<td>-138.2±2.0</td>
<td>-87.6±2.4</td>
<td>-130.1±7.9</td>
<td>-29.4±7.2</td>
<td>-49.4±12.1</td>
</tr>
<tr>
<td>Allyl isobutyl</td>
<td>-113.8±1.1</td>
<td>-83.9±2.1</td>
<td>-130.1±7.9</td>
<td>-6.8±6.1</td>
<td>-11.4±10.2</td>
</tr>
</tbody>
</table>

(*: These are the best estimates of interaction energies as of the filing time of this dissertation)

Maleamic acid isobutyl POSS has the lowest ratio and also the ever best miscibility and distribution in the PEO film. Thus our calculations and experimental data support each other.

Aminopropyl isobutyl POSS has higher interaction value with PEO compared with octaisobutyl POSS’ interaction with PEO as it is expected from its amine group. However its self-interaction is the highest value as well. Thus, aminopropyl isobutyl ratio is the highest one among the isobutyl-POSS comparisons. This is also supported as aminopropyl isobutyl POSS created big phase domains inside the film, which lowered both of its mechanical and thermal properties.

Lastly, allyl-isobutyl POSS and octaisobutyl POSS molecules have almost same ratio. This is interesting since their films have distinctly different surface topography. However we might be able to interprete this ratio similarity with the $z$-axis level of agglomeration within the film. While octaisobutyl POSS forms honeycomb-like structures,
allyl-isobutyl POSS forms plaques. Nevertheless cross-sectional SEM-EDS images show that they both make clusters at the surface of the film. This might be the common feature that the interaction ratio tells us. But, even this assumption is correct, these calculations could not explain the delayed crystallization of allyl-isobutyl POSS-PEO film and its interesting PLM image. That is why, we compared allyl-isobutyl and octaisobutyl POSS molecules from the perspective of quantum mechanics below.

According to Figure 3.25 to Figure 3.31 below, allyl group is sterically less hindered compared with the isobutyl groups. This feature might allow allyl-isobutyl POSS molecules stay closer. Besides this average atomic charge of the end group hydrogens is almost 3 times higher compared with the ones on the isobutyl group which can not be observed by force field based molecular mechanics calculations. Finally, when the electron charges in the Si-O cages of these molecules are compared, Si-O-Si bridging oxygens in allyl-isobutyl POSS have higher atomic charge as well.

![Figure 3.25 Comparison of octaisobutyl and allyl-isobutyl POSS molecules in terms of molecular connoly surfaces.](image-url)
Figure 3.26 Illustrations of octaisobutyl POSS (left) and allylisobutyl POSS molecules according to their atomic Van der Waals volumes.

Figure 3.27 Atomic charge comparison between isobutyl (left) and allyl groups (right).
Figure 3.28 Atomic charge comparison between an octaisobutyl (left) and allyl isobutyl POSS (right) Si-O frameworks

Figure 3.29 Lowest energy structure for the self-interaction of octaisobutyl POSS

As a result all these differences, octaisobutyl POSS molecules can come closest to each other as shown in Figure 3.29, while allyl-isobutyl POSS molecules might be able stay closer as shown in Figure 3.30 below. Allyl-isobutyl POSS molecules can sort of interlock each other (Figure 3.30) or stay after another like in Figure 3.31. Considering very delayed crystallization of allyl-isobutyl POSS/PEO film, its interesting PLM image, and plaque formations at the surface, which are determined to be POSS rich regions, we have reason to speculate that these structures are possible.
Figure 3.30 Lowest energy structure for the self-interaction of allyl-isobutyl POSS

Figure 3.31 Possible arrangement of allyl-isobutyl POSS molecules interacting by using allyl groups
3.2.5 Thermogravimetric Analysis

![TGA graph](image)

**Figure 3.32 TGA results for the Isobutyl-POSS-PEO films.**

In Figure 3.32, we can see that maleamic acid isobutyl POSS, which has the best miscibility in PEO matrix among the samples in this study, got the best thermal stability. While allyl- and aminopropyl isobutyl composites are almost same as pure PEO, octaisobutyl containing sample has clearly worst stability. Considering this study, we can say that the non-functional POSS had the worst thermal stability compared to the mono-substituted POSS samples.

3.2.6 Mechanical Analyses

As data from mechanical analysis, we are sharing only tensile strength. The reason is that the other results had pretty large standard error thus we cannot make clear judgement
by using them. We will test more sample for each composite film in order to lower the deviation in the results.

Figure 3.33 Tensile strength comparison of the Isobutyl-POSS/PEO films.

Tensile strength results of isobutyl POSS family is more exciting. (See Figure 3.33) Aminopropyl isobutyl POSS has the lowest value and it reminds us its agglomeration within the film and not on the surface. That might be a strong reason. Allyl isobutyl did not affect the pure PEO’s value as it was agglomerating as plaques on the surface of the film. However, maleamic acid isobutyl POSS has the ever best value and clearly higher than pure PEO as well. It was the best mixing POSS for this comparison set and it is solid powder at room temperature.
3.3 Conclusion

In this chapter, we compared four isobutyl-POSS molecules’ behavior in PEO matrix by solvent-casting method. While we were focusing on octaisobutyl POSS’ hexagonal phase domains, we found out another interesting phase domain with allyl isobutyl-PEO nanocomposite. Moreover, when we applied our classic computer calculations to get a normalized molecular interaction parameter for that particular composite, allyl isobutyl POSS got similar results with octaisobutyl POSS. After doing several quantum mechanical calculations we get some understanding about allyl isobutyl POSS but we still could not understand the main difference between allyl and octaisobutyl POSS that will lead to difference like hexagon- and plaque- like formations. For this purpose, we are going to make one more study, which is described in chapter 4.
Chapter 4  Understanding Allyl isobutyl POSS behavior

In the previous chapter, we examined the difference between isobutyl POSS molecules, which were identical with core POSS cage and seven isobutyl legs but different only on the eighth leg, which are either aminopropyl, maleamic acid, allyl, or isobutyl.

As observed in several cross-polarized, SEM-EDS, and confocal images, they differ both in crystal size, distribution, shapes, location within the polymer film, and also surface topography. By using Monte Carlo and quantum mechanical computer simulations, we interpreted their macro-behavior from the molecular interaction perspective. Nevertheless, we have found very similar (POSS-POSS/POSS-PEO) interaction energy ratio for allyl isobutyl and octaisobutyl POSS containing PEO films, while these films distinctly differ in morphology.

In order to observe POSS crystals in a polymer matrix more easily, we used amorphous polymer and, dissolved PMMA and allyl isobutyl POSS together in chloroform. By using same concentration and ratios, we compared it with octaisobutyl POSS-PMMA-chloroform solution.

Figure 4.1 PLM images of solvent-casted 10wt% octaisobutyl POSS (left) and 10wt% allyl isobutyl POSS (right) in PMMA and CHCl₃
Figure 4.2 PLM images of solvent-casted 10wt% octaisobutyl POSS (left) and 10wt% allyl isobutyl POSS (right) in PMMA and CHCl₃.

As it can be clearly seen from Figures Figure 4.1 and Figure 4.2, there are distinct differences between PMMA-allyl isobutyl and PMMA-octaisobutyl films, like in PEO films. Moreover, we can observe plaque-like allyl isobutyl POSS crystals in amorphous PMMA film. This is also similar with the PEO-allyl isobutyl POSS film, which had large POSS plaques on its surface.

Considering the computational results for interaction energy of PEO-allyl isobutyl POSS and PEO-octaisobutyl POSS are very similar, we thought the dominant effect might not be polymer-POSS interaction in this experiment. After observing similar allyl isobutyl POSS crystals this time in PMMA matrix, we changed our point of view and decided to investigate solvent effect, if there is any. By this time, in all experiments, chloroform was used as only solvent. As POSS has three major solvents, which are chloroform, THF, and hexane, we investigate in this chapter both of the POSS types’ crystals in these three solvents without using any polymer.
Figure 4.3 PLM images of pure allyl isobutyl POSS in CHCl₃ in different magnifications

Figure 4.3 supports our suspicion about the solvent, as the pure allyl isobutyl POSS molecules formed plaque-like crystals as well. In order to check the allyl group’s effect, we prepared same solution ratio for octaisobutyl POSS, too. In Figure 4.4, octaisobutyl POSS crystals are seen, which are casted from same concentration chloroform solution as in Figure 4.3. In Figure 4.5, we compare octaisobutyl POSS and allyl isobutyl POSS crystals under same low magnification in order to observe a larger area of crystals. It is obvious that they have very different crystal characteristics and actually, octaisobutyl POSS behavior explains a little about the honeycomb-like formations in PEO, when the solution has high enough viscosity.
Figure 4.4 PLM images of pure octaisobutyl POSS in CHCl$_3$ in different magnifications

Figure 4.5 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in CHCl$_3$ in low magnification

If chlorine is the dominant group to form plaques of allyl isobutyl POSS, then non-chlorinated POSS solvents, THF and hexane, are expected to behave differently.
Figure 4.6 PLM images of pure allyl isobutyl POSS in THF in different magnifications

Figure 4.7 PLM images of pure octaisobutyl POSS in THF in different magnifications

Figure 4.8 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in THF in low magnification
We know from the computational calculations that the allyl isobutyl POSS’ self-interaction is stronger compared with octaisobutyl POSS’, which makes expectable we get larger crystals of allyl isobutyl POSS. That might be the reason of difference in Figure 4.8. However, dendrimer-like crystals are very similar for both molecules, especially when compared the highest magnification images in Figure 4.6 and Figure 4.7. As a non-chlorinated solvent, THF did not cause a major difference between these two molecules’ crystal structures.

**Figure 4.9** PLM images of pure allyl isobutyl POSS in hexane in different magnifications

**Figure 4.10** PLM images of pure octaisobutyl POSS in hexane in different magnifications
With the second non-chlorinated solvent, hexane, we get different type of crystals, but again there is no major difference between octaisobutyl POSS and allyl isobutyl POSS except allyl isobutyl POSS has larger crystals. Especially in Figure 4.11, even the spread characteristics on to glass slide is very similar.

![Image](image.png)

**Figure 4.11 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in hexane in low magnification**

In Figure 4.6 to Figure 4.11, it is clear that similar type of crystals are formed with both POSS types with THF, and hexane, while chloroform used POSS solutions end up with distinctly different crystals which is similar with the differences of the PEO films with these POSS molecules.

These results narrowed down our research to the chloroform’s effect, as it was the only solvent among three of them causing distinct differences in crystal behavior. We have been suspicious about a possible interaction of chlorine and allyl groups. Between octaisobutyl and allyl isobutyl POSS molecules, allyl group is the only difference and this causes an obvious difference in crystallinity only when dissolved in chloroform.

In order to make a more detailed research about chlorine effect, we use solvents with various numbers of chlorines and similar molecular structure with chloroform, which
are dichloromethane and carbon tetrachloride. The hypothesis is, if allyl group of allyl isobutyl POSS and chlorine groups of chloroform have a special interaction, this might be the reason that allyl isobutyl POSS forms plaque-like crystals both as pure crystal and within polymer films. (See Figure 4.1 to Figure 4.3). Each of three chlorine groups of the chloroform might be attracting and gathering up to three allyl isobutyl POSS molecules and make a densely packed plaque-like crystal structure. If the hypothesis is correct then dichloromethane, which has similar molecular structure with chloroform but two chlorine groups only, is not likely to form a POSS network. However, we also note that it has lowest boiling point (39.6°C) among the solvents we used in this study, which might hinder the crystallization by having very fast evaporation at RT. If this hypothesis is correct, then carbon tetrachloride is even more likely to form a network, and maybe allyl isobutyl POSS films, by using its four carbons and relatively high boiling point (76.7°C).

Figure 4.12 PLM images of pure allyl isobutyl POSS in CH₂Cl₂ in different magnifications

In Figures Figure 4.12 to Figure 4.14 we can observe allyl isobutyl and octaisobutyl POSS crystals casted from dichloromethane (CH₂Cl₂). Compared with non-chlorinated solvents, THF and hexane, we see here distinctly different crystal characteristics between two POSS
types. As expected, dichloromethane cannot form plaque-like structures with allyl isobutyl POSS as it has only two chlorine groups per molecule. The ring like structures are also worth to be noted. On the other hand, octaisobutyl POSS does not form much different crystal structure than it forms in chloroform. Major difference between chloroform and dichloromethane are the boiling points, which are 61.2 and 39.6°C, respectively.

Figure 4.13 PLM images of pure octaisobutyl POSS in CH$_2$Cl$_2$ in different magnifications

![Image](image1.png)

![Image](image2.png)

Figure 4.14 Comparison of PLM images of pure octaisobutyl POSS (left) and allyl isobutyl POSS (right) in CH$_2$Cl$_2$ in low magnification

Final comparison is made with carbon tetrachloride (CCl$_4$). In Figure 4.15 we can observe pretty interesting crystal formation with allyl isobutyl POSS. As expected, carbon
tetrachloride caused to form a network structure, eventually an allyl isobutyl POSS film with its four chlorine groups.

Figure 4.15 PLM images of pure allyl isobutyl POSS in CCl$_4$ in different magnifications

Figure 4.16 PLM images of pure octaisobutyl POSS in CCl$_4$ in different magnifications

Figure 4.16 shows also a film like surface. We can understand it from the cracks at the surface. However, it is way more amorphous compared with allyl isobutyl POSS. In Figure 4.17, big difference can be seen.
In conclusion, allyl group is considered to have strong interaction with chlorine group and this hypothesis is examined by using five different solvents under same conditions. In order to understand whether solvent co-crystallized with POSS or not, SEM-EDS analyses were done.

Finally, computational calculations will help to quantify the interaction energy difference between allyl-chlorine and isobutyl-chlorine couples, thus we will be able understand the real fact beyond these different crystal structures.

Figure 4.18 shows elemental analysis for solvent-casted allyl isobutyl POSS sample using EDS detector. Cl amount is seen as 0.1%, which is neglectable amount. Thus
practically, we prove that there is no chlorine left in the sample. We did this analysis for every sample in this study and result did not change.

4.1.1 Computational Calculations

In order to explain experimentally observed significant difference between allyl isobutyl POSS and octaisobutyl POSS polymer nanocomposite morphology, phase organisation and dynamics of formation theoretical studies were conducted. One to one and three to one ratio of POSS structure to chloroform molecular models were prepared. At least five different initial structures were prepared for each structure which is followed by geometry optimization. Interaction energies between POSS and chloroform structures were calculated for the lowest energy structures for both 3:1 and 1:1 ratios for both allyl isobutyl POSS and octaisobutyl POSS structures. Density Functional Theory (DFT) and semi empirical methods were used in these calculations.

In Figure 4.19, we can observe the lowest energy state for allyl isobutyl POSS molecules around one chloroform molecule, where Chloroform is trapped in between three allyl and three isobutyl layers. This might be the reason why ally isobutyl and chloroform containing solutions were staying amorphous for hours and also crystallizing very slowly. Though every chlorinated solvent eventually evaporates (Figure 4.18), while they stay for hours between the molecules, their strong interactions can be able to orient the POSS structures. This might be the reason how allyl isobutyl POSS molecules can form plaque-like domains either as pure or in a polymer matrix.
Figure 4.19 Lowest energy state calculated with semi empirical method for allyl isobutyl POSS molecules around one chloroform molecule.
4.2 Conclusions and Future work

With these two sets of experimental ways, we aimed to have a deeper understanding about the effect of hydrocarbon groups (methyl-, isobutyl-, isoctyl- comparisons) and also the effect of functional groups on the mono-substituted POSS molecules (octaisobutyl, aminopropyl isobutyl, maleamic acid isobutyl and allyl isobutyl) on the same polymer matrix (PEO).

As there many other POSS molecules commercially available and also POSS can be tailored by chemists in any they way as well, it is hard to predict, which POSS type to be the best option for a particular application, for a particular polymer or blend. Thus, molecular modeling plays an important role about this prediction ability.

In this study, we aimed to build a bridge between the experimental results and computational calculations, expecting there might be a correlation between the structure of the composite and interaction values between that particular POSS type and polymer matrix. If such a correlation can be found, then a small database can be made of these computational calculation ratios for main class of polymers and commercially available POSS molecules, which can be produced by Hybrid Plastics, Inc.

Besides these bigger aims, we tried to have an understanding about the behavior of allyl isobutyl POSS in PEO film by using quantum mechanics as well and brought some assumptions to be discussed. In future, long crystallization process of allyl-isobutyl POSS/PEO film will be video-recorded.

Results of the chapter 4 make us suspicious about solvent effect on special phase domain formation by particular POSS types. If there that large effect by solvent, it is important to note that as most of the POSS types are dissolved by similar type of solvents. The
By now, as polymer matrix only PEO was used. Future work will be making similar trials with poly (methyl methacrylate) (PMMA), which is chloroform-soluble as well. By doing these future experiments, it is expected to observe especially octaisobutyl POSS’ and allyl-isobutyl POSS’ behavior in another polymer matrix, which is miscible with PEO. Also there will be double-check with the power of computational calculations.
Chapter 5  Use of compatibilizer polymer in an immiscible polymer-POSS blend

In the second and third chapters, we investigated poly (ethylene oxide) (PEO) – POSS blends. They were dissolved in chloroform as common solvent and then solvent casted on both glass and Teflon substrates for further analyses.

According to polarized light microscope (PLM), confocal laser scanning microscope (CLSM), and scanning electron microscope with energy-dispersive x-ray spectroscopy (SEM-EDS), we observed macro-phase separation between octamethyl-, octaisobutyl-, allyl isobutyl-, aminopropyl isobutyl POSS and PEO, while isooctyl- and maleamic acid isobutyl POSS molecules mixed with PEO well. These experimental results were supported also with the Monte Carlo fashion computer simulations and calculations (See Table 5.1).
Table 5.1 Molecular interaction energy results for several POSS-Polymer couples using Monte Carlo computer simulations

<table>
<thead>
<tr>
<th></th>
<th>Polymer+POSS</th>
<th>Polymer</th>
<th>POSS</th>
<th>Interaction (a.u.)</th>
<th>Interaction (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octamethyl POSS-PEO</td>
<td>-4365.92</td>
<td>-844.34</td>
<td>-3521.56</td>
<td>-0.03</td>
<td>-17.88</td>
</tr>
<tr>
<td>Octaisobutyl POSS-PEO</td>
<td>-5304.36</td>
<td>-844.34</td>
<td>-4459.99</td>
<td>-0.03</td>
<td>-21.88</td>
</tr>
<tr>
<td>Isooctyl POSS-PEO</td>
<td>-6555.58</td>
<td>-844.33</td>
<td>-5711.20</td>
<td>-0.04</td>
<td>-25.61</td>
</tr>
<tr>
<td>Allyl isobutyl POSS-PEO</td>
<td>-5264.02</td>
<td>-844.33</td>
<td>-4419.65</td>
<td>-0.04</td>
<td>-22.97</td>
</tr>
<tr>
<td>Aminopropyl Isobutyl POSS-PEO</td>
<td>-5320.29</td>
<td>-844.34</td>
<td>-4475.92</td>
<td>-0.04</td>
<td>-24.97</td>
</tr>
<tr>
<td>Maleamic acid Isobutyl POSS-PEO (with -COOH)</td>
<td>-5697.52</td>
<td>-844.34</td>
<td>-4853.15</td>
<td>-0.04</td>
<td>-25.17</td>
</tr>
<tr>
<td>Maleamic acid isobutyl-PEO (with -NH)</td>
<td>-5697.53</td>
<td>-844.34</td>
<td>-4853.15</td>
<td>-0.05</td>
<td>-28.41</td>
</tr>
<tr>
<td>Octaisobutyl POSS-PMMA</td>
<td>-6024.43</td>
<td>-1564.40</td>
<td>-4459.99</td>
<td>-0.05</td>
<td>-28.99</td>
</tr>
<tr>
<td>PEO-PMMA</td>
<td>-2408.78</td>
<td>-844.33</td>
<td>-1564.39</td>
<td>-0.05</td>
<td>-33.26</td>
</tr>
</tbody>
</table>

As we can see, there is a critical interaction energy boundary at around 25 kcal/mol. The lower this interaction energy is, the larger phase domains of POSS are formed in the polymer films. Beyond this level there is no macro-phase separation observed.

Among these POSS-PEO films, octaisobutyl POSS containing one formed honeycomb-like phase domains, which brought up the third chapter studies in order to further investigate this interesting behavior.
In this chapter, we will try to understand octaisobutyl POSS interactions with another chloroform soluble polymer: PMMA. From the results of the third chapter, we understood the sensitivity of substituted organic group in POSS-polymer interaction. None of the substituted POSS molecules formed hexagonal phase domains in PEO film, though they had still seven isobutyl groups out of eight organic legs. We also understood strong dependence of solution viscosity if this formation which was shown in the second chapter.

As first step, octaisobutyl POSS-PMMA interaction energy is calculated with the same computational techniques and shown also in Table 5.1. This energy level is even higher than the best POSS-PEO couples, which makes us to expect a good miscibility.

Figure 5.1 PLM images of pure PMMA film (10g 996k PMMA, 50ml Chloroform)

PLM images of pure PMMA film can be seen in two different magnifications in Figure 4.1. As known, it is 100% amorphous film. Due to fast evaporation rate of chloroform and high solution viscosity a lot of bubbles are formed in the film.
Figure 5.2 PLM images of 10% Octaisobutyl POSS-PMMA film (10g 996k PMMA, 1g octaisobutyl POSS, 50ml Chloroform)

Due to amorphous nature of PMMA we can easily observe POSS crystals in PMMA film. Figure 5.2 shows PLM images of 10 wt.% octaisobutyl POSS containing PMMA film. We use only 10%, since this % level was the one causing hexagonal phase domains in PEO films. The images support the simulation calculations. There is no macro-phase separation, nor POSS chunks. Crystal distribution is homogeneous as well.

Figure 5.3 Comparison of CLSM images of pure PMMA film (left) and 10% Octaisobutyl POSS-PMMA film (right) (10g 996k PMMA, 1g octaisobutyl POSS, 50ml Chloroform)
Figure 5.3 shows us 2D confocal image comparison between pure PMMA film and 10% octaisobutyl POSS containing one. Bubble formation is very clear on both samples. Octaisobutyl POSS increases opacity but there is no distinct visible phase domain.

The reason of this good level miscibility between octaisobutyl POSS and PMMA can be seen in Figure 5.4. According to our simulations, while every hydrogen on the isobutyl legs are interacting with carbonyl group of PMMA, hydrogens on the PMMA’s side group interact with the oxygen in the POSS framework. This mutual interaction prevents macro phase separation even at 10wt.% POSS loading.

Figure 5.4 Interacting sites of PMMA and octaisobutyl POSS

It is well known that PMMA and PEO are miscible polymers. So in this case, we have a POSS molecule, which is highly miscible with PMMA but not with PEO. Our research question is: “If we have an immiscible polymer-POSS couple, can we use another polymer, which is miscible both with the polymer and POSS, as a compatibilizer?” The
result of this question is especially important for the polymer-POSS couples, which are both important for a particular application but immiscible with each other. Though we know well the miscibility of PMMA and PEO, we wanted to compare their interaction energy level under same conditions with the previous computational comparison set. In table 5.1, we can see the interaction energy between PMMA and PEO, which is even higher than all POSS-polymer interaction energies. Below in figure 5.5, we can also see the interaction sites between these polymers.

![Figure 5.5 Interacting sites of PMMA and PEO](image)

There is a mutual interaction just like in the PMMA and octaisobutyl POSS. While hydrogens of methylene group in PEO are interacting with carbonyl group on PMMA, hydrogens on the PMMA’s side group interact with the oxygen in PEO.

**Experimental**

**Materials**

996,000 g/mol poly (methyl methacrylate) (PMMA) and 1000,000 g/mol poly (ethylene oxide) (PEO) from Sigma-Aldrich, octaisobutyl POSS (MS0825) from Hybrid Plastics,
and chloroform (99.8%+) were purchased from Alfa Aesar. All products were used without further purification. Recipe of each solution can be found in Table 5.2.

Table 5.2 Sample set and recipes

<table>
<thead>
<tr>
<th>Sample name</th>
<th>PEO (g)</th>
<th>PMMA (g)</th>
<th>POSS (g)</th>
<th>Chloroform (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0PEO-N</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>0PEO-P</td>
<td>-</td>
<td>10</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>30.5PEO-N</td>
<td>2</td>
<td>4.54</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>30.5PEO-P</td>
<td>2</td>
<td>4.54</td>
<td>0.654</td>
<td>100</td>
</tr>
<tr>
<td>40PEO-N</td>
<td>2</td>
<td>3</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>40PEO-P</td>
<td>2</td>
<td>3</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>50PEO-N</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>50PEO-P</td>
<td>2</td>
<td>2</td>
<td>0.4</td>
<td>100</td>
</tr>
<tr>
<td>70PEO-N</td>
<td>2</td>
<td>0.857</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>70PEO-P</td>
<td>2</td>
<td>0.857</td>
<td>0.286</td>
<td>100</td>
</tr>
<tr>
<td>100PEO-N</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>100PEO-P</td>
<td>2</td>
<td>-</td>
<td>0.2</td>
<td>100</td>
</tr>
</tbody>
</table>

We gradually increase the PEO % in the solutions and eventually get 100% PEO films like in the previous chapters. While we were using 900k g/mol PEO sample in the previous chapters 1000k g/mol is used for this in order to have almost same Mw as PMMA (996k g/mol). As clearly seen, all PEO containing samples have constant amount of PEO and chloroform, while PMMA amount is changing. The reason behind this is, keeping the
solution viscosity as similar as possible. PMMA has no major effect on viscosity. Thus we had to make 20wt.% PMMA solution for the pure PMMA sample in order to make the viscosity high enough to mimic PEO solution’s viscosity. POSS amount is always 10% of the total polymer amount in each sample. We always keep 10wt.% POSS/polymer ratio constant. Among the sample set, the most interesting sample name might be PEO30.5. It is 30.5% PEO because this ratio makes almost same amount of PEO and PMMA repeating units in the sample. This gives statistically almost same level of chance for both polymers to interact with each other and/or with POSS molecules.

Figure 5.6 PLM images of PEO30.5-N samples

With 30.5% PEO, we see macro-phase separation in both samples. In Figure 5.6 we observe phase separation even without POSS, only between PMMA and PEO. This might be due to high molecular weight of both polymers. We can recognize PMMA phase domain from the bubbles inside. By adding 10wt% octaisobutyl POSS to this sample, polymer phase separation is reduced, however we get some POSS agglomerations, which are the black spots in the film. (See Figure 5.7)
Figure 5.7 PLM images of PEO30.5-P samples

Figure 5.8 CLSM images of PEO30.5-N(left) and PEO30.5-P(right) samples
40% PEO samples are the most important samples in this chapter. When there is no POSS in this concentration, we cannot observe macro-phase separation. (See Figure 5.9) Thus, we basically found the best PEO:PMMA ratio for highest level of miscibility for this high Mw polymers. However once we add octaisobutyl POSS, we get the film composition shown in Figure 5.10 which has visible phase domains. Likewise in Figure 5.11 we can observe the change on the surface topography of the films.
Figure 5.11 CLSM images of PEO40-N(left) and PEO40-P(right) samples

Figure 5.12 PLM images of PEO50-N samples
50%PEO-PMMA film keeps showing distinct phase separation. In Figure 5.13 with the addition of octaisobutyl POSS, we get thicker phase domains and POSS crystals can be seen clearly.

**Figure 5.13 PLM images of PEO50-P samples**

We can understand the dark regions in Figure 5.13 by looking at Figure 5.14. On the left column images of figure 5.14 PEO50-N film can be observed. Phase separation is very clear. When we add octaisobutyl POSS to that sample, we obtain PEO50-P, which is presented on the right column of Figure 5.14. PEO50-P is around 2 times thicker than PEO50-N. We see cubical POSS crystals on the film, which was supported also by Figure 5.13.
Figure 5.14 Comparison of CLSM images of PEO50-N (left column) and PEO50-P (right column) samples. First row is for real color, second row shows height difference.

In order to be sure about which phase domain belongs to PMMA and which one to PEO, we simply immerse the film into distilled water for 24 h and retake CLSM images, which is shown in Figure 5.15.
Figure 5.15 CLSM images of PEO50-P after staying for 24h in DI water

As it can be seen in Figure 5.15, web-like phase domain mostly remain. This we can understand that those regions were PMMA-rich, while underneath layer is PEO-rich domain.

Below in Figure 5.16 we have SEM image of PEO50-P film under CBS detector, which shows Si containing POSS compounds in a brighter way. Figure 5.17 has same samples’ higher magnification image with its EDS map for silicon element to show POSS-rich domains to understand on which side more POSS were accumulated.
As it is seen in Figure 5.17, octaisobutyl POSS crystals are both in PMMA-rich domain and on the PEO-rich domain. While POSS is not macro-phase separated in PMMA domain, its cubical crystals are visible in PEO-rich domain.

Figure 5.17 SEM-EDS image(left) and silicon map (right) of PEO50-P film
70%PEO samples have the same phase behavior as previous ones except the PMMA-rich domains have more uniform structures. POSS makes the phase boundaries thicker and some of POSS crystals stay again individually on PEO rich side.
Figure 5.20 Comparison of CLSM images of PEO70-N (left) and PEO70-P (right) samples.

Figure 5.21 PLM images of PEO100-N samples

Figure 5.22 PLM images of PEO100-P samples
Figure 5.23 Comparison of CLSM images of PEO100-N (left) and PEO100-P (right) samples.

As it is known from the second and third chapters, when pure PEO is mixed with octaisobutyl POSS above 7.5wt%, it ends up with honeycomb-like surface topography with the phase domain of POSS. This structure is observed again in Figure 4.21.

Figure 5.24 Modulus vs. PEOwt% plots for both w/ and w/o POSS series.
Figure 5.24 is the modulus plot for all samples in this study. X-axis shows the PEO wt% in each sample. Orange series is for the samples containing 10wt% octaisobutyl POSS, while blue set is for without POSS films.

Addition of octaisobutyl POSS reduces the modulus only for 100% PEO sample. Except that, all samples’ modulus values were increased significantly. By investigating microscope images and computational calculations, we know about the incompatibility of octaisobutyl POSS and PEO. Likewise, we also know the compatibility of PMMA and octaisobutyl POSS. This information is supported here with the mechanical test data, too. 100% PMMA film’s modulus is increased with the help of octaisobutyl POSS. As we blended PEO and PMMA in different ratios, modulus kept increasing up to 40wt% PEO. After this peak value, it is reduced as PEO ratio was increased in the blend. However, we should note that the samples with POSS had always higher modulus compared with the same samples without POSS. This proves the compatibilizer effect of PMMA in PEO-octaisobutyl POSS blend.
Figure 5.25 Tensile Strength vs. PEOwt% plots for both w/ and w/o POSS series.

Figure 5.25 presents tensile strength data in the same way as in the figure 5.24. Again, pure PEO loses its strength with the addition of octaisobutyl POSS while pure PMMA has an increase with POSS. While the PEO-PMMA blend has a clear increase up to 40wt%PEO, it has not the same fashion with the POSS added series. When POSS was added, tensile strength constantly decreases with the increase of PEO amount in the blend. When we look from the point of view of compatibility, 40PEO-P sample has almost same tensile strength as the pure PMMA film and 140% increase compared with pure PEO film strength. Thus, PMMA is successful in being compatibilizer in terms of tensile strength as well.
Finally, in Figure 5.26, breaking strain (%) is shown. Addition of octaisobutyl slightly decreases strain of PMMA while increases strain of PEO. There is no big difference between POSS added samples versus not added ones up to 40% PEO samples. Beyond that POSS effect is more visible.

Conclusions

Due to high Mw of PEO and PMMA (1000k, and 996k respectively) there is macro-phase separation in every blend ratio of these polymers, though they are known as miscible. According to mechanical results, phase separation of polymers does not have a significant negative effect. As it is understood in the previous chapters, PEO is not miscible with octaisobutyl POSS, while PMMA is. By keeping 10wt% octaisobutyl POSS constant in every different PEO-PMMA blend, we compared morphology and mechanical properties of the resulting solvent-casted films. The major aim was the make an incompatible
polymer-POSS couple (in this case PEO-octaisobutyl POSS) more compatible, miscible and stronger by using another polymer as compatibilizer (in this case PMMA), which is miscible both with the matrix polymer and that particular POSS type. According to mechanical tests, especially in modulus results, this aim is succeeded. While PEO loses modulus and tensile strength with the addition of 10wt% octaisobutyl POSS, same values increase for PMMA. For all blend ratios POSS-added samples show higher modulus compared with no-POSS samples. Especially 40%PEO-60%PMMA blend seems optimum one under these conditions. As last step, DSC results will be added. DSC results might show a common Tg as a result of miscibility and addition of POSS might shift that value as well as overall crystallinity.
Chapter 6  Conclusions and Future work

With these two sets of experimental ways, we aimed to have a deeper understanding about the effect of hydrocarbon groups (methyl-, isobutyl-, isoctyl- comparisons) and also the effect of functional groups on the mono-substituted POSS molecules (octaisobutyl, aminopropyl isobutyl, maleamic acid isobutyl and allyl isobutyl) on the same polymer matrix (PEO).

As there are many other POSS molecules commercially available and also POSS can be tailored by chemists in any way as well, it is hard to predict, which POSS type to be the best option for a particular application, for a particular polymer or blend. Thus, molecular modeling plays an important role in this prediction ability.

In this dissertation, we aimed to build a bridge between the experimental results and computational calculations, expecting there might be a correlation between the structure of the composite and interaction values between that particular POSS type and polymer matrix. If such a correlation can be found, then a small database can be made of these computational calculation ratios for main class of polymers and commercially available POSS molecules, which can be produced by Hybrid Plastics, Inc.

Besides these bigger aims, we tried to have an understanding about the behavior of allyl isobutyl POSS in PEO film by using quantum mechanics as well and brought some assumptions to be discussed. With deeper analysis using allyl isobutyl and octaisobutyl POSS molecules alone with five different solvents, we understood that chlorinated solvents have a major effect on these molecules. It is also supported with further computer calculations. In order to be positive, further computational techniques will be applied. This is very important because, while dealing with POSS engineered materials, solvent type is
generally neglected. Especially in case that the functional group of a POSS has special interaction with any group of the solvent, dramatically different results might happen by using different solvents. As chloroform family is generally a good solvent for POSS structures, scientists should be careful while using it.

Final study was done to use another polymer as a potential compatibilizer in a POSS-polymer nanocomposite, which are initially incompatible. For this purpose, PMMA is dissolved together with PEO and octaisobutyl POSS. Pretty interesting results came out. It is especially promising technique for lower molecular weight polymers and also for functional materials. Future studies will be done also to use a particular POSS type as compatibilizer in an incompatible polymer blend.
References


[8] Markovic E, Constantopolous K, Matisons JG. Polyhedral Oligomeric Silsesquioxanes: From Early and Strategic Development through to Materials


doi:10.1016/j.progpolymsci.2015.01.003.


[58] Decker B, Hartmann-Thompson C, Carver PI, Keinath SE, Santurri PR. Multilayer Sulfonated Polyhedral Oligosilsesquioxane (S-POSS)-Sulfonated


methacrylate–polyhedral oligomeric silsesquioxane hybrid polymeric coating. 


[123] Mya KY, Li X, Chen L, Ni X, Li J, He C. Core–Corona Structure of Cubic Silsesquioxane-Poly(Ethylene Oxide) in Aqueous Solution: Fluorescence, Light
doi:10.1021/jp050287s.

doi:10.1021/ma062327b.


[130] Chae Jung Y, Hwa So H, Whan Cho J. Water-Responsive Shape Memory Polyurethane Block Copolymer Modified with Polyhedral Oligomeric


[138] Chinnam PR, Zhang H, Wunder SL. Blends of Pegylated Polyoctahedralsilsesquioxanes (POSS-PEG) and Methyl Cellulose as Solid


