2010

Polymer/mesoporous metal oxide composites

Melissa Ann Ver Meer
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/etd

Part of the Materials Science and Engineering Commons

Recommended Citation
Ver Meer, Melissa Ann, "Polymer/mesoporous metal oxide composites" (2010). Graduate Theses and Dissertations. 11479.
https://lib.dr.iastate.edu/etd/11479

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Polymer/mesoporous metal oxide composites

by

Melissa Ann Ver Meer

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

Program of Study Committee:
Surya Mallapragada, Major Professor
Brent Shanks
Balaji Narasimhan
Michael Kessler
Zhiqun Lin

Iowa State University
Ames, Iowa
2010

Copyright © Melissa Ann Ver Meer, 2010. All rights reserved.
DEDICATION

I would like to dedicate this dissertation to my beloved husband, Michael Ver Meer.
Without his support, patience and love this work would not have been possible.
TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................... vi
LIST OF FIGURES ........................................................................................................ vii
ACKNOWLEDGMENTS ................................................................................................. x
ABSTRACT .................................................................................................................... xii

CHAPTER 1: GENERAL INTRODUCTION ................................................................. 1
  1.1 Introduction ........................................................................................................... 1
  1.2 Research Objectives .......................................................................................... 1
    1.2.1 Synthesis and characterization of polymer composites based on mesoporous
          metal oxides blended within a polymer matrix .............................................. 2
    1.2.2 Synthesis and characterization of polymer composites with polymer chains
          grafted to the surface of the mesoporous metal oxides ................................ 2
    1.2.3 Synthesis and characterization of polymer composites with polymer chains
          grafted to the interior of the mesoporous metal oxides ................................ 2
  1.3 Dissertation Organization ................................................................................ 3
  1.4 References .......................................................................................................... 3

CHAPTER 2: BACKGROUND AND LITERATURE REVIEW ................................... 4
  2.1 Introduction ........................................................................................................ 4
    2.1.1 Polymer composites ............................................................................... 4
    2.1.2 Synthesis of polymer composites ............................................................ 7
    2.1.3 Atom transfer radical polymerization ....................................................... 8
    2.1.4 Silica fillers ............................................................................................ 11
  2.2 References ......................................................................................................... 13

CHAPTER 3: MELT BLENDED POLYSTYRENE MICRO AND
        NANOCOMPOSITES ................................................................................. 16
  3.1 Abstract ........................................................................................................... 16
  3.2 Introduction ....................................................................................................... 16
  3.3 Experimental ................................................................................................... 18
    3.3.1 Synthesis of mesoporous silica (MCM-41) ........................................... 18
    3.3.2 Preparation of PS-grafted MCM-41 ....................................................... 19
    3.3.3 Surface preparation and synthesis of 3-aminopropyltrimethoxy-
          functionalized MCM-41 particles ............................................................... 19
    3.3.4 Preparation of initiator and synthesis of 2-bromoisobutyrate-bunctionalized
          MCM-41 particles ......................................................................................... 20
    3.3.5 Polymerization and grafting of styrene from 2-bromoisobutyrate-
          functionalized MCM-41 particles ............................................................... 21
5.3.1 Materials .......................................................................................................67
5.3.2 ATRP of styrene from APMSS ................................................................67
5.3.3 Preparation of polystyrene-grafted-silica....................................................68
5.3.4 Particle characterization...............................................................................68
5.3.5 Polystyrene characterization ......................................................................69
5.3.6 Thermal properties .....................................................................................69
5.3.7 Mechanical properties ...............................................................................69
5.4 Results and Discussion ....................................................................................69
  5.4.1 Silica characterization ...............................................................................69
  5.4.2 Initiator grafting density ...........................................................................71
  5.4.3 Polystyrene-graft-APMMS particles .......................................................72
  5.4.4 Thermal stability .....................................................................................74
  5.4.5 Mechanical behavior and glass transition .................................................76
5.5 Conclusions ....................................................................................................82
5.6 Acknowledgments ............................................................................................83
5.6 References ......................................................................................................83

CHAPTER 6: GENERAL CONCLUSIONS ................................................................86
LIST OF TABLES

Table 3-1 Tensile property data of PS nanocomposites - ASTM D638 type V tensile samples, 190°C melt temp, 3 min mix, 200 rpm ..............................................32
Table 3-2 GPC data for as received and melt blended PS and unfilled, processed PS.....33
Table 3-3 Tensile property data of PS nanocomposites - ASTM D638 type I tensile samples, 190°C melt temp, 2 min mix, 150 rpm.....................................................34
Table 4-1 Results for the ATRP synthesis of polystyrene-silica... ...........................53
Table 4-2 Sample identification, composite preparation and relative silica loading levels........................................................................................................53
Table 5-1 Results for the ATRP synthesis of polystyrene-APMMSS... ....................73
Table 5-2 Sample identification and relative silica loading levels... ..........................74
Table 5-3 Thermal decomposition temperatures for polystyrene and PS-g-APMMSS composites........................................................................................................75
Table 5-4 Glass transition temperature comparison as defined by loss modulus (E”) peak ..................................................................................................................78
Table 5-5 Comparison of molecular weight distributions for polystyrene chains before and after thermal aging due to the annealing and molding processes ..........80
LIST OF FIGURES

Figure 2-1 15 ml twin screw extruder for batch operations........................................8
Figure 2-2 ATRP, “grafting-from” steps for forming polymer-inorganic particles where [M]₀ is the monomer, CuX is the transition metal and L is the ligand...............10
Figure 2-3 Formation of MCM-41 particles: (a) surfactant micelle; (b) micellar rod; (c) hexagonal array; (d) silicate; (e) MCM-41. .................................................................12
Figure 3-1 Surface area/volume ratios for various reinforcing filler geometries (particle, fiber, layered) ..................................................................................................17
Figure 3-2 Ligand for atom transfer radical polymerization, 2,2’-bipyridyl (Bipy)........20
Figure 3-3 Synthetic approach for polystyrene-grafted silica particles by ATRP.........21
Figure 3-4 SEM image of TEOS-derived agglomerated mesoporous silica particles (no grinding or sonication) .................................................................25
Figure 3-5 TGA comparison of MCM-41 particles and Stöber synthesized silica particles ................................................................................................................26
Figure 3-6 Polystyrene PS 1220 1% MCM-41 silica above and 1% Cloisite 10A nanoclay ...........................................................................................................27
Figure 3-7 Polystyrene PS 1510 1% MCM-41 silica above and 1% Cloisite 10A nanoclay ...........................................................................................................28
Figure 3-8 Polystyrene PS 1220 5% MCM-41 silica above and 5% Cloisite 10A nanoclay ...........................................................................................................29
Figure 3-9 Polystyrene PS 1510 5% MCM-41 silica above and 5% Cloisite 10A nanoclay ...........................................................................................................30
Figure 3-10 High magnification TEM image of PS 1510 1% MCM-41 (above) and PS1510 1% Cloisite 10A composite .................................................................31
Figure 3-11 FTIR spectra of grafting process of MCM-41 particles as measured by ATR: (a) MCM-41; (b) APTMS-functionalized MCM-41; (c) 2-bromoisobutyryl-functionalized MCM-41; (d) polystyrene-grafted MCM-41; (e) polystyrene-grafted MCM-41 ................................................................................33
Figure 3-12 TEM image of PS 1510 blended with polystyrene-grafted MCM-41 (2 wt% MCM-41 overall) ..................................................................................34
Figure 3-13 Tensile curves for PS 1510-based PNCs, including Cloisite 10A, MCM-41 and grafted MCM-41 particles .................................................................35
Figure 3-14 A comparison between glass transition responses for composites filled with layered silicate (Cloisite 10A) and mesoporous silica (MCM-41) ........36
Figure 4-1 Tri-functional ligand, tris[(2-pyridyl)methyl]amine (TPMA) .................43
Figure 4-2 SEM images of Stöber, on the left, and mesoporous silica (MCM-41), on the right ..........................................................48

Figure 4-3 (Top) Adsorption-desorption isotherm of nitrogen at 77K for MCM-41. (■ Adsorption, ● Desorption). (Bottom) BJH pore-size distribution plot from adsorption branch for MCM-41 ..........................................................49

Figure 4-4 Polystyrene with MCM-41 incorporated, after melt compounding. Single particles present in polymer matrix with larger aggregates still present ........50

Figure 4-5 TGA thermograms of weight loss as a function of temperature. (● Stöber, ○ Br-grafted-Stöber, ■ MCM-41, □ Br-grafted-MCM-41) ..............................................52

Figure 4-6 Polystyrene-graft-Stöber silica, after melt compounding. Single particles present in polymer matrix with smaller aggregates still present ...............................54

Figure 4-7 Polystyrene-graft-MCM-41 after melt compounding. Single particles present in polymer matrix with smaller aggregates still present ...............................55

Figure 4-8 Storage modulus (E’) as a function of temperature (■ SiO2-g-PS, □ M41-g-PS, ◆ 0.9 SiO2-PS, ● 2.6 SiO2-PS, ○ 2.0 M41-PS) ..............................................56

Figure 4-9 Loss modulus (E”) as a function of temperature (■ SiO2-g-PS, □ M41-g-PS, ◆ 0.9 SiO2-PS, ● 2.6 SiO2-PS, ○ 2.0 M41-PS) ..............................................57

Figure 4-10 Loss tangent (tan δ) as a function of temperature (■ SiO2-g-PS, □ M41-g-PS, ◆ 0.9 SiO2-PS, ● 2.6 SiO2-PS, ○ 2.0 M41-PS) ..............................................58

Figure 4-11 TGA thermograms of weight loss as a function of temperature (■ SiO2-g-PS, ◆ 0.9 SiO2-PS, ● 2.6 SiO2-PS) ..............................................59

Figure 4-12 TGA thermograms of weight loss as a function of temperature (□ M41-g-PS, ○ 2.0 M41-PS) ..............................................60

Figure 5-1 SEM image of APMMSS ........................................................................70

Figure 5-2 Adsorption-desorption isotherm of nitrogen at 77K for APMMSS. (□ Adsorption, ○ Desorption) ..............................................70

Figure 5-3 BJH pore-size distribution plot from adsorption branch for APMMSS ........71

Figure 5-4 TGA thermogram of weight loss as a function of temperature for the aminopropyl-functionalized mesoporous silica after initiator grafting ..........72

Figure 5-5 Polystyrene-grafted-APMMSS particle after annealing ..........................73

Figure 5-6 Representative dispersion of PS-g-APMMSS 50 sample .......................74

Figure 5-7 Samples are 6.6, 11.8 and 16.6 wt% mesoporous silica with polystyrene (see chart for GPC data) grafted from the interior of the particle .............76

Figure 5-8 Loss modulus (E") as a function of temperature ..................................77

Figure 5-9 Loss tangent (tan δ) as a function of temperature .................................79
Figure 5-10 Loss tangent (tan δ) as a function of temperature for pure polystyrene with various heat histories .................................................................81

Figure 5-11 Loss modulus (E’’) as a function of temperature for pure polystyrene with various heat histories .................................................................................82
ACKNOWLEDGMENTS

I am extraordinarily grateful to Dr. Surya Mallapragada for stepping forward and accepting the responsibility of a non-traditional doctoral student. Her patience, wisdom, encouragement and guidance navigated me through the entire process. I will take all that she has taught me, technically, professionally and personally on my continued journey. I would also like to thank Dr. Balaji Narasimhan and Dr. Brent Shanks for coming together as my co-advisors, with their inspirational ideas, sage advice and heavy doses of patience during this long trek. Additionally, I am grateful to Dr. Michael Kessler and Dr. Zhiqun Lin for their time and shared technical expertise while serving on my advisory committee.

Schlumberger Technology Corporation, specifically the Lawrence Technology Center, graciously provided the financial support and facilities for this work. Schlumberger’s Lawrence management, particularly Greg Manke, Barry Landon and Howard Oswald, provided both encouragement and flexibility.

I would particularly like to thank the many graduate students who have aided me over the years in one manner or another. They include Dr. Michael Determan, Dr. Umai Kanapathillai, Dr. Isa Mbaraka, Brenda Carrillo-Conde, Bret Ulery and Ryan Snell. I would also like to express my gratitude to Tracey Pepper, Dr. Tanya Prozarov and Warren Straszheim for their time and expertise in electron spectroscopy. And I am very appreciative for the continued technical conversations with my Schlumberger colleagues, Dr. William Goertzen, Jason Holzmueller, Dr. Huilin Tu, Dr. Agathe Robisson and Dr. Alan Humphreys as well as Linda Williams for her continuous laboratory assistance.
Finally, I would like to offer thanks to my family for their love and support. I want to thank my parents for my first chemistry set and for keeping my scientific curiosity alive. And I have been blessed with two wonderful sons, Alexander and Liam. I hope I can continue to fuel their scientific spirits. Most of all, I am eternally grateful for my marvelous husband, Michael, who is the foundation that made all of this possible. Thank you.
ABSTRACT

Understanding the nature of the interfacial region between an organic polymer matrix and an inorganic filler component is essential in determining how this region impacts the overall bulk properties of the organic/inorganic hybrid composite material. In this work, polystyrene was used as the model polymer matrix coupled with silica-based filler materials to investigate the nature of structure-property relationships in polymer composites.

Initial work was conducted on synthesis and characterization of colloidal and mesoporous silica particles melt blended into the polystyrene matrix. Modification of the interface was accomplished by chemically bonding the silica particles with the polystyrene chains through polymerization from the particle surface via atom transfer radical polymerization. High molecular weight polystyrene chains were formed and bulk test samples were evaluated with increased thermal stability of the grafted polymer composite system versus equivalent melt blended polymer composites.

Polymer grafting was also conducted from the internal pores of mesoporous silica, further improving the thermal stability of the composite system without degrading dynamic mechanical properties. Characterization of the polymer composites was conducted with gel permeation chromatography, transmission electron microscopy, thermogravimetric analysis and dynamic mechanical analysis.

It was also discovered during the polystyrene-silica composite studies that amorphous polystyrene can possess a less mobile phase, evident in a second peak of the loss tangent (tan δ). The long annealing times necessitated by the mesoporous silica
composites were replicated in as received polystyrene. This new, less mobile phase is of particular interest in determining the mobility of polymer chains in the interfacial region.
CHAPTER 1. INTRODUCTION

1.1 Introduction

The combination of high surface area inorganic mesoporous materials with organic polymer systems is an emerging class of hybrid materials with numerous potential applications.\textsuperscript{1-3} Mesoporous silica can have ordered pores ranging in diameter from 2 to 50 nm and specific surface areas over 1000 m\textsuperscript{2}/g.\textsuperscript{4} Composite materials can be formed through polymerization in the presence of the mesoporous materials,\textsuperscript{3,5} covalently bonded to the polymer matrix through grafting techniques\textsuperscript{2} or simply blended into a polymer melt.\textsuperscript{6}

Due to the control that can be exerted in mesoporous materials, such as MCM-41, well studied particle surfaces and chemistry can be controlled and manipulated. MCM-41 particles in particular are spherical in shape with ordered nano-scale pores. These high surface area particles can be directly compared to similar diameter colloidal silica or functionalized for further use. This arrangement provides an ideal model system to study the influence of the interface between the polymer and inorganic component with the elimination of the particle size influence.

1.2 Research Objectives

The central focus of this work is development of model systems to better understand the influence of the interface and interfacial region on the bulk properties of polymer composite systems. The well-studied system of polystyrene as the polymer matrix and silica as the inorganic component was selected due to its ease of processing, established procedures for grafting polystyrene from the surface of silica and its
ubiquitous nature in literature. Manipulation of the silica particle through variations in surface area, surface interaction and interior versus exterior surfaces were studied to determine the impact of the interfacial region on the overall thermomechanical properties of the composite system. This work includes the first known investigation of polymer grafting exclusively from the interior surface of mesoporous silica particles.

1.2.1 Synthesis and characterization of polymer composites based on mesoporous metal oxides blended within a polymer matrix

The objective of this stage of work was to study the high surface area particle mesoporous silica as the inorganic component in a polystyrene-based polymer composite. The polystyrene-mesoporous silica composite was compared with another well studied high surface area inorganic component, nanoclay.

1.2.2 Synthesis and characterization of polymer composites with polymer chains grafted to the surface of the mesoporous metal oxides

Atom transfer radical polymerization was employed to graft polystyrene chains to the surface of mesoporous silica as well as similar diameter colloidal silica particles. Similar melt blended composites were manufactured to compare thermal and mechanical properties.

1.2.3 Synthesis and characterization of polymer composites with polymer chains grafted to the interior of the mesoporous metal oxides

This portion of the work involved grafting polystyrene chains from the interior pore surface of co-condensed mesoporous silica particles.
1.3 Dissertation organization

This dissertation is organized into 6 chapters. Chapter 2 is general background into polymer composites and nanocomposites and their synthesis via melt blending or grafting processes. The intention of this review is to provide context for the specific materials and methods used to generate composite materials in the subsequent chapters. Chapter 3 involves physical property testing of polymer composites consisting of colloidal silica as well as mesoporous silica melt blended into a polystyrene matrix and comparisons with nanoclay-filled polymer nanocomposites. Chapter 4 is a paper published in the journal *ACS Applied Materials & Interfaces* that focuses on grafted silica particles, both colloidal and mesoporous, in comparison to melt blended equivalents. Chapter 5 is a paper to be submitted that includes grafted mesoporous silica particles in which the polystyrene chain is initiated from the interior pore of the particle. The final chapter includes general conclusions and a summary of contributions of this work.

1.4 References

2.1 Introduction

2.1.1 Polymer composites

Polymers are widely used in applications because they are lightweight, easily processed and allow for design flexibility. Polymer composites, consisting of the polymer phase and an additional component or components, generally balance performance, mechanical properties, cost and processability. The additional component, or filler, may be of reinforcing or non-reinforcing type. Reinforcing fillers aid in improving mechanical properties and abrasion resistance whereas non-reinforcing fillers may decrease the cost, modify density, improve barrier properties or change color.  

Fillers are typically inorganic, rigid materials that are immiscible in the polymer matrix in both solid and molten states and form distinct morphologies. Small fillers are used in polymer composites to increase the surface area available for interaction with the polymer matrix. High filler content, typically above 20% volume fraction, normally is required to positively impact mechanical properties for micron sized fillers. At higher concentrations the filler can negatively affect the processability and appearance of the polymer composite.

Polymer nanocomposites (PNCs) are polymer composites with one dimension of the inorganic component in the nano-scale, typically less than 100 nm. In the last two decades PNCs have attracted the attention of researchers due to the allure of dramatically improved properties, including higher modulus, increased solvent resistance, greater thermal stability and reduction in gas permeation at very low filler levels (5 wt% or
lower). PNCs can contain various structures such as nanospheres, nanoplatelets, nanofibers, nanotubes, nanocages, nanococoons, nanoropes, nanocoils, nanorods, nanowires, and fullerene structures. One advantage of each of these nanoparticle structures is the extremely high surface to volume ratio in comparison to standard polymer composites. PNCs, with equivalent or superior performance to classically filled systems and filler loadings of 1-5%, allow for greater retention of processability and toughness of the neat polymer.\textsuperscript{13,14} Together with relatively simple processing techniques such as melt intercalation, PNCs are appearing in applications that were limited to costlier, lightweight materials. Tailored materials are increasing in possibility due to the number of organic-inorganic systems and the processing methodologies available.

There are several fundamental challenges that still exist in the development of polymer composites and nanocomposites, including prediction of bulk properties from model equations and an absence of structure-property relationships including the mechanism of reinforcement.\textsuperscript{15-21} To achieve a customizable material a complete understanding of the system must be achieved, including component properties, composition, structure and interfacial interactions.\textsuperscript{22} These characteristics determine the mechanical strength and other properties of the material. Therefore to understand polymer-based composite systems, and make predictive assumptions about the properties of such materials, each of the four characteristics should be fully understood.

Overall polymer composite properties are determined by the properties of the polymer, including structure, molecular weight and chemistry, the surface properties of the filler, including chemistry and morphology, and their ability to interact. Interfacial interaction between the two components provides effective stress transfer from the
continuous polymer matrix to the dispersed fillers. Polymer composite properties are also dominated by the ratio of the polymer to the filler particle. The overall structures of the particles within the polymer matrix, including inter-particle interactions such as aggregation and agglomeration, as well as dispersion of the particles also strongly influence the overall composite characteristics.\textsuperscript{23-26}

Polymer composite theories presume that the modulus of a composite is a function of properties of constituents, volume fraction, shape and interaction of particles, and the matrix-particle interface but independent of particle size.\textsuperscript{27} Theories in composite reinforcement predict that improved bonding between polymer and matrix typically lead to improved mechanical properties.\textsuperscript{28} The properties of the interphase, defined as the region directly near the interface of the filler and the polymer matrix, can differ dramatically from the bulk and influence the mechanical properties of the composite.\textsuperscript{29} Characteristics that the interphase can influence include the degree of filler particle aggregation\textsuperscript{30,31} and the efficiency of load and stress transfer between matrix and filler.

It is hypothesized that the main reason for improved properties in PNCs is the strong interfacial interactions between the nanoparticle and the polymer matrix.\textsuperscript{32} The high number of nanoparticle-polymer interfaces enables the majority of polymer chains to be located near a particle surface. In PNCs the entire polymer matrix may be considered to be a confined polymer due to only a few volume percent of dispersed nanoparticles.\textsuperscript{4} Dispersion of inorganic nanoparticle filler in a polymer is not easily achieved because nanoparticles have a strong tendency to agglomerate to reduce their surface energy, eliminating any improvements in any benefits due to the nanoscale filler. Due to the comparable dimension of the polymer radius of gyration and the nanoparticle,
Balazs et al. theorize that nanoparticles are repelled by polymer chains due to conformational entropy resulting in a low density region around the particle. A modified Flory-Huggins theoretical model was developed to describe the impact on mechanical properties. Dispersion is also impacted by interfacial chemistry, matrix interactions and processing such that nanoparticles with poor interfacial interaction with the polymer matrix tend to aggregate. The enthalpic interaction between the nanoparticle and polymer chains, due to van der Waals forces or covalent bonding, influences the stress transfer across the interface.

Aggregation depends on the relative magnitude of adhesion and shear forces which depend on the size of the particles. Aggregation tendency of fillers increases strongly with decreasing particle size. The quality of the interphase and the formed structure from aggregation control the properties of the composite. The size and volume of the particles factor into the strength of the aggregates. Aggregation leads to increased permeability, reduced interphase, decreased stiffening, and changes in the mechanical properties. The primary means to control aggregation is surface modification of the filler particle.

2.1.3 Synthesis of polymer composites

Processing conditions also influence interfacial interactions and aggregation within polymer composites. Polymer composites can be generated by physical mixtures of the particles in the polymer matrix, development of interpenetrating networks or by modification of particle surface to graft polymers to or from the particle. Direct blending of the filler particles into the polymer matrix is, however, the simplest method of incorporating the inorganic component into the organic component. One of the
simplest and commercially reproducible methods for PNC fabrication is polymer melt intercalation. It is a conventional polymer processing technique that has been used to produce PNCs since approximately 1993.\textsuperscript{38} Composites are formed by heating the mixture of polymer and nanocomposite filler above the melt point of the polymer. Blending of the organic and inorganic components is typically done with shear generated by a mixing mechanism such as a twin screw extruder.

![Twin screw extruder](image)

**Figure 2-1. 15 ml twin screw extruder for batch operations.**

2.1.4 Atom transfer radical polymerization

Polymerization from the particle surface involves preparation of the surface as an initiator. The grafting step can then be conducted on the functionalized particle.

Initiating groups anchored to the inorganic particle permit grafting of polymers from the surface of the inorganic component. CRP is a desirable polymerization method as it proceeds in a controlled manner until all of the monomer present in the system is consumed. \textsuperscript{39-41} Of the three major CRP processes Atom Transfer Radical Polymerization (ATRP), Stable Free Radical Polymerization (SFRP), and Degenerative Transfer (DT),
ATRP has been most widely used to polymerize from the surface of silica nanoparticles since its development in 1995 by Matyjaszewski and Wang and Sawamoto. ATRP systems are comprised of monomer, initiator and catalyst (which consist of a transition metal and ligand). The polymerization takes place in two steps: initiation and propagation. The overall reaction proceeds at a rate of $K_{eq}$, with a propagation rate constant, $k_p$. The reaction involves an initiator consisting of one transferable atom or group, generally a halogen atom, such as Cl or Br, a transition metal, a ligand that forms a complex with the transition metal and a radically polymerizable monomer.

Initiation

$$R - X + Cu(I)X / ligand \xrightleftharpoons[K_{eq}]{k_p} R^* + X - Cu(II)X / ligand \quad (X=Cl, Br)$$

$$R^* + \text{monomer} \xrightarrow{k_p} P_1^* \quad (P=\text{Polymer chain})$$

Propagation

$$P^* - X + Cu(I)X / ligand \xrightleftharpoons[K_{eq}]{k_p} P_n^* + X - Cu(II)X / ligand$$

$$P_n^* + \text{monomer} \xrightarrow{k_p} P_{n+1}^*$$

Termination

$$P_n^* + P_m^* \xrightarrow{k_p} P_{n+m}^*$$

ATRP kinetics are described by the following equations:

$$K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{[P^*Cu(II)X_2]}{[Cu(I)X][PX]}$$

($k_{act} = \text{rate of activation, } k_{deact} = \text{rate of deactivation}$)
To graft polymers from the surface of silica particles, the surface of the silica must be prepared and developed as the initiator. The first step involves reacting the silanol groups on the surface of the silica particle, creating a reactive functional surface. The amine groups are then converted to initiators for ATRP. The polymerization step can then be conducted on the functionalized particles.

\[
R_p = k_p [P^*]_{monomer} = k_p K_{eq} [RX] \frac{[Cu(I)X]}{[Cu(II)X_2]} [monomer]
\]

\(R_p = \text{rate of polymerization}\)

To the author’s knowledge, there have not been studies conducted that directly compare polymer composites generated by melt processing techniques with those prepared by grafting from the surface of the particle. The polystyrene-silica system was chosen as the model composite for this study, due to its relative ease of melt blending and
the availability of established procedures for grafting polystyrene from the surface of colloidal silica. 42-44, 49, 50

2.1.2 Silica fillers

Spherical particles simplify polymer composite models and the interaction between the polymer matrix and the particle interface. Silica spherical particles are a suitable template in which to study the impact of spherical inorganic particles in a polymer matrix with varying surface chemistries. Using the Stöber synthesis (reactions 1 and 2), an ammonia-catalyzed reaction of tetraethyl orthosilicate (TEOS) with water in simple alcohols, monodisperse, spherical silica particles can be synthesized, ranging in diameter from 40 nm to a few micrometers.

Hydrolysis reaction

\[ Si(OR)_4 + H_2O \rightarrow (OR)_3Si(OH) + ROH \] (1)

Condensation to form silica

\[ (OR)_3Si(OH) + H_2O \rightarrow SiO_2 \downarrow +3ROH \] (2)

Recently, the introduction of mesoporous silica as reinforcement for polymer composites has generated great interest due to its unique properties, such as high surface area, large pore volume, uniform pore size, and good chemical and thermal stability. 54-60 The M41S family of mesoporous silicas, including MCM-41 (hexagonal), MCM-50 (lamellar) and MCM-48 (cubic) was first reported by the Mobil Research group in 1992. 61,62 These materials are synthesized under basic conditions using a micelle
template, such as cetyltrimethylammonium bromide (CTAB), around which tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) can self-assemble as it undergoes hydrolysis and condensation into a silicate structure. As shown in Figure 2-3, the resulting structure is a highly ordered hexagonal arrangement of unidirectional pores. High temperature calcination or solvent extraction is necessary to remove the surfactant template.

![Figure 2-3. Formation of MCM-41 particles: (a) surfactant micelle; (b) micellar rod; (c) hexagonal array; (d) silicate; (e) MCM-41.](image)

The surface of MCM-41 provides a unique interface, whereas it is not continuous but marked with mesopores and surface hydroxyl groups, known as silanols. The density of the surface silanols depends on the method of synthesis. The network of pores also creates an internal surface in addition to the external surface of the particle. The surface silanols can be reacted after removal of the surfactant template, allowing for grafting of an organic group to the silica surface.

Alternatively, co-condensation can be used to produce selected functionalized silica surfaces. Rather than grafting the organic species to the silica particle after surfactant removal, the silane, such as 3-aminopropyltrimethoxysilane (APTM), is added during the mesoporous silica synthesis. The functional group homogeneously coats the interior
surface of the pores due to the preference for the micelles. Grafting can be performed selectively on the internal and external surfaces, allowing for functionalization of each surface type within the same particle.

2.2 References

CHAPTER 3. MELT BLENDED POLYSTYRENE MICRO AND
NANOCOMPOSITES

A paper to be submitted

Melissa A. Ver Meer, Balaji Narasimhan, Brent H. Shanks and Surya K. Mallapragada

3.1 Abstract

PS-mesoporous silica composites were prepared through melt blending and compared with PS-layered silicate nanocomposites and PS-silica composites of similar surface area or geometry, respectively. For composites containing 5.0 wt % inorganic component, the mechanical properties of the MCM-41 mesoporous silica and nanoclay materials were similar under large deformations. However, modification of the MCM-41 particle surface with grafted polystyrene significantly altered the stress-strain curve and created a higher modulus composite material.

3.2 Introduction

Polymer composites consisting of a polymer matrix and micron-sized inorganic particles are common commercial composite materials.\(^1\) Particles are added to the matrix to improve mechanical properties such as elastic modulus and yield strength while maintaining the desirable processing properties of the polymer. Optimal mechanical properties are achieved when the interaction between the polymer matrix and filler particle is maximized. Increasingly, smaller particles, with one-dimension in the nanometer scale, are utilized to increase surface area similar to the micron-scale particles
but at lower total volume fractions, therefore maintaining more of the inherent polymer processing properties and appearance.²

Layered silicate polymer nanocomposites have been of particular interest in the recent past with literature emphasizing improvements in mechanical, thermal, permeation and flammability over the pure polymer matrix.³⁻⁵ Processing of the layered silicate materials is critical to the reinforcement contribution to the overall composite. The maximum specific surface area, approximately 750 m²/g, is achieved when the layers of the silicate are completely exfoliated and individual layers of the silicate interact with the polymer matrix.⁶ In a practical sense, this complete exfoliation is difficult to achieve on a commercial scale.

Comparatively, larger spherical particles with similar specific surface areas, over 1000 m²/g can be synthesized.⁷⁻⁸ Mesoporous metal oxides, in particular the MCM-41 mesoporous silica can be generated in comparison with layered silicate filled composite systems to decouple the shape factor from the surface area.

\[
\frac{3}{r} \quad \frac{2}{r} + \frac{2}{l} \quad \frac{2}{t} + \frac{4}{l}
\]

Figure 3-1. Surface area/volume ratios for various reinforcing filler geometries (particle, fiber, layered).
Polymer nanocomposites typically have mechanical properties that are below the expected values based on their individual components as calculated by theory, except at low volume fractions. The discrepancy between theory and full-scale experiments lies in the inability of most processes to develop composites with well dispersed inorganic fillers at large volume fractions. This lack of dispersion affects the ability of the filler to interact with the polymer matrix. The specific surface area and the interfacial region immediately surrounding the filler component are of importance in composites due to the influence of this stiff interphase on the overall composite properties. Properties measured at larger deformations, like tensile yield stress and tensile strength are more sensitive to structure and interaction between the polymer matrix and the filler component.

This study includes a comparison between a nanoclay, quaternary ammonium salt modified natural montmorillonite (Cloisite 10A®, Southern Clay Products, Gonzales, Texas, USA), and mesoporous silica of similar specific surface area. Determination of the influence of particle geometry and surface chemistry was conducted in comparison with the mesoporous silica as well as modification of the MCM-41 particle through grafting.

3.3 Experimental

3.3.1 Synthesis of mesoporous silica (MCM-41)

The filler particles used in this study consist of the commercially available layered silicate Cloisite 10A, mesoporous silica MCM-41. Mesoporous silica particles were prepared using a procedure developed by Deng et al to synthesize spherical MCM-41 particles with diameters of approximately 300 nm. 1.2 g of cetyltrimethylammonium
bromide (CTAB, Aldrich) was dissolved in 105 ml of deionized water and 45 ml of ethanol (99.5%, Sigma-Aldrich). While stirring the mixture vigorously at 500 rpm, 2 ml of ammonium hydroxide (28-30%, Sigma-Aldrich) were added and the solution was heated to 30°C. 5.5 ml of tetraethyl orthosilicate (TEOS) (98%, Sigma-Aldrich) was added and the mixture was stirred for 3 hours at 30°C. The resulting slurry was filtered with a 4-5.5 µm Büchner funnel with a fritted disc and washed with ethanol, allowed to dry overnight. The dried particulate cake that formed was ground with a mortar and pestle, sonicated for 30 minutes in approximately 200 ml ethanol, re-filtered and dried again.

3.3.2 Preparation of PS-grafted MCM-41

Polystyrene-grafted MCM-41 particles were prepared using a modified procedure from Nystrom et al. The procedure was manipulated to accommodate MCM-41 particles, rather than fumed silica particles with diameters on average of 7 nm. The grafting technique first involved preparation of the MCM-41 particle to accept the grafted PS chains prior to the polymerization.

3.3.3 Surface preparation and synthesis of 3-aminopropyltrimethoxy-functionalized MCM-41 particles

The MCM-41 particles were dried under vacuum at 60°C for 24 hours prior to use. The dried mesoporous silica particles (1.2 g) were added to a 250 ml round-bottomed flask containing a stir bar, anhydrous tetrahydrofuran (THF) (99.9%, Sigma-Aldrich) (125 ml), 3-Aminopropyltrimethoxysilane (APTMS) (97%, Aldrich) (0.9 ml) and a stir bar. The solution was refluxed for 48 hours at 65°C. The particles were then separated
from the reaction mixture via centrifugation, and then decanted. Fresh THF was added to
the particles. The procedure was repeated four times to remove excess APTMS. The
functionalized particles were dried under vacuum at 60°C for 24 hours and analyzed via
FT-IR.

3.3.4 Preparation of initiator and synthesis of 2-bromoisobutyrate-functionalized MCM-
41 particles

Add 3-Aminopropyltrimethoxy-functionalized mesoporous silica particles to a
round-bottomed flask containing dichloromethane (DCM) (99.8%, Sigma-Aldrich) (120
ml), triethylamine (99.5% Aldrich) (1.167 g), 2-bromoisobutyryl bromide (98%, Aldrich)
(2.232 g), and a catalytic amount of 4-(dimethlamino)pyridine (DMAP) (99%, Aldrich).
The reaction was quenched after 12 hours by addition of ethanol. The particles were
separated from the reaction mixture via centrifugation, decanted, and fresh DCM was
added. The decanting procedure was repeated four times. The 2-bromoisobutyrate
functionalized particles were dried under vacuum at 60°C for 24 hours.

Figure 3-2. Ligand for atom transfer radical polymerization, 2,2’-bipyridyl (Bipy)
3.3.5 Polymerization and grafting of styrene from 2-bromoisobutyrate-functionalized MCM-41 particles

The polymerization was conducted in a flask sealed with a rubber septum under argon atmosphere. The particles (754 mg) were added to a flask, then 2,2'-bipyridyl (Bipy) (99%+, Aldrich) (120 mg) and styrene (99%, Acros) (30 ml). A small amount of Copper(0) (99%+, Fisher) was added. The solution was allowed to dissolve and stirred. Argon was then added to the flask. Copper(I) bromide (Cu(I)Br) (98%, Aldrich) (102 mg) was added and immediately capped. The copper bromide was allowed to dissolve and then the flask was placed in liquid nitrogen, frozen completely, pumped (~2 minutes) and thawed. The freeze, pump, thaw procedure was repeated three times. The reaction
temperature was set to 110°C for 22 hours. The flask was allowed to cool. The grafted particles were diluted in chloroform and recovered by drop wise precipitation in methanol and subsequent filtration.

3.3.6 Synthesis of polymer nanocomposites

Two grades of commercial polystyrene (M_n 84,000, INEOS NOVA Crystal PS 1510 and M_n 119,000, INEOS NOVA Crystal PS 1220) were air dried in oven and stored in a desiccator over a desiccant prior to use. The nanocomposites were prepared via extrusion melt intercalation. The PS was premixed with the organoclay, mesoporous silica, or grafted mesoporous silica and blended/extruded using a DSM microcompounder at under two sets of test conditions, 200 rpm at 190 °C for 3 minutes mixing and 150 rpm at 190°C for 2 minutes, both under a steady stream of nitrogen. The melt stream immediately entered a heated cylinder and transferred to the injection molder, where tensile bars and elements for flex testing were molded. The melt stream was also extruded directly from the microcompounder.

3.3.7 Scanning electron microscopy

All scanning electron microscope (SEM) images were obtained using a JEOL JSA-840A SEM. Samples were prepared with carbon sticker mounting and a gold sputter coating of approximately 10 to 20 nm using a Denton Vacuum Desk II sputter coating system.
3.3.8 Transmission Electron Microscopy

All PS nanocomposites samples were sectioned (70nm) with a diamond knife on a Reichert Ultracut S ultramicrotome. Sections were collected onto copper grids and images obtained at 80 kV using a JEOL 1200 EXII scanning and transmission electron microscope (STEM) with a Megaview III digital camera and SIS Pro software.

3.3.9 Gel permeation chromatography

Conventional gel permeation chromatograph (GPC) data were collected on a system that consisted of a Waters 510 pump, Waters 717 autosampler, a Wyatt Optilab DSP refractometer and a Wyatt Dawn EOS light scattering detector. The mobile phase was THF at a flow rate of 1 ml/min. Samples and standards were dissolved in THF at 1 mg/ml.

3.3.10 Fourier transform infrared spectroscopy

Infrared spectra were obtained using a Mattson GL-3020 Fourier transform infrared (FT-IR) spectrometer equipped with a Thermo Electron Thunderdome single-reflection ATR using a germanium crystal. Data were analyzed using Thermo Nicolet Ominic software.

3.3.11 Measurement of thermal properties

Differential scanning calorimetry (DSC) data were collected using a TA Instruments Q1000. The materials were first annealed under nitrogen under with an initial ramp at 20 °C to 150 °C and held for 2 minutes at temperature. The samples were cooled at a rate of 20 °C/min to 40 °C and then tested from 40 °C to 150 °C at 10 °C/min.
Thermogravimetric analysis (TGA) was conducted with a TA Instruments Q5000 (New Castle, DE). The materials were tested under a nitrogen atmosphere from 40 °C to 600°C at 10°C/min.

3.3.12 Measurement of mechanical properties

Mechanical evaluation was conducted on an Instron 5500R instrument with a cross-head speed of 50 mm/min. Dumbbell specimens with waist dimensions of 12.7 x 3.2 mm² were used for tensile mechanical tests following ASTM D638 test method with Type I specimens as well as Type V specimens with waist dimensions of 3.2 x 1.6 mm². Stress-strain curves were recorded from which the modulus, stress and elongation at break were evaluated.

3.4 Results and discussion

The MCM-41 particles were first characterized to evaluate their properties prior to incorporation in further processes. The SEM image, Figure 3-4, show the MCM-41 particles formed and their relative size distribution. Each particle is approximately 300 nm in diameter.
Stöber colloidal silica particles generated using a two-step growth process\textsuperscript{14} were prepared to compare thermal stability versus MCM-41 particles of similar diameter. Thermogravimetric analysis (TGA) also revealed physisorbed and chemisorbed water on the surface of the Stöber and MCM-41 particles and within the pores of the MCM-41 particles. Noted in Figure 3-5 is the MCM-41 weight loss between 200 °C and 300 °C, indicating that the pore structure retains water but ultimately releases the water and an overall weight loss similar to Stöber silica is seen.
Melt blended polystyrene composites were generated with MCM-41 silica particles, including grafted MCM-41. As a comparison to published literature, nanoclay was also used for verification of the melt intercalation procedure. As can be noted in Figures 3-6 through 3-9, nanoclay does not disperse well in polystyrene and forms tactoids. This is a significant drawback in the nanoclay-based PNC and largely due to the lack of interaction between the sodium montmorillonite modified with an ammonium cation and the chemistry of the polystyrene. MCM-41, on the other hand, forms fairly well dispersed polymer composites with smaller aggregates. PS 1510, which is a higher
molecular weight polystyrene, was chosen for further investigation over PS 1220 due to its ability to more evenly disperse higher weight percentage fillers.

![Figure 3-6. Polystyrene PS 1220 1% MCM-41 silica above and 1% Cloisite 10A nanoclay. Scale bar is 5 µm.](image-url)
Figure 3-7. Polystyrene PS 1510 1% MCM-41 silica above and 1% Cloisite 10A nanoclay.

Scale bar is 5 μm.
Figure 3-8. Polystyrene PS 1220 5% MCM-41 silica above and 5% Cloisite 10A nanoclay.

Scale bar is 5 µm.
Figure 3-9. Polystyrene PS 1510 5% MCM-41 silica (above) and 5% Cloisite 10A nanoclay (below). Scale bar is 5 µm.
Figure 3-10. High magnification TEM image of PS 1510 1% MCM-41 (above) and PS1510 1% Cloisite 10A composite. Scale is 100 nm (above) and 500 nm (below).
Mechanical testing was also conducted on the samples generated by melt intercalation. It was observed that the ultimate tensile strain and tensile stress values did not agree well with the values provided by the supplier of the polystyrene. After comparison of the tensile properties of the PS nanocomposites versus the published data from the supplier it was suspected that the polystyrene was thermally degrading during mixing. It was also observed that the unfilled PS that had undergone the mixing process but lacked any fill material was noticeably discolored in comparison to the unprocessed, virgin material.

Table 3-1. Tensile property data of PS nanocomposites - ASTM D638 type V tensile samples, 190°C melt temp, 3 min mix, 200 rpm.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler</th>
<th>Filler wt %</th>
<th>Tensile strain (%)</th>
<th>Tensile stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1220</td>
<td>none</td>
<td>0</td>
<td>5.8 ± 0.4</td>
<td>58.9 ± 2.0</td>
</tr>
<tr>
<td>PS1220</td>
<td>Cloisite 10A</td>
<td>1</td>
<td>6.1 ± 0.4</td>
<td>57.2 ± 0.9</td>
</tr>
<tr>
<td>PS1220</td>
<td>Cloisite 10A</td>
<td>3</td>
<td>5.2 ± 0.5</td>
<td>57.2 ± 2.6</td>
</tr>
<tr>
<td>PS1220</td>
<td>Cloisite 10A</td>
<td>5</td>
<td>4.5 ± 0.4</td>
<td>56.7 ± 2.5</td>
</tr>
<tr>
<td>PS1220</td>
<td>MCM-41</td>
<td>1</td>
<td>5.4 ± 0.3</td>
<td>60.5 ± 1.9</td>
</tr>
<tr>
<td>PS1220</td>
<td>MCM-41</td>
<td>3</td>
<td>4.8 ± 1.1</td>
<td>57.5 ± 6.8</td>
</tr>
<tr>
<td>PS1220</td>
<td>MCM-41</td>
<td>5</td>
<td>4.0 ± 0.6</td>
<td>51.2 ± 1.6</td>
</tr>
<tr>
<td>PS1510</td>
<td>none</td>
<td>0</td>
<td>4.5 ± 0.4</td>
<td>55.8 ± 2.7</td>
</tr>
<tr>
<td>PS1510</td>
<td>Cloisite 10A</td>
<td>1</td>
<td>5.7 ± 0.4</td>
<td>54.5 ± 2.6</td>
</tr>
<tr>
<td>PS1510</td>
<td>Cloisite 10A</td>
<td>3</td>
<td>5.6 ± 1.0</td>
<td>53.9 ± 1.6</td>
</tr>
<tr>
<td>PS1510</td>
<td>Cloisite 10A</td>
<td>5</td>
<td>4.8 ± 0.7</td>
<td>52.1 ± 1.5</td>
</tr>
<tr>
<td>PS1510</td>
<td>MCM-41</td>
<td>1</td>
<td>5.3 ± 0.8</td>
<td>56.4 ± 1.6</td>
</tr>
<tr>
<td>PS1510</td>
<td>MCM-41</td>
<td>3</td>
<td>4.9 ± 0.3</td>
<td>54.9 ± 1.9</td>
</tr>
<tr>
<td>PS1510</td>
<td>MCM-41</td>
<td>5</td>
<td>3.6 ± 0.9</td>
<td>50.1 ± 1.4</td>
</tr>
</tbody>
</table>

Gel Permeation Chromatography (GPC) analysis of the PS samples showed changes in the average molecular weight, $M_n$, before and after processing. Upon investigation, this phenomenon was found in literature. The recommended remedy to
decrease the thermal degradation was to run the melt intercalation process under a nitrogen atmosphere with minimal shear and mix times.

Table 3-2. GPC data for as received and melt blended PS and unfilled, processed PS.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melt Blended?</th>
<th>$M_n$</th>
<th>$M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1510</td>
<td>no</td>
<td>84,000</td>
<td>264,000</td>
</tr>
<tr>
<td>PS1510</td>
<td>yes</td>
<td>63,000</td>
<td>163,000</td>
</tr>
<tr>
<td>PS1220</td>
<td>no</td>
<td>119,000</td>
<td>320,000</td>
</tr>
<tr>
<td>PS1220</td>
<td>yes</td>
<td>70,000</td>
<td>183,000</td>
</tr>
</tbody>
</table>

Figure 3-11. FTIR spectra of grafting process of MCM-41 particles as measured by ATR: (a) MCM-41; (b) APTMS-functionalized MCM-41; (c) 2-bromoisobutyryl-functionalized MCM-41; (d) polystyrene-grafted MCM-41; (e) polystyrene-grafted MCM-41.

Samples were re-run at a slow mix rate, 150 rpm versus 200 rpm, as well as for a shorter duration, 2 minutes versus 3 minutes. The melt temperature was held constant. One additional change was the size of the tensile samples, which changed from ASTM
D638 type V to type I. The set of samples under these conditions also included a set of samples generated with polystyrene-grafted MCM-41 particles, blended with PS 1510 polystyrene matrix. The overall weight percent of MCM-41 was 2 wt %, based on the availability of material and the batch sizes required for the twin screw extruder.

![Figure 3-12. TEM image of PS 1510 blended with polystyrene-grafted MCM-41 (2 wt% MCM-41 overall). The scale bar is 5 µm. White area in the middle is contamination.](image)

### Table 3-3. Tensile property data of PS nanocomposites - ASTM D638 type I tensile samples, 190°C melt temp, 2 min mix, 150 rpm.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler</th>
<th>Filler wt %</th>
<th>Tensile strain (%)</th>
<th>Tensile stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1510</td>
<td>none</td>
<td>0</td>
<td>8.1 ± 0.2</td>
<td>47.7 ± 0.9</td>
</tr>
<tr>
<td>PS1510</td>
<td>Cloisite 10A</td>
<td>1</td>
<td>6.3 ± 0.5</td>
<td>47.1 ± 1.1</td>
</tr>
<tr>
<td>PS1510</td>
<td>Cloisite 10A</td>
<td>3</td>
<td>5.0 ± 0.2</td>
<td>43.7 ± 0.2</td>
</tr>
<tr>
<td>PS1510</td>
<td>Cloisite 10A</td>
<td>5</td>
<td>4.4 ± 0.0</td>
<td>40.9 ± 1.9</td>
</tr>
<tr>
<td>PS1510</td>
<td>MCM-41</td>
<td>1</td>
<td>6.3 ± 0.5</td>
<td>49.4 ± 0.9</td>
</tr>
<tr>
<td>PS1510</td>
<td>MCM-41</td>
<td>3</td>
<td>4.1 ± 0.5</td>
<td>40.2 ± 4.0</td>
</tr>
<tr>
<td>PS1510</td>
<td>MCM-41</td>
<td>5</td>
<td>3.6 ± 0.3</td>
<td>36.8 ± 1.3</td>
</tr>
<tr>
<td>PS1510</td>
<td>MCM-41-g-PS</td>
<td>2</td>
<td>2.5 ± 0.3</td>
<td>42.3 ± 2.1</td>
</tr>
</tbody>
</table>
The relative tensile results were similar to the previous study as shown in Table 3-3; however, the tensile strain was higher, likely due to the larger geometry of the tensile bar and the induced stress in the polymer chains due to injection molding. Tensile testing comparison shows that there is a significant impact on the overall tensile properties imparted by the grafted particles in the PS 1510 matrix. The samples were stiffer, with a higher Young’s modulus and more brittle, as can be seen in Figure 3-13.

![Figure 3-13. Average tensile curves for PS 1510-based PNCs, including Cloisite 10A, MCM-41 and grafted MCM-41 particles.](image)

The influence of particle geometry on thermal properties was measured via differential scanning calorimetry. The glass transition temperature was measured for the PS1510 polystyrene-based composite samples filled with MCM-41 or Cloisite 10A. Results are shown in Figure 3-14 and indicate that MCM-41 decreases the glass transition
temperature at a slower rate than the layered silicate. The behavior is similar to results for 14 nm diameter colloidal silica with similar loadings and polystyrene with an average molecular weight of 282,000 g/mol.\textsuperscript{17}

![Graph showing glass transition temperature (C) vs. Filler wt % for Cloisite 10A and MCM-41](image)

**Figure 3-14.** A comparison between glass transition responses for composites filled with layered silicate (Cloisite 10A) and mesoporous silica (MCM-41).

### 3.5 Conclusions

There is significant damage imparted on the polystyrene samples due to the melt blending process as well as stress induced by the injection molding process. The heat history of polystyrene is critical in obtaining repeatable results. While comparative
analysis can be conducted on samples with similar heat history and blending regimes, analysis versus other published literature is difficult without full knowledge of processing conditions.

Overall the MCM-41 particles, due to their large diameter, dispersed well within the polystyrene matrix in comparison to Cloisite 10A layered silicate tactoids. However, no significant improvements were noted in the blended MCM-41 particles versus Cloisite 10A layered silicate with the tested blending cycles. Alternatively, grafted polystyrene on the surface of MCM-41 particles showed a significant modification in overall mechanical properties, including increased modulus.

3.6 References

4 Szazdi, L.; Pukanszky, B.; Vancso, G. J.; Pukanszky, B. Polymer 2006, 47, 4638-4648


4.1 Abstract

In this study, mesoporous or colloidal silica particles were incorporated into polystyrene matrices via melt blending or by styrene polymerization initiated from the particle surface. The relationships between the surface morphology of filler particles in polymer composites and their thermomechanical properties were investigated. High molecular weight polystyrene-silica hybrids were generated by modifying the surfaces of monodisperse colloidal silica and templated mesoporous silica nanoparticles. The functionalized silica surfaces were grafted with alkyl halide initiators for atom transfer radical polymerization. Polymerization was conducted without free initiator present. The physical properties of these composites were studied by dynamic mechanical analysis, thermogravimetric analysis, transmission electron microscopy, and scanning electron microscopy. Results indicate that colloidal and mesoporous silica polymer composites generated by atom transfer radical polymerization have similar grafted polymer characteristics, indicating that polymer growth from the surface of the particle does not allow for significant polymer chain growth in the interior of the mesoporous silica particles.
4.2 Introduction

In polymer composite systems, the interfacial interactions between the polymer and the particles dictate the overall properties. Despite the wide array of inorganic particles available for composite preparation, two difficulties continually arise: 1) aggregation and 2) the lack of a strong interaction between the polymer matrix and filler. Dispersion of inorganic nanoparticles in a polymer is not easily achieved because nanoparticles have a strong tendency to agglomerate to reduce their surface energy, eliminating the potential benefit of the nanoscale filler. Recently, the introduction of mesoporous silica as reinforcement for polymer composites has generated great interest due to its potential to address the difficulties of both aggregation and interfacial interaction.\textsuperscript{1-7} Mesoporous silica has high specific surface area, uniform nano-scale pore sizes and a high concentration of surface hydroxyl groups. Additionally, the interfacial interactions between the mesoporous silica and the polymer matrix can be improved through functionalization and grafting from the surface hydroxyl groups.

Processing conditions also influence interfacial interactions and aggregation within polymer composites. Polymer composites can be generated by melt blending of the particles in the polymer matrix, in situ sol-gel methods\textsuperscript{8} or by polymerization from particle surfaces. Melt blending of the filler particles into the polymer matrix is the simplest method of incorporating the inorganic component into the organic component, usually by polymer melt processing. Polymerization from the particle surface involves...
preparation of the surface as an initiator. The grafting step can then be conducted on the functionalized particle. There is a lack of direct comparisons between the properties of polymer composites generated by melt processing techniques and those prepared by grafting from the surface of the particle. The polystyrene-silica system was chosen as the model composite for this study, due to its relative ease of melt blending and the availability of established procedures for grafting polystyrene from the surface of colloidal silica.\textsuperscript{9–13}

In this work, we synthesized polymer composites with the inorganic phase based on mesoporous silica, as well as Stöber silica, by atom transfer radical polymerization (ATRP), allowing for a unique polymer-particle interface. High polymer brush density was required on the surface of the polystyrene-grafted-silica particles to compare similar filler content between melt blended and grafted polymer composites. The mesoporous silica-based polymer composite could potentially clarify underlying relationships revolving around interfacial interactions of the polymer matrix and filler particles, as well as the structure and dependence of dispersion on the bulk properties including mechanical properties and thermal stability. Using this model system, these unique silica-based filler particles were investigated.

**4.3 Experimental**

**4.3.1 Materials**

The filler particles used in this study consist both of the mesoporous silica, MCM-41, as well as its non-porous equivalent; spherical monodisperse colloidal silica generated using the Stöber method.\textsuperscript{14} The colloidal silica measured 470 nm in diameter.
Mesoporous silica particles were prepared using a procedure developed by Deng et al\textsuperscript{15} to synthesize spherical MCM-41 particles with 360-nm diameters. They were characterized using scanning electron microscopy (SEM) (for surface morphology) and sorption experiments (for pore size characterization).

4.3.2 ATRP of styrene from SiO\textsubscript{2} colloidal and mesoporous initiators

In addition to the interface derived from the chemical interaction of the bulk polymer and the surface of the silica particles, it was desired to covalently bond the silica particles to the bulk polymer. This was achieved by preparing the surface of the silica particles to behave as initiators for ATRP synthesis of polystyrene. Using a relatively pH insensitive ligand\textsuperscript{16}, high molecular weight polystyrene polymer chains were grafted to the surface of both the colloidal and mesoporous silica. The grafting technique was a step-by-step process, allowing for the formation of the initiator on the surface of the particle.

4.3.3 Preparation of polystyrene-grafted-silica

Polystyrene-grafted Stöber and MCM-41 particles were prepared using a modified procedure from Nystrom et al.\textsuperscript{17} The grafting technique first involved preparation of the Stöber and MCM-41 particles to accept the grafted PS chains prior to the polymerization.

The silica particles were dried under vacuum at 60°C for 24 h prior to use. The dried mesoporous silica particles (1.2 g) were added to a 250 mL round-bottomed flask containing 125 mL of anhydrous tetrahydrofuran (THF) (99.9%, Sigma-Aldrich) and 0.9 mL of 3-aminopropyltrimethoxysilane (APTMS) (97%, Aldrich) (0.9 mL). The solution
was refluxed for 48 h at 65°C. The particles were then separated from the reaction mixture via centrifugation and decanted. Fresh THF was added to the particles. The procedure was repeated four times to remove excess APTMS. The functionalized particles were dried under vacuum at 60°C for 24 h.

The 3-aminopropyltrimethoxy-functionalized silica particles were added to a round-bottomed flask containing 120 mL of dichloromethane (DCM) (99.8%, Sigma-Aldrich), 1.167 g of triethylamine (99.5% Aldrich), 2.232 g of 2-bromoisobutyryl bromide (98%, Aldrich), and a catalytic amount of 4-(dimethylamino)pyridine (DMAP) (99%, Aldrich). The reaction was quenched after 12 h by adding ethanol. The particles were separated from the reaction mixture via centrifugation, decanted, and fresh DCM was added. The decanting procedure was repeated four times. The 2-bromoisobutyrate functionalized particles were dried under vacuum at 60°C for 24 h.

![Tri-functional ligand, tris[(2-pyridyl)methyl]amine (TPMA).](image)

Tris[(2-pyridyl)methyl]amine (TPMA) (Figure 4-1) was synthesized as described previously. The functionalized particles (313 mg) were added to 120 mg of TPMA, 30 mL of styrene (99%, Acros), 129 mg of elemental copper(0) (99%+, Fisher) and 13.6 mg of copper(II) bromide (Cu(II)Br) (98%, Aldrich) and immediately capped. The reaction
temperature was carried out at 110°C for 18.5 h. The grafted particles were diluted in chloroform and recovered by drop wise precipitation in methanol and subsequent filtration.

4.3.4 Preparation of polystyrene-silica composites

The composites were prepared via extrusion melt intercalation. For comparison, commercial polystyrene (Mn = 84,000, M_w/M_n = 3.1, NOVA Chemicals Crystal PS 1510) was dried in vacuum oven and stored in a desiccator prior to use. The PS 1510 was premixed with the Stöber or MCM-41 mesoporous silica particles (between 0.9 and 2.6% by wt.) and blended/extruded using a DSM Xplore 15 ml Microcompounder (Geleen, Netherlands) at 150 rpm at 190°C for 2 min. The polystyrene-grafted particles were processed using the microcompounder under the same conditions without any additional polystyrene. The melt stream immediately entered a heated cylinder and transferred to the injection molder and molded into rectangular bars. Due to the residual stress present in the molded components, the rectangular bars were annealed under vacuum above the glass transition temperature at 177°C. Samples were compressed into plaques at 177°C.
4.3.5 Particle characterization

Scanning electron microscopy (SEM) images were obtained using a JEOL JSA-840A SEM. The samples were prepared with carbon sticker mounting and a gold sputter coating of approximately 10 to 20 nm using a Denton Vacuum Desk II (Mooresetown, NJ) sputter coating system.

The PS composite samples were sectioned (70 nm) with a diamond knife on a Reichert Ultracut S ultramicrotome. Sections were collected onto copper grids and images obtained at 80 kV using a JEOL 1200 EXII scanning and transmission electron microscope (STEM) with a Megaview III digital camera and SIS Pro software.
Silica particle size was determined by using a Malvern Zetasizer ZS90 at 25°C in methanol. The size data from dynamic light scattering (DLS) was the z-average size.

4.3.6 Polystyrene characterization

Gel permeation chromatography (GPC) data was carried out using a Waters 510 pump, Waters 717 autosampler, a Wyatt Optilab DSP refractometer and a Wyatt Dawn EOS light scattering detector. The mobile phase was THF at a flow rate of 1 mL/min. PS samples and standards were dissolved in THF at 1 mg/mL.

4.3.7 Thermal properties

Thermogravimetric analysis (TGA) was conducted with a TA Instruments Q5000 (New Castle, DE). The materials were tested under a nitrogen atmosphere from 40°C to 600°C at 10°C/min.

4.3.8 Mechanical properties

Dynamic mechanical properties of the composites were measured using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA). Rectangular samples with dimensions of 2 x 7 x 18 mm³ were used in a single cantilever bending mode. The experiments were carried out by varying the temperature from 30°C to 150°C at a heating rate of 1°C/min, strain of 0.05% and frequency of 1 Hz.
4.4 Results and discussion

4.4.1 Silica characterization

The morphologies of the colloidal and mesoporous silica were observed using SEM (Figure 4-2). While the relative diameters of the two forms of silica particles are similar (380 nm diameter for Stöber particles and 460 nm for MCM-41 particles, as measured by dynamic light scattering), the specific surface area for the mesoporous silica was 1031.9 m²/g, as shown in Figure 4-3. In contrast, the surface area for Stöber silica was 8.2 m²/g with no measured porosity. The mesoporous silica surface morphology allows for greater interaction with the polymer matrix based on the increased surface area. The surface interactions are also impacted by aggregation, which can control the mechanical properties of the final composite. Previous studies have indicated that silica particles should not be dried prior to polymerization to eliminate aggregation.19 However, due to the porous nature of mesoporous silica, it was determined that the silica particles would be dried to remove excess chemical species and solvents. The silica particles were dried but not calcined to minimize rigid aggregate formation.
Figure 4-2. SEM images of Stöber (above) and mesoporous silica (MCM-41). Scale bars are 0.5 µm
Figure 4-3. (Top) Adsorption-desorption isotherm of nitrogen at 77K for MCM-41. (■ Adsorption, ● Desorption). (Bottom) BJH pore-size distribution plot from adsorption branch for MCM-41.
Figure 4-4. Polystyrene with MCM-41 incorporated, after melt compounding. Single particles present in polymer matrix with larger aggregates still present. Scale bars are 5 \( \mu \text{m} \) (left) and 0.5 \( \mu \text{m} \) (right), respectively.
4.4.2 Melt blending

Colloidal and mesoporous silica particles were melt blended in polystyrene, creating polymer composites with spherical inorganic components of variable surface area. Melt processing via a twin screw extruder has been used to form polymer nanocomposites where layered silicates are dispersed in molten polymer. This technique eliminates the need for solvent and allows the polymer to diffuse from the bulk onto or into the surface of spherical silica particles. The TEM images in Figure 4-4 show individual mesoporous silica particle dispersion within the polystyrene matrix with the presence of large aggregates.

4.4.3 Initiator grafting density

Thermogravimetric analysis (TGA) was used to calculate the grafting density of the initiators, as shown in Figure 4-5, based on the method described by Save et. al. The weight loss between 30°C and 200°C was excluded, as it is due to physisorbed water on the silica surface. For the colloidal silica this constituted 1.97% and for the mesoporous silica this was 1.78% by weight. The weight loss between 30°C and 600°C was determined and the physisorbed water was subtracted from the total weight loss. The weight of initiator was 7.43% on the colloidal silica and 26.46% on the mesoporous silica, which amounts to 0.35 mmol of initiator grafted onto the colloidal silica and 1.28 mmol grafted onto the mesoporous silica per gram of sample.
The initiator grafting per gram of silica is nearly four-fold for mesoporous silica versus colloidal silica, indicating that the interior pore space was indeed grafted with the ATRP initiator based on the weight loss indicated during the TGA tests. While the number of potential initiator sites is significantly higher on the MCM-41 particles, the actual polymerization is remarkably similar to the monodisperse spherical silica of similar overall diameter as listed in Table 4-1. It appears that the growth of the polymer from the surface on the mesoporous silica prevents the interior pores from participating in the grafting process and the system behaves like spherical particles.
### Table 4-1. Results for the ATRP synthesis of polystyrene-silica

<table>
<thead>
<tr>
<th>Sample</th>
<th>Styrene</th>
<th>Silica</th>
<th>CuBr$_2$</th>
<th>TPMA</th>
<th>Cu(0)</th>
<th>T(°C)</th>
<th>t (h)</th>
<th>$M_n$,$\text{GPC}$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$-g-PS</td>
<td>200</td>
<td>Stöber</td>
<td>0.030</td>
<td>0.1</td>
<td>1</td>
<td>110</td>
<td>18.5</td>
<td>156868</td>
<td>1.29</td>
</tr>
<tr>
<td>M41-g-PS</td>
<td>200</td>
<td>MCM-41</td>
<td>0.030</td>
<td>0.1</td>
<td>1</td>
<td>110</td>
<td>18.5</td>
<td>240805</td>
<td>1.30</td>
</tr>
</tbody>
</table>

$^a$ All polymerizations were performed in 50% (v/v) toluene.

$^b$ CuBr$_2$ = copper (II) bromide; Cu(0) = elemental copper; T(°C) = reaction temperature; t(h) = reaction time; $M_n$,$\text{GPC}$ = average molar mass of grafted chains; $M_w/M_n$ = polydispersity index

### Table 4-2. Sample identification, composite preparation and relative silica loading levels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silica</th>
<th>Preparation</th>
<th>wt.% Silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$-g-PS</td>
<td>Stöber</td>
<td>Graft</td>
<td>1.1</td>
</tr>
<tr>
<td>M41-g-PS</td>
<td>MCM-41</td>
<td>Graft</td>
<td>1.3</td>
</tr>
<tr>
<td>0.9 SiO$_2$-PS</td>
<td>Stöber</td>
<td>Blend</td>
<td>0.9</td>
</tr>
<tr>
<td>2.6 SiO$_2$-PS</td>
<td>Stöber</td>
<td>Blend</td>
<td>2.6</td>
</tr>
<tr>
<td>2.0 M41-PS</td>
<td>MCM-41</td>
<td>Blend</td>
<td>2.0</td>
</tr>
</tbody>
</table>

#### 4.4.4 Silica dispersion and morphology

The ATRP results for the colloidal and mesoporous silica are shown in Table 4-1. TPMA was selected as a ligand based on temperature and pH stability for ATRP in the presence of limited amount of air. The use of TPMA resulted in fast polymerizations that initially gelled. Toluene was introduced to dilute the styrene and allow for high molecular weight (> $M_n = 150,000$, $M_w/M_n < 1.3$) composites, which could then be compared to commercial polystyrene. As shown in Figure 4-6 and Figure 4-7, aggregation was minimized and single particle dispersion was prevalent. There was only slight improvement in the dispersion and aggregation between the polymer composites generated purely by blending versus the polymer composites generated by surface-initiated polymerization. The structure of the silica, relative to the amount of aggregation, was primarily determined prior to blending or polymerization processes.
Figure 4-6. Polystyrene-graft-Stöber silica, after melt compounding. Single particles present in polymer matrix with smaller aggregates still present. Scale bars are 1 µm (left) and 0.5 µm (right), respectively.
Figure 4-7. Polystyrene-graft-MCM-41 after melt compounding. Single particles present in polymer matrix with smaller aggregates still present. Scale bars are 1 µm (left) and 0.5 µm (right), respectively.
4.4.5 Mechanical behavior and thermal stability

DMA was used to measure the temperature dependence of the storage modulus (E’), loss modulus (E’’), and loss factor (tan δ, E’’/E’), varying both the surface morphology of the silica particles as well as the chemical interaction between the particle and the polymer matrix. Figure 4-8 shows the storage moduli of the colloidal and mesoporous silica-grafted as well as the blended samples. The grafted mesoporous silica composites (open squares) show improved thermo-mechanical stability over the blended silica-polystyrene composites at high temperatures with the same inorganic content. This is consistent with the electron micrographs in Figure 7, which show single particle dispersion and low aggregation. Interestingly, the SiO$_2$-g-PS composite shows two
transitions, one with an onset at ~63°C and the second at ~102°C, which is the glass transition temperature. The M41-g-PS has only a slight discernible shift in storage modulus (E’) at ~65°C and the glass transition onset is at ~102°C. The blended composites also showed small shifts at ~65°C. This shift at ~65°C is attributed to chain mobility, a behavior seen in other polymer-silica composite systems.¹,²,³

Figure 4-9. Loss modulus (E’’) as a function of temperature (■ SiO₂-g-PS, □ M41-g-PS, ◆ 0.9 SiO₂-PS, ● 2.6 SiO₂-PS, ○ 2.0 M41-PS)
Glass transition temperatures were 2-5°C higher for the grafted particles versus the blended components based on the peaks of the loss modulus (E'') values, as shown in Figure 4-9. However, as shown in Figure 4-10, the blended mesoporous sample showed a dramatic increase in loss tangent (tan δ) as a function of temperature in comparison with other samples. This large tan δ is indicative of a material that will dissipate energy when stress is applied. Blending mesoporous silica into the polystyrene matrix results in an increased tan δ while maintaining the stiffness. This result also suggests that the blended and annealed mesoporous materials have an interpenetrating organic-inorganic network.\textsuperscript{24} In contrast, the M41-g-PS samples merely have the polystyrene chains adhered to the outer surface of the composites, resulting in a material with low dissipative
energy. Interestingly, the potential penetration of the polystyrene into the pores of the melt blended and annealed polystyrene/mesoporous silica composite results in a material that has the potential to absorb more energy than comparable colloidal silica composites. Broadening the interfacial region appears to create a highly viscoelastic material.

Figure 4-11. TGA thermograms of weight loss as a function of temperature (■ SiO$_2$-g-PS, ◆ 0.9 SiO$_2$-PS, ● 2.6 SiO$_2$-PS)
TGA studies for the polymer composites show enhanced thermal stability of the grafted composites in comparison to the blended composites. For the Stöber silica-based composites, the grafted sample did not lose 5 wt.% until 387°C whereas the blended samples lost 5% of their weight between 363°C and 365°C, shown in Figure 4-11. As for the mesoporous silica-based composites, the grafted sample lost 5 wt-% at 383°C compared to 365°C for the blended sample, as shown in Figure 4-12. Despite the relatively low filler loading, the presence of grafted versus unbound polystyrene resulted in a nearly 20°C increase in degradation temperature. This is likely due to the fact that the polystyrene chain is bound on one surface and degradation occurs from the outer surface inward.


4.5 Conclusions

A customizable set of polymer composites was developed by employing either colloidal or mesoporous silica particles whose surfaces were modified and used as initiators for ATRP of styrene. The grafted polymer composites were compared with conventional melt blended composites to study the relationships between component properties, composition, structure, and interfacial interactions. While the initiator grafting density was considerably higher for mesoporous silica versus colloidal spherical silica, the polymerization was limited to the accessibility of the initiator sites on the surface of the silica particles. It was demonstrated that the higher surface area inorganic component in mesoporous silica, as well as the covalently bonded polymer matrix and silica particles, increased the storage modulus and enhanced the thermal stability of the composites. These studies provide a basis for rationally designing composite materials based on polystyrene with controlled properties for specific applications.

4.6 Acknowledgements

This project was financially supported by Schlumberger Lawrence Technology Center. The authors would like to thank Tracey E. Pepper (Iowa State University Bessey Microscopy Facility) and Warren Straszheim (Iowa State University Materials Analysis Research Laboratory) for their expert assistance with electron microscopy. Additionally, the authors would like to thank Jason Holzmueller and Dr. William Goertzen of Schlumberger for thoughtful discussions.
4.7. References


CHAPTER 5. SYNTHESIS OF AMINOPROPYL-MODIFIED MESOPOROUS SILICA COMPOSITES

A paper to be submitted

Melissa A. Ver Meer, Balaji Narasimhan, Brent H. Shanks and Surya K. Mallapragada

5.1 Abstract

Polystyrene-graft-mesoporous silica composites were generated by functionalization of the interior pore structure of mesoporous silica. The co-condensed monodisperse amino-propyl-functionalized mesoporous silica was further modified with alkyl halide initiators within the pores for atom transfer radical polymerization. High molecular weight polystyrene chains were formed without free initiator present. The physical properties of these composites were studied by dynamic mechanical analysis, thermogravimetric analysis, transmission electron microscopy and scanning electron microscopy. Results indicate improved thermal stability of the composites generated by atom transfer radical polymerization from the interior pore structure of the mesoporous silica, including lower weight loss at elevated temperature and an increase in glass transition temperature, over similar molecular weight polystyrene. A new, less mobile polymer phase was also observed based on the loss modulus data for the polystyrene-graft-mesoporous silica composite samples as well as the polystyrene samples after long annealing times.

Keywords: polymer composites, atom transfer radical polymerization, mesoporous silica, polystyrene, dual peak tan delta
5.2 Introduction

Polymer composites, particularly polymer nanocomposites, offer the potential for tailored materials with improved mechanical, electrical, optical and thermal properties through proper selection of the polymer matrix and filler components. Improvement of polymer thermomechanical properties by the addition of inorganic filler particles is a function of particle distribution, size, geometry and interaction of the particle and the polymer matrix. The compatibility between the surface of the particle, local polymer chains and the interfacial region that is formed can dictate overall bulk properties of the composite. The interfacial region, or interphase, and its influence on the bulk thermomechanical properties of polymer composites is still not fully understood. Recent literature has sought to better determine structure-property relationships in polymer composites by studying polymer chain entanglements and mobility, modeling the interphase and determination of the effects of particles on thermomechanical properties.

The behavior of the polymer chains in the interfacial region differs from the bulk polymer due to confinement effects and interaction with the particle surface. While there is limited experimental measurement of interphase, it has been shown to change bulk properties of the polymer composite, including the glass transition, $T_g$. Filler size, loading and distribution determine the amount of polymer affected in the interphase but the degree of interaction between the polymer matrix and the filler particles is determined by the surface properties of the particle including surface structure and chemistry. Weak interactions between the filler particles and the polymer matrix have
shown to decrease the $T_g$ \cite{17,18} whereas there is evidence that strong interactions, including polymer-grafted-particles can increase the $T_g$ \cite{19-22}. Manipulation of the $T_g$ of a polymer composite can provide insight into the influence of the interphase on the overall characteristics of the polymer composite.

Measurement of local polymer interfaces have largely been constructed from thin polymer film studies with the polymer either supported on one surface or sandwiched between two inorganic plates.\cite{4,7} These results have been compared with changes in $T_g$ for polymer nanocomposites with good correlation. Particles have also been grafted with polymer, where $T_g$ has been shown to be affected by the wetting behavior of the particles with the polymer matrix.\cite{8,23} In the Bansal et. al. study it was shown that higher molecular weights had a negative influence on the bulk polymer composite $T_g$ due to dewetting of the grafted polymer particle from the matrix polymer chains.

In a previous study\cite{24} it was demonstrated that grafted silica particles with high molecular weight polystyrene were more thermally stable than melt blended composites of the same composition. Additionally, mesoporous silica exhibited superior thermal stability over similar sized colloidal silica particles. However, polymerization was limited to the external surface of the mesoporous silica and full advantage of the initiator sites within the pore structure was not possible.

In this work, we explore the glass transition temperatures of polymer grafted high surface area particles to examine the interphase of high molecular weight brushes without the influence of a free polymer matrix. High surface area mesoporous silica particles, functionalized on the interior of the pores, were utilized to alleviate inaccessibility to the initiator sites for polymerization in the pore opening. Polystyrene was grafted from the
interior of the particle, creating a completely synthesized polymer composite. Thermomechanical testing was conducted and compared to polystyrene of similar molecular weight.

5.3 Experimental

5.3.1 Materials

The filler particles used in this study were aminopropyl-functionalized monodisperse mesoporous silica spheres (APMMSS) prepared using a procedure developed by Suzuki et al.\textsuperscript{25} The cocondensation method produced mesoporous silica spheres containing 3-aminopropyltrimethoxysilane (APTMS) functionalized surfaces on the walls of the radially-aligned pores. The particles were 330 nm in diameter as measured from SEM images. They were characterized using scanning electron microscopy (SEM) (for surface morphology) and sorption experiments (for pore size characterization).

5.3.2 ATRP of styrene from APMMSS

In addition to the interface derived from the chemical interaction of the bulk polymer and the surface of the silica particles, it was desired to covalently bond the silica particles to the bulk polymer. This was achieved by preparing the interior pores of the mesoporous particles to behave as initiators for ATRP synthesis of polystyrene. Using a relatively pH insensitive ligand\textsuperscript{26}, high molecular weight polystyrene polymer chains were grafted to the functionalized interior pores of the mesoporous silica. The grafting technique was a step-by-step process, allowing for the formation of the initiator on the interior of the particle.
5.3.3 Preparation of polystyrene-grafted-silica

Polystyrene-grafted-APMMSS particles were prepared using the same procedure described in earlier work, without the step to add APTMS first. Error! Bookmark not defined. The grafting technique involved preparation of the APMMSS particles to accept the grafted PS chains prior to the polymerization.

After polymerization the polystyrene-grafted-APMMSS particles were annealed in a vacuum oven at 200°C for close to 100 hours to remove all residual solvent from the silica pore interiors. The composite material was then molded into a 1 mm thick sheet at 200°C for 3 hours to remove all residual stress. The unfilled polystyrene samples were manufactured in the same manner.

5.3.4 Particle characterization

Scanning electron microscopy (SEM) images were obtained using a JEOL JSA-840A SEM. The samples were prepared with carbon sticker mounting and a gold sputter coating of approximately 10 to 20 nm using a Denton Vacuum Desk II (Moorestown, NJ) sputter coating system.

The PS composite samples were sectioned (70 nm) with a diamond knife on a Reichert Ultracut S ultramicrotome. Sections were collected onto copper grids and images obtained at 80 kV using a JEOL 1200 EXII scanning and transmission electron microscope (STEM) with a Megaview III digital camera and SIS Pro software.
5.3.5 *Polystyrene characterization*

Gel permeation chromatography (GPC) data was obtained using a Waters 510 pump, Waters 717 autosampler, a Wyatt Optilab DSP refractometer and a Wyatt Dawn EOS light scattering detector. The mobile phase was THF at a flow rate of 1 mL/min. PS samples and standards were dissolved in THF at 1 mg/mL.

5.3.6 *Thermal properties*

Thermogravimetric analysis (TGA) was conducted with a TA Instruments Q5000 (New Castle, DE). The materials were tested under a nitrogen atmosphere from 40°C to 600°C at 10°C/min.

5.3.7 *Mechanical properties*

Dynamic mechanical properties of the composites were measured using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA). Rectangular samples with dimensions of 1 x 7 x 18 mm³ were used in a single cantilever bending mode. The experiments were carried out by varying the temperature from 30°C to 150°C at a heating rate of 1°C/min, strain of 0.05% and frequency of 1 Hz.

5.4 Results and Discussion

5.4.1 *Silica characterization*

The morphology of APMMSS was observed using SEM (Figure 5-1). The diameter of the APMMSS particles measured 330 nm with a specific surface area of 933 m²/g, as shown in Figure 5-2 and an average pore diameter of 3.1 nm as shown in Figure 5-3. Due to the porous nature of aminopropyl-functionalized mesoporous silica the particles
dried to remove excess chemical species and solvents from the internal pores. The APMMSS particles were dried but not calcined to minimize rigid aggregate formation.

Figure 5-1. Scanning electron microscopy image of APMMSS

Figure 5-2. Adsorption-desorption isotherm of nitrogen at 77K for APMMSS. (□ Adsorption, ○ Desorption).
5.4.2 Initiator grafting density

Thermogravimetric analysis (TGA) was used to calculate the grafting density of the initiators, as shown in Figure 5-2, based on the method described by Audouin et. al. The weight loss below 120°C was excluded, as it is due to physisorbed water on the silica surface. The weight of the initiator was 22.83% on the APMMSS particles, which amounts to 1.10 mmol of initiator grafted within the particle per gram of sample. Samples were prepared for polymerization with 50:1, 100:1 and 200:1 ratios of monomer initiator based on the TGA calculations. The samples are labeled PS-g-APMMSS 50, PS-g-APMMSS 100 and PS-g-APMMSS 200 to reflect their respective monomer: initiator ratios.

While the potential concentration of initiator in the ATRP polymerization process was doubled for each sample, the overall actual polymerization is nearly identical as
shown in Table 5-1. It appears that the available sites for polymerization are limited to the point that the polymerization is less ideally controlled ($\frac{M_w}{M_n} > 1.3$). The monomer concentration is in fact, much higher than calculated, with the pores of the mesoporous silica blocked by the growing polymer chains, excluding internal initiators from the polymerization process.

Figure 5-4. TGA thermogram of weight loss as a function of temperature for the aminopropyl-functionalized mesoporous silica after initiator grafting.
Table 5-1. Results for the ATRP synthesis of polystyrene-APM MSS\(^b\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Styrene</th>
<th>Silica (mg)</th>
<th>CuBr(_2)b</th>
<th>TPMA</th>
<th>Cu(0)b</th>
<th>T(°C)b</th>
<th>t (h)b</th>
<th>(M_n,GPC^b) g \cdot mol(^{-1})</th>
<th>(M_w/M_n^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-g-APM MSS 50</td>
<td>200</td>
<td>2359</td>
<td>0.030</td>
<td>0.1</td>
<td>1</td>
<td>110</td>
<td>22</td>
<td>156,913</td>
<td>1.47</td>
</tr>
<tr>
<td>PS-g-APM MSS 100</td>
<td>200</td>
<td>1180</td>
<td>0.030</td>
<td>0.1</td>
<td>1</td>
<td>110</td>
<td>22</td>
<td>188,226</td>
<td>1.47</td>
</tr>
<tr>
<td>PS-g-APM MSS 200</td>
<td>200</td>
<td>590</td>
<td>0.030</td>
<td>0.1</td>
<td>1</td>
<td>110</td>
<td>22</td>
<td>187,731</td>
<td>1.53</td>
</tr>
</tbody>
</table>

\(^a\) All polymerizations were performed in 50% (v/v) toluene.
\(^b\) CuBr\(_2\) = copper (II) bromide; Cu(0) = elemental copper; T(°C) = reaction temperature; t(h) = reaction time; \(M_n,GPC\) = average molar mass of grafted chains; \(M_w/M_n\) = polydispersity index

5.4.3 Polystyrene-graft-APMMS particles

The polystyrene grafted particles, shown in Figure 5-3, were well dispersed and maintained relatively small aggregates. This is due to the large size of the particle, the fact that the particles were not calcined and the presence of grafted polymer from within the particle interior. The three composites had 6.6, 11.8 and 16.6 wt% silica loadings with relatively similar molecular weight polystyrene chains grafted.

![Figure 5-5. Polystyrene-grafted-APMMS particle after annealing.](image)
5.4.4 Thermal stability

The thermogravimetric curves provided in Figure 5-4 show that the thermal stability of the polystyrene is improved relative to a similar commercial polystyrene, Ineos Nova Crystal PS1220 polystyrene, (Mn=146,426 PDI=2.08) and also consistent with other published polystyrene data.29 As shown in Table 5-3, the decomposition temperature for 5% weight loss (T_{5wt%}) for the grafted particles was improved 7 to 10 °C over pure
polystyrene. At 50% weight loss, the effect of higher loadings of silica was evident with PS-g-APMMSS 50 sample, containing 16.6 wt % silica, had the highest decomposition temperature ($T_{50\text{wt\%}}$) of 431 °C versus pure polystyrene at 415 °C. Polystyrene decomposition takes place due to random scissions of the polymer chain, creating lower molecular weight by-products and eventually complete depolymerization at higher temperatures. The grafted polystyrene chains are bound to one surface, so degradation occurs from the outside of the grafted particle inward.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_{5\text{%}}$ °C</th>
<th>$T_{50\text{wt%}}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-g-APMMSS 50</td>
<td>387</td>
<td>431</td>
</tr>
<tr>
<td>PS-g-APMMSS 100</td>
<td>390</td>
<td>426</td>
</tr>
<tr>
<td>PS-g-APMMSS 200</td>
<td>390</td>
<td>424</td>
</tr>
<tr>
<td>PS1220</td>
<td>380</td>
<td>415</td>
</tr>
</tbody>
</table>

Table 5-3. Thermal decomposition temperatures for polystyrene and PS-g-APMMSS composites.
Figure 5-7. Samples are 6.6, 11.8 and 16.6 wt% mesoporous silica with polystyrene (see chart for GPC data) grafted from the interior of the particle.

5.4.5 Mechanical behavior and glass transition

The dynamic mechanical properties of PS-g-APMMSS composites were determined over the temperature range of 40-150°C. For PS-g-APMMSS composites the Tg of each material was approximately 4-5°C higher than pure polystyrene listed in Table 5-4. This result is inconsistent with results found by Bansal et. al.\(^7\) for polystyrene molecular weight near 200,000. In fact, their data showed that at this molecular weight the glass transition should decrease approximately 4°C at silica concentrations above 5 wt%. The fundamental difference between this study and the Bansal study is that there is
no free polymer matrix in which to dewet, and further proves that the polystyrene present in the composite is bound to the particle. The relationship between wetting behavior is related to the correlations between molecular weight of the matrix and the molecular weight of the grafted polymer.

Figure 5-8. Loss modulus (E’’) as a function of temperature.
Table 5-4. Glass transition temperature comparison as defined by loss modulus (E") peak.

<table>
<thead>
<tr>
<th>sample</th>
<th>Glass transition temperature (T_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-g-APMMSS 50</td>
<td>109.8</td>
</tr>
<tr>
<td>PS-g-APMMSS 100</td>
<td>109.8</td>
</tr>
<tr>
<td>PS-g-APMMSS 200</td>
<td>109.1</td>
</tr>
<tr>
<td>PS1220</td>
<td>105.0</td>
</tr>
</tbody>
</table>

Loss tangent (tan δ) data from the PS-g-APMMSS samples versus the pure polystyrene also reveal behaviors not typically seen in dynamic mechanical analysis (DMA) results for polystyrene. All sets of samples, including the pure polymer exhibited a dual peak tan δ. Figure 5-8 again shows the positive shift in glass transition temperatures for the composite materials but also reveals a second peak approximately 10°C higher than the first peak for each sample. To our knowledge this behavior for polystyrene has not been documented before in a DMA test, though slight signs of similar behavior were present in our previous study.²⁴ It is presumed that this is evidence of another transition, possibly the liquid-liquid transition (T_ll) for polystyrene as described by Boyer.³⁰ However, Boyer’s study predicted this transition at 131°C for MW=110,000. The heat history of polymers influences the T_g.³¹,³² With the long anneal and mold times, which are atypical but necessary for the mesoporous material, the heat history was significant for each sample and the cooling times were very slow (<1°C/min). It is possible that the extended time above the T_g of the polystyrene sample, as well as the slow cool rate allowed for some alignment in the polymer chains creating an additional transition. This transition could also be described by the twinkling fractal theory (TFT) with the formation of dynamic percolating fractal structures near the T_g.³³ Interestingly, this secondary peak is predicted by Brinson’s group in a model to determine the
thermomechanical impact of the interphase in a polymer nanocomposite.\textsuperscript{5} The model for a two-phase systems, consisting of the bulk polymer matrix and the less mobile interphase, showed a two peak tan δ at approximately 50% percolation of the interphase and was deemed a concern due to lack of evidence in experimental data.

![Figure 5-9. Loss tangent (tan δ) as a function of temperature.](image)

Verification that the heat history did influence the emergence of the dual peak tan δ was conducted on the pure polystyrene sample. Two additional samples were prepared aside from the original sample (PS1220) that was prepared as per the procedure for PS-g-
APMMSS samples. Shown in Figure 5-10, removal of the long annealing period removed distinct evidence of a secondary peak. However, molding the original PS1220 sample a second time revealed a more distinct secondary peak while decreasing the initial peak. While the two peaks become more distinct with additional heat history, the overall base of the tan δ curve does not significantly broaden; however, the molecular weight of the polystyrene after heat aging does significantly decrease. The Tg for the three samples, as defined by the peak of the loss modulus shown in Figure 5-11 changes from 105.4°C for the sample that was not annealed to 104.7°C for the sample that was annealed and molded twice.

Table 5-5. Comparison of molecular weight distributions for polystyrene chains before and after thermal aging due to the annealing and molding processes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anneal</th>
<th>Mold</th>
<th>$M_{n,GPC}$ g·mol⁻¹</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-g-APMMSS 50</td>
<td>no</td>
<td>no</td>
<td>156,913</td>
<td>1.47</td>
</tr>
<tr>
<td>PS-g-APMMSS 50</td>
<td>yes</td>
<td>yes</td>
<td>89,615</td>
<td>1.80</td>
</tr>
<tr>
<td>PS-g-APMMSS 100</td>
<td>no</td>
<td>no</td>
<td>188,226</td>
<td>1.47</td>
</tr>
<tr>
<td>PS-g-APMMSS 100</td>
<td>yes</td>
<td>yes</td>
<td>99,094</td>
<td>1.86</td>
</tr>
<tr>
<td>PS-g-APMMSS 200</td>
<td>no</td>
<td>no</td>
<td>187,731</td>
<td>1.53</td>
</tr>
<tr>
<td>PS-g-APMMSS 200</td>
<td>yes</td>
<td>yes</td>
<td>79,963</td>
<td>2.00</td>
</tr>
<tr>
<td>PS1220</td>
<td>no</td>
<td>no</td>
<td>146,426</td>
<td>2.08</td>
</tr>
<tr>
<td>PS1220</td>
<td>no</td>
<td>yes</td>
<td>79,218</td>
<td>2.54</td>
</tr>
<tr>
<td>PS1220</td>
<td>yes</td>
<td>yes</td>
<td>43,127</td>
<td>4.31</td>
</tr>
</tbody>
</table>
Figure 5-10. Loss tangent (tan $\delta$) as a function of temperature for pure polystyrene with various heat histories.
5.5 Conclusions

We synthesized polymer composites of aminopropyl-functionalized monodispersed mesoporous silica spheres with polystyrene grafted from the interior of the particles in order to improve thermomechanical properties, including thermal degradation and glass transition. For the first time, polymer chains were grafted exclusively from the interior surface of a mesoporous silica particle. An increase in the glass transition at high molecular weight was measured without evidence of dewetting.
Due to the long thermal processing conditions of the samples a new peak for polystyrene was identified in the loss tangent of the dynamic mechanical analysis at the expense of molecular weight and an increase in polydispersity. There is some evidence this may be a less mobile phase with its own, higher glass transition temperature.

5.6 Acknowledgements

This project was financially supported by Schlumberger Lawrence Technology Center. The authors would like to thank Tracey E. Pepper (Iowa State University Bessey Microscopy Facility) and Warren Straszheim (Iowa State University Materials Analysis Research Laboratory) for their expert assistance with electron microscopy. Additionally the authors would like to thank Brenda Carrillo-Conde, Bret Ulery and Ryan Snell for their assistance in gel permeation chromatography and BET analysis.

5.7 References


CHAPTER 6. GENERAL CONCLUSIONS

This work has contributed to the field of materials science and engineering through the development of robust methodologies to synthesize and characterize mesoporous silica-based polymer composites. The use of atom transfer radical polymerization to polymerize from the surface of mesoporous materials was developed concurrently by other groups, however, the methods developed within this work allowed for the presence of limited amounts of oxygen as well as the absence of free initiator. Composites were developed strictly from the particle-based initiators and grafted high molecular weight polystyrene chains.

Hexagonal array mesoporous silica, MCM-41, was shown to disperse well within a polystyrene matrix in comparison to a typical nanocomposite filler, Cloisite 10A nanoclay. While no significant improvements in properties were observed in large deformations through tensile testing of melt blended composites, a noticeable difference was obtained for MCM-41 particles that contained polystyrene grafted to the surface of the particle. The grafted particles increased the modulus of the composite system. Chapter 3 also illustrates the importance of understanding the degree of degradation of polystyrene due to the sample preparation process. Determination of the heat history of polystyrene was shown to be critical in analyzing the behavior of the polystyrene samples within the study as well as samples from literature. Assessment of the molecular weight of polystyrene samples before and after sample preparation is not typically reported.

MCM-41 was also compared with colloidal silica of similar size in melt blended and grafted particle composites in Chapter 4. The colloidal or mesoporous silica particle
surfaces were modified and used as initiators for ATRP of styrene and compared with conventional melt blended composites. A study was conducted to determine the relationships between component properties, composition, structure and interfacial interactions. The polymerization was limited to the accessibility of the initiator sites on the surface of the silica particles despite the fact that the initiator grafting density was improved for the MCM-41 particles. Storage modulus and thermal stability was improved in the MCM-41 based composites versus similar colloidal silica composite samples.

In Chapter 5, aminopropyl-functionalized mesoporous silica, formed through co-condensation, was used as the filler component for the generation of polymer composites. Polystyrene was grafted to the interior pores of the mesoporous silica through atom transfer radical polymerization. Improvements were seen in the glass transition at high molecular weight without evidence of dewetting that has been observed elsewhere in literature. Dynamic mechanical analysis, specifically the loss tangent (\( \tan \delta \)), also showed evidence of two peaks. While allusion to the two peak tan \( \delta \) was seen in our previous study, it was not fully characterized. The long annealing times required for sample preparation for mesoporous silica-graft-polystyrene composites allow for complete relaxation of the polystyrene chains within the sample. The long heat history of the sample due to the annealing and molding processes did result in a significant decrease in polystyrene molecular weight and an increase in polydispersity. However, the resultant mesoporous silica-based composites showed improved thermal stability with increased amounts of filler as compared to similar molecular weight commercial polystyrene.

The resulting techniques, materials and observations within this thesis illustrate the potential for the generation of well-controlled and tailored composite materials.
Composites can be completely synthesized from nano-scale building blocks with improved properties over similar composition composites generated from traditional techniques. Further understanding of the polymer matrix-particle interface was achieved by modifying the structure of the particle, chemical bonding as well as dispersion and the impact of the interface on the bulk properties of the composite was measured.

Further manipulation of the mesoporous silica interface is needed to fully understand the capability of these new composite materials. In particular, modification of the interior pore space as well as the exterior surface is necessary for generation of more sophisticated grafted particles and ultimately more sophisticated, tailored composites. Specific surface preparation could facilitate use of these tailored materials for applications ranging from controlled drug delivery to environmentally responsive composites.