Hierarchical
Layered-Silicate – Lamellar Triblock Copolymer Nanocomposites

by
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ABSTRACT

The fundamental role of the layered-silicates in a styrene-butadiene-styrene triblock
copolymer (SBS) as a function of layered-silicate dispersion during deformation was
investigated. Predominantly immiscible composites of mixed morphology provided the
initial proof that dramatic alteration of the SBS deformation behavior exists, but a clear
understanding of the nature of reinforcement was precluded due to the fiber symmetric
orientation of the SBS and the mixed clay morphologies.

Following the theory of Vaia and Giannelis, use of a more hydrophobic organically
modified clay resulted in an intercalated morphology with a near single crystalline texture
of the SBS due to roll-casting. Significant heterogeneous deformation was observed at
ambient conditions as well as at elevated temperature as verified through Cohen’s affine
deformation model in combination with Kratky’s scattering pattern model. The
intercalated morphology shows little or modest mechanical property enhancements at all
temperatures studied.
Exfoliated nanocomposite was produced by functionalization of the clay surfaces with polystyrene, altering the enthalpic interactions. Entropic interactions were also controlled by varying the molecular weight of the surfactant and the grafting density and shows remarkable agreement with the theory proposed by Balazs et al. Due to the increase surface volume ratio of the clay, a flipping transition of the block copolymer morphology was observed during roll-casting producing a near single crystalline parallel/parallel clay/BCP orientation. The modulus was relatively unaffected whereas the toughness increased significantly due to an earlier onset of strain hardening.

Thesis Supervisor: Edwin L. Thomas
Title: Morris Cohen Professor of Materials Science and Engineering
To my beloved...
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Deep and far away in my old age – with all the memories, wisdom, and experiences under my belt – I will probably look back upon these last five years as one of the most endearing times of my life. It has been filled with so many firsts and so many lasts, so many lessons learned and revealed to be learned, so much bliss as well as tribulation, so much verve and so little lethargy, and most importantly, so many valuable faces which will forever be engraved in my memories – whether those faces be a source of curiosity or a face which will transform and grow old with me through the years of my journey in life.

Someone claimed to me once that life is simply a series of chance events combined to make a cohesive story. I have also heard that whereas choice makes friends, chance makes family. And lastly, that chance is nothing but a master puppeteer orchestrating the events of our lives beyond our comprehension... If so, chance must also be called a blessing as the parents and the sister which God has bestowed upon me fills my heart with greater riches than any worldly possession can. They have been my wall of defense and my pool of solace. They have been my ardent cheerleaders, my sternest teachers. My best friends... The love, support, patience, and understanding they have given me, silently and wholeheartedly, through the years of my life cannot be explained with the words that I know.

Family however begins with one conscious choice – a communion between man and woman promising to share the ups and downs of life together. About eight years ago, I chanced upon Beethoven’s letter beseeching his immortal beloved – a moving cry of love which defies time and heard by people living centuries after, and I can still recall seeing my immortal beloved for the first time. She is my first true love and will be my
last. She is my one and only, but also my all. She is the sweetness I taste in my intellect, and the fragrance which fills my life. She is the essence of my very existence. I have fallen in love with her for what she has shown me, and fall in love again and again with every passing image in my eyes. She brings order into my chaos and balance into my extremities. Without her, I feel nothing is possible anymore and with her, everything is possible. Her unconditional sacrifice for my happiness, her infinite consideration, the wisdom which is beyond the scope of my comprehension, and her unflinching love towards me... I truly owe my all to you, and without you, this would not have been possible.

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FOREWORD

Introduction

Clay based organic-inorganic nanocomposites have generated intense scientific interest principally due to the potential these materials offer for improved properties in mechanical, electronic, packaging, ablation, and fire-retardant applications. Despite the intense excitement for the potential of these nanocomposites and an enormous body of literature concerning their preparation and their resultant physical properties, understanding of the fundamental mechanisms of the property enhancements and in particular the deformation behavior of the nanocomposites is still noticeably absent.

The motivation of this study arises from our ability to make model nanocomposites via the unique templating and processing of block copolymer thermoplastic elastomers. The presence of the block copolymer microstructure possessing a size scale approximately one order of magnitude larger than the size of the individual clay nanosheets results in a hierarchical nanocomposite system. The principle notion of this thesis is that the block copolymer domains allow the possibility to create an “ideal” nanocomposite where a clay layer may be preferentially confined to a single block copolymer domain. The average spacing of the clay layers can be precisely controlled by simply varying the molecular weight of the block copolymer and the volume loading of the clay component. Our ability to study the deformation behavior of a block copolymer in-situ using small angle x-ray scattering (SAXS) allows the possibility to contrast the deformation of the clay-polymer nanocomposite system with prior deformation studies on the same neat block copolymer. By comparing the detailed mechanical behavior of BCP and a clay-BCP nanocomposite a more fundamental understanding of the principles of
property enhancement of nanocomposites should be possible and new opportunities based on these principles should arise in other applications.

**Thesis Structure**

Chapter 1 introduces and describes the broad background related to the current study. The large amount of previous work on clay-polymer nanocomposites including fabrication methods, morphology, and physical properties is reviewed. The previously measured deformation behavior of near single crystal lamellar triblock copolymer is then discussed. This is followed by reviewing the relatively small amount of previous work (mostly rheological studies) on clay-block copolymer nanocomposites.

Materials and various experimental methods used in this work are discussed in chapter 2. Methods for clay-block copolymer (CBCP) nanocomposite fabrication are detailed, with emphasis on surface functionalization of the clay to produce an exfoliated clay-polymer nanocomposite. Other characterization techniques such as mechanical property measurements, x-ray diffraction (XRD), in-situ small angle x-ray scattering (SAXS) deformation, and transmission electron microscopy (TEM) are also briefly discussed.

Flow field assisted production of uniaxially oriented CBCP possessing a mixture of immiscible, intercalated, and exfoliated clay structures is discussed in chapter 3. We find that a significant (greater than 100%) enhancement in mechanical properties (such as tensile modulus, tensile stress, and toughness) occurs with only a small loading of the clay. Moreover, new deformation mechanisms of the block copolymer-clay containing domains arise.
Chapter 4 discusses the temperature dependent deformation behavior of a near-single crystalline fully intercalated clay triblock copolymer nanocomposite. We find that an enhancement in the mechanical modulus contrast between the BCP domains is present and that higher temperatures are required to erase the mechanical contrast as compared to the neat triblock. However, due to the lack of exfoliation, overall mechanical properties of the nanocomposite improve only modestly (approximately 40%) with respect to those of the neat triblock copolymer. We suggest that this is due to the significantly lower surface to volume ratio which leads to smaller degree of interactions between the clay-BCP at the interfaces as compared to that of the exfoliated state. However, the microstructural evolution during deformation at various temperatures is significantly different from that of the neat triblock due to the role of the oriented layered-silicates in suppressing layer dilation of the nanocomposite system.

Chapter 5 discusses the interaction of a polystyrene modified layered-silicate with the block copolymer which we believe forms the first truly model clay-block copolymer nanocomposite. Results show that a certain critical density of the polystyrene brush on the layered-silicates is required to induce exfoliation, and that the method of polystyrene attachment also dictates the density of the polymer brush. Furthermore, the interaction of the layered-silicate with the block copolymer leads to a flipping of the orientation of the block copolymer from a perpendicular to a parallel orientation during roll casting. The nanocomposite shows an increased toughness as compared to the neat triblock although the modulus is approximately the same.

Chapter 6 summarizes current on-going work and suggestions for future work. The chapter outlines some of the thoughts, predictions, and visions I see on these
hierarchical layered-silicate nanocomposites and hopefully will serve a good starting point for someone else who will continue on the work.
CHAPTER 1: Background and Motivation

1.1 Layered-Silicate Polymer Nanocomposites

Ever since the seminal work by the Toyota researchers in 1993 demonstrating dramatic improvements in the tensile modulus, tensile strength, and the heat distortion temperature of Nylon 6 by the addition of a mere 4wt% clay [1], an intense scrutiny of the production and property measurements of clay based nanocomposites has ensued. Through numerous investigations, three distinct types of composite structure have emerged:

- **immiscible microcomposites** where the clay layers have not been interpenetrated by the polymer matrix and act as conventional micron sized filler particles.
- **intercalated nanocomposites** consisting of polymer chains confined in between the clay layers
- **exfoliated nanocomposites** where the individual silicate layers are well dispersed in the polymer matrix

The three types of possible morphologies are shown in Figure 1.1. Researchers have attributed the dramatic improvement in properties to the exfoliated structure (Figure 1.1c).

1.1.1 Background

The term “layered-silicates” has been used to refer to natural clays such as montmorillonite, but technically, “layered-silicates” encompasses all layered structures possessing a silicate chemistry. The main components are silicon and oxygen, with significant amounts of other cations such as aluminum, magnesium, and iron – as the building blocks of the layers. Some examples, with the corresponding idealized chemical formulas, are hectorite \((\text{Na}_{0.3}(\text{Mg},\text{Li})_5\text{Si}_4\text{O}_{10}(\text{OH})_2)\), muscovite mica
(KAl₂(Si₃Al)O₁₀(OH,F)₂), laponite (Si₈(Mg₅.₅Li₀.₄H₄O₂₄)Na₀.₇), magadiite (NaSi₇O₁₃(OH)₃·4(H₂O)), and many other minerals – some which are natural and some of which are synthetic. Various types of minerals have successfully been used in polymer nanocomposites, but the natural clay termed montmorillonite is the most widely used. Montmorillonites were first discovered in 1847 by two French scientists in the area called Montmorillon, France but are now found in numerous other areas [2]. Typically,
Figure 1.1: The three possible structures of clay nanocomposites: a) immiscible, b) intercalated, and c) exfoliated states.
montmorillonites are formed by the weathering of natural minerals such as tuffs and volcanic ash and in their natural form are contaminated by many other minerals. Thus a purification step is required prior to any further handling for nanocomposite work. Companies such as Nanocor and Southern Clay Products sell purified natural and organically modified montmorillonites in addition to other synthetically produced layered-silicates for nanocomposite work.

1.1.2. Morphology

1.1.2.1 Crystallographic Structure

The building blocks of clay minerals are based on the combination of \((\text{Si}_2\text{O}_5)_n\) layers of silica tetrahedral units joined at the corners with \(\text{AlO(OH)}_2\) layers where the alumina are at the octahedral positions (see Figure 1.2a). Montmorillonites consist of a central \(\text{AlO(OH)}_2\) layer sandwiched by two outer layers of \((\text{Si}_2\text{O}_5)\) sharing common oxygen ions resulting in the composition \(\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4\) [3]. A typical thickness of this layer combination is about 1 nm and typical diameters of the native montmorillonite particles are approximately 100 – 200 nm (see Figure 1.2b). Different clay minerals are built with different layer combinations and with different cations – all of which affect the nature, size, and properties of the clay. A thorough discussion on the various types of layered-silicates and their crystal structure are outlined in the books by Brindley [2] and Brown [4].

An interesting feature of clay minerals is the potential for isomorphous substitution of cations in the octahedral or tetrahedral sites. Commonly, \(\text{Si}^{4+}\) ions, located in the tetrahedral sites, are substituted by \(\text{Al}^{3+}\) or \(\text{Fe}^{3+}\); \(\text{Al}^{3+}\) ions, located in the octahedral sites, are substituted by \(\text{Mg}^{2+}\) or \(\text{Fe}^{2+}\). Isomorphous substitution leads to an overall
negative charge on the surface of the clay layers that then requires balance by positive counterions near the surface of the clay, creating an electrostatic attraction and leading to stacking of the layers (see Figure 1.2c).

The hydrophilicity of clay minerals usually leads to the presence of some water in addition to the positive counterions in between the layers. These regions are termed the “gallery”. In montmorillonites, Na\(^+\) ions are the most commonly found positive counterions. These positive counterions are in an exchangeable state – a property that has been crucial in the development of layered-silicate polymer nanocomposites, and is discussed further in section 1.1.3.

1.1.2.2 Microstructure

In general, the individual clay layers, possessing an overall negative charge, are termed lamellae (not to be confused with the same term used by polymer researchers to denote the common two layer repeat structure found in diblock copolymers), and are approximately 1 nm thick. The exact thickness depends upon the type of clay. The widths of the lamellae vary considerably, ranging in diameter from approximately 20 nm, for synthetic laponites, to approximately 5 \(\mu\)m, for natural fluorohectorites. The typical sizes of montmorillonites yield an aspect ratio of a single montmorillonite layer of approximately 100 – 200 : 1.

Ten to twenty lamellae are typically associated with each other through counterion interactions and are termed primary particles (“tactoids”). The resulting tactoid thicknesses, in the direction parallel to the lamellar normals, are approximately 8 – 20 nm. These primary particles are then clumped together to form a turbostratic texture and are termed aggregates. The width and height dimensions of these aggregates range
from 0.1 – 10 μm in size and are the commonly found “dust-like” particles of clay purchased from various commercial vendors. The various schematics of the morphology are illustrated in Figure 1.2.

1.1.3 Cation Exchange Reactions

Clays possess the ability to exchange their positive counterions located in the gallery with other cations in the nearby environment. Thus, if the clay is placed in an electrolyte solution, an exchange reaction occurs between the positive counterions in the clay with the positive counterions located in an electrolyte solution. The reaction is generally not a balanced reaction, but qualitatively follows the Le Chatelier’s principle. Thus, increasing the amount of ions in the electrolyte will generally increase the amount of exchanged ions.

There is however a maximum amount of ions which can be exchanged, defined as the cation exchange capacity (CEC). It is commonly measured in milliequivalents per
Figure 1.2: Schematic of the hierarchical nature of the layered-silicates. a) Atomic model of an individual layered-silicate. b) Schematic showing the negative charge on the surface of the clay. Thickness of the lamellae is approximately 1 nm. c) Primary particle showing the stacking of a few layers of the lamellae. Approximately 10 layers stack together to form an 8 – 10 nm stack. d) Aggregates showing the turbostratic structure of the clay. These range in 0.1 – 10 μm. e) A scanning electron microscope image of a montmorillonite aggregate which has been dried at 80 °C for 1 week.
gram (meq/100g) where 1 meq/g is equivalent to 96.5 C/g. This value can vary depending on the pH of the system, and thus is measured normally at the neutral pH of 7. This is done by saturating the clay with positive counterions and determining the amount held at pH of 7 by conductometric titration. Another popular method of measurement commonly used is to saturate the clay with alkylammonium ions and measure the amount ignited through thermogravimetric analysis (TGA). Typical values of CEC for montmorillonites vary from 80 to 150 meq/100g.

1.1.4 Compatibilization

Compatibilizers have a rich history in composite work. Essentially, they are a method to change the surface property of the dispersant so as to be more favored by the matrix material. The fact that clays possess exchangeable cations has been exploited to change their inherent hydrophilic nature to a hydrophobic nature in order to enhance its interaction with an organic (i.e. polymeric) matrix. Essentially, the procedure is to employ a molecule which possesses a positive endgroup as the exchangeable ion (see Figure 1.3). The approach was first carried out by Fukushima and Inagaki [5] in 1987 when they used an amino acid to functionalize the montmorillonite and subsequently polymerized caprolactam to form a nylon-6-montmorillonite nanocomposite. Intragallery polymerization allowed exfoliation of the clay to occur and remarkable property enhancements were observed a few years later [1].
**Figure 1.3:** Schematic illustration of compatibilization process using a cation exchange reaction of alkylammonium ions.

The most popular compatibilizer is based on alkylammonium ions due to their ease of synthesis and excellent intercalation behavior. The most commonly used are primary alkylamines possessing the chemical structure \( \text{CH}_3 - (\text{CH}_2)_n - \text{NH}_2 \) where \( n \) varies normally from 1 to 18. Lan et al. \[6\] have shown that molecules with \( n > 8 \) tend to exfoliate the clay layers, whereas those alkylamines with \( n < 8 \) usually tend to lead to an intercalated nanocomposite.

Variations of the compatibilizer chemistry have been also utilized, and specifically for polystyrene nanocomposites, aminomethylstyrenes have been used as compatibilizers \[7\]. More recently, living free radical polymerization \[8\] and anionic synthesis \[9\] has been used to functionalize the surfaces of clay layers with polystyrene. In general, various types of compatibilized clays have been commercialized by companies such as Southern Clay Products and Nanocor and are available with varying degrees of hydrophobicity and chemistry for dispersion in various types of host polymer matrix. For a detailed review on other compatibilizing agents, the reader should refer to the good review by Ogawa et al. \[10\].

1.1.5 Methods of Production
There are three principal methods of nanocomposite production: in-situ polymerization, solution blending, and melt blending. Nanocomposite formation by each method of production is outlined in the next three sections.

1.1.5.1 In-situ Polymerization

In-situ polymerization was the first method utilized to produce Toyota’s breakthrough clay-nylon 6 nanocomposites [1,5,11,12]. The basis of fabrication is to first swell the functionalized clay with the monomer for a suitable period of time to allow monomer saturation into the galleries. This is followed by the addition of an agent to kick off the reaction, such as an initiator or a curing agent, depending on the type of monomer used. Alternatively, it may be possible to initiate the reaction using temperature or UV irradiation. This method of production usually results in exfoliated clay layers given that the rate of polymerization within the layers is favored over the polymerization outside the particle. It is postulated that the polarity within the gallery decreases during polymerization and a replenishment of monomer within the gallery occurs to equilibrate the polarity difference which eventually leads to the desirable delamination (exfoliation) of the layered-silicates. This method is commonly used now for the production of thermoset nanocomposites where the monomer and the crosslinking agent both enter the galleries and subsequently react. This method has been utilized for many other polymer matrices [6,13-15].
Figure 1.4: In-situ polymerization method for nanocomposite is illustrated. Organically modified clay is swollen with a monomer M for a sufficient time. This is followed by the addition of a reaction initiator which leads to the polymerization of the monomer. The final structure can result in exfoliated nanocomposite structure.

1.1.5.2 Solution Blending

Solution blending involves the use of solvents which can both swell the functionalized clay and dissolve the polymer. Typically, polar solvents are favored such as tetrahydrofuran (THF) or N,N-dimethylformamide. If the polymer can dissolve in water, even unfunctionalized clay can also be used [16]. The method of synthesis is thus to dissolve or suspend the clay aggregates in the solvent to form isolated layers and to add in the polymer solution. This allows both the solvent and the polymer chains to be situated in between clay layers. It is postulated that the layers are actually exfoliated at this stage. This is followed by solvent removal by evaporation which unfortunately usually leads to reassembly to a final intercalated nanocomposite [17-19].

The primary driving force for polymer intercalation is believed to be the entropy gained by the desorption of solvent molecules, which compensates the loss of
conformational entropy of the intercalated polymer chains. This indicates that a large quantity of solvent is needed for intercalation to occur properly. However, this approach to nanocomposites is not favored by industry due to the large quantity of solvent required.

Figure 1.5: Solution blending method for producing a nanocomposite is illustrated. Two dilute and separate solutions of organically modified clay and the polymer to be used as the matrix material are mixed together. The mixture leads to the presence of solvent and polymer in between layered-silicates. The intercalated morphology is usually maintained with the evaporation of the solvent.
1.1.5.3 Melt Blending

This technique was pioneered by Vaia et al. [20] and involves using elevated temperatures to mainly intercalate clays although clay exfoliation has also been reported [21]. This was a surprising result since the typical radius of gyration of the polymers employed is about an order of magnitude greater than the typical gallery height [22]. This leads to a huge loss of conformational entropy of the intercalated polymer chains. Nevertheless, it is believed that the enthalpic interaction offered by the functionalized clay offers enough decrease in the overall free energy to lead to the most commonly observed intercalated structure. This process is the most favored processing route for industry as it incorporates much of the currently used polymer processing techniques.

![Diagram of Melt Blending Process]

**Figure 1.6:** Melt blending method for producing a nanocomposite. Organically modified clay is mixed a polymer, and under appropriate temperature and mixing conditions, intercalated nanocomposite usually results. This is believed to occur since the tremendous penalty in the conformational entropy of the polymer chains are offset by the enthalpic interaction between the polymer chains and the organic modifiers on the clay.
1.1.6 Properties of Nanocomposites

The ardent interest in nanocomposites is due to the dramatic physical property improvements with only a few weight percent addition of the extremely inexpensive and easily processible inorganic particles. The researchers at Toyota revolutionized the polymer-filler blend field when they reported the numerous property enhancements in their clay-nylon 6 hybrids (see Table 1.1). There have been many studies on the production and measurements of the resulting properties. This section outlines the most important property enhancements that are observed for clay-polymer nanocomposites with the intent of citing the first publications accompanied by a brief introductory explanation of the observed phenomenon.

<table>
<thead>
<tr>
<th>Composite Type</th>
<th>Wt% Clay</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Impact Strength (kJ/m²)</th>
<th>HDT (°C) at 18.5 kg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exfoliated</td>
<td>4.2</td>
<td>107</td>
<td>2.1</td>
<td>2.8</td>
<td>145</td>
</tr>
<tr>
<td>Immiscible</td>
<td>5</td>
<td>61</td>
<td>1.1</td>
<td>2.2</td>
<td>89</td>
</tr>
<tr>
<td>Nylon 6</td>
<td>0</td>
<td>69</td>
<td>1.0</td>
<td>2.3</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 1.1: The remarkable property enhancements observed in clay nylon 6 nanocomposites as reported by Kojima et al. [1].

1.1.6.1 Mechanical Properties

Kojima et al. [1] were the first to report the astonishing and totally unanticipated increase in the mechanical properties of exfoliated clay-nylon 6 nanocomposites. The
tensile modulus increased two-fold and the tensile strength increased by approximately 40% with the incorporation of only 4.2wt% of exfoliated layered-silicates. Importantly, the toughness (impact strength) also increased, contrary to the usual trade-off between strength and toughness. Perhaps expectedly, even a more dramatic improvement was reported by Lan et al. where 15wt% exfoliated clay in a rubbery epoxy increased the tensile modulus and strength by more than ten-fold [23]. Whereas, for intercalated systems, 20wt% clay was needed to achieve a 60% increase in the tensile modulus for PMMA nanocomposite [24]. Furthermore, in addition to the beneficial property enhancements in tension, there are enhancements in the compression behavior of these nanocomposites. Massam et al. have shown that with 10wt% fully exfoliated layers in an epoxy matrix, compressive yield strength and modulus of elasticity increased nearly 20% and 30% respectively [25]. Unfortunately, the increased fracture toughness demonstrated by Kojima et al. [1] for the clay-nylon 6 system has not been translated into most systems. The nanocomposite system in general possess lower impact strength than the native homopolymer, and Manias et al. have revealed in intercalated and immiscible systems that the fracture mechanisms occur mainly near the polymer clay interface [26].

In general, results show that the degree of exfoliation, the type of matrix polymer used, and the actual percentage of clay used all contribute to the observed mechanical properties. Furthermore, the interfacial interactions between the polymer and the clay surface are also crucial in the overall mechanical properties of the nanocomposites. However, to date, there have not been any studies of ideal systems where the degree of exfoliation, distance between the silicates, orientation of the clay layers, and interfacial interactions between clay and polymer matrix have been controlled. The creation of such an ideal system should enable deeper insights into the mechanical properties of the
nanocomposites and the role of the layered-silicates in the overall deformation mechanisms of the nanocomposite. This is the aim of my thesis.

1.1.6.2 Optical Properties

Nanocomposites are optically transparent while most traditional composites are opaque due to scattering of the larger particulates. The nanometer sized clay particles are sufficiently smaller than the wavelength of light that scattering does not occur as is the case with most micron sized composite particulates [27] which tend to be translucent or opaque. Further improvements in transparency can be obtained by reducing the refractive index difference between the clay used and the matrix polymer [28].

1.1.6.3 Barrier Properties

Another major thrust in nanocomposite research has been to create a high barrier (low permeation) materials system for packaging applications. Permeation is defined as the flux of the diffusant divided by the pressure difference across the film membrane. It can be expressed as the combination of diffusion coefficient multiplied by the solubility coefficient \((P = D \times S)\). Generally, the diffusion coefficient in nanocomposites with relatively low percentage filler is the term which is most sensitive to the shape, size, and orientation of the dispersant relative to the diffusing solute. The volume fraction is another term of interest, but somewhat misleading in the case of layered-silicates since the degree of exfoliation will strongly dictate the diffusive path of the diffusing solute. Thus, a better descriptor would be the \textit{surface to volume ratio of the individual nanoparticles}. These various parameters can be grouped together to describe what is called the tortuosity factor. It is generally believed that the increased tortuosity of the
diffusing molecules through the film (thereby lowering its diffusivity) is the source of decreased permeability. This suggests that fully exfoliated, large aspect ratio, silicates are desired for enhanced barrier properties.

The Toyota group first reported a 40% decrease in the water permeation in 4wt% clay nylon 6 nanocomposites [29]. The sample was oriented such that the layered-silicates were aligned with the layer normals along the diffusion gradient. They show that the degree of crystallinity is similar to the neat nylon-6 and the decrease in permeability is mainly due to a significantly decreased diffusion coefficient. They furthermore show that the diffusion coefficient is lower for larger sized layered-silicates suggesting that tortuosity is the main reason for the observed phenomenon. Messersmith et al. have reported an even more dramatic decrease of 80% in 5vol% clay ε-polycaprolactam nanocomposite [30]. These samples were simple cast which typically leads to an in-plane orientation of the layered-silicates. They also attribute the decreased permeability to come from increased tortuosity of the diffusing water vapors. Gas permeabilites were also observed to decrease by 30% with only 4vol% exfoliated clay in a vulcanized acrylonitrile butadiene rubber matrix which was compression molded [31]. The authors also attributed an increase in tortuosity to be the main factor in decreasing the hydrogen and water permeation. Most recently, studies on polyimide nanocomposites by Yano et al. [32] using varying particle diameters of layered-silicates which were all exfoliated and contained the same volume fraction clearly showed that indeed tortuosity plays the dominant role in decreasing the permeability.

1.1.6.4 Thermal Properties
Another exciting discovery of the Toyota research group was the gigantic 80 °C increase in the heat deflection temperature (HDT) of the nanocomposite to 145 °C from that of pure nylon 6 (65 °C). The clay-nylon 6 material also exhibited a 45% decrease in the thermal expansion coefficient [1]. They envisioned the use of these nanocomposites in under-the-hood applications where polymer materials had been unable to withstand the hot environment. Kojima et al. also showed that the HDT of the nanocomposite increases with increasing length and content of the silicates [1]. In general, the increase in HDT has been accompanied by an increase in the glass transition temperature of the matrix polymer which suggests that the presence of the layered-silicates strongly constrains the movement of the polymer chains.

Another interesting property of the nanocomposite is the enhancement of fire retardancy and char formation over that of the neat polymer [33]. The presence of the layered-silicates leads to a thermal barrier layer where flammability is significantly reduced and the material self-extinguishes. Similarly, at extremely high temperatures, the formation of a char layer helps to maintain the overall shape of the material during combustion and prevents flow. The char layer prohibits further combustion and thus nanocomposite polymers are being pursued for use as a rocket case-lining materials [34].

1.1.7 Summary

The study of clay nanocomposites has generated tremendous excitement in both the academic and the industrial arena. This arises mainly from the fact that significant property enhancements are observed despite a very low content of the layered-silicates – sometimes affectionately called the “magic dust”. There have been nearly 800 publications discussing the creation and property enhancements of clay-homopolymer
nanocomposites. Interestingly enough, it is only very recently that interest has turned to using block copolymer as the matrix material for a clay nanocomposite. In the next section, I discuss in detail the previous, much more limited work on clay-block copolymer nanocomposites.

1.2 Clay-Block Copolymer Nanocomposites

1.2.1 Experimental Work

Relatively little work has been devoted to combining clay and block copolymer materials to produce a hierarchical nanocomposite structure. The first report of a block copolymer-clay nanocomposite appears to be that of Laus et al. [35], who in 1997 studied melt (120 °C) processed blends of a SBS triblock containing 30wt% PS (total molecular weight of 70,000) both with an organically modified montmorillonite clay and with an unmodified clay for 10, 20 and 30wt% clay loadings. Given the polymer composition and molecular weight, the material was processed well below the order-disorder transition temperature (ODT). The unmodified clay-SBS composites showed almost no change in properties whereas for the modified clay-SBS composites, the PS plateau modulus increased significantly (3.3x) and the PS glass transition temperature broadened and increased (50°C increase) considerably with clay content and with longer annealing times (at 120 °C). X-ray scattering showed an increase in the silicate layer spacing for the modified clays indicating some intercalation by the triblock into the clay particles. No further morphological characterization of the samples was done but presumably the PS formed cylindrical microdomains typical of triblocks of this composition. The important information on the location and dispersion of the clay particles is thus unknown. The glass transition temperature of the PB was unaffected by
the addition of either type of clay whereas the \( T_g \) of the PS as measured by DMTA increased and broadened systematically only with organically modified clay content indicating that perhaps some of the PS chains were preferentially localized in the clay regions which lead to constraint on the motion of the PS. No large strain behavior was investigated but the authors concluded that the addition of clay would help raise the application temperatures for thermoplastic elastomers.

Galanti et al. [36] have also studied melt-processed blends of a cylindrical microdomain (31wt% styrene) triblock copolymer (total molecular weight of 166,000) with a montmorillonite modified by a coupling agent, isopropyl tristearoyl titanate. They showed that the addition of the organophilic clay allows lower mixing temperatures and smaller torques as compared to blends using the unmodified clay. The composite system exhibited a significantly higher heat deflection temperature (up to 75 °C increase) than the neat triblock. Unfortunately, neither TEM nor x-ray analysis were carried out to determine whether the clay particles were intercalated or exfoliated. DMTA analysis shows that whereas the PB glass transition temperature does not change, the PS relaxation shifts and broadens toward higher temperature. The storage modulus increases with increasing clay content between \(-140 \, ^\circ\text{C}\) and the temperature at which the samples lost their dimensional stability (approximately 100 – 150 °C). Despite the fact that the cylindrical PS domain morphology may preclude the insertion of the large montmorillonite layers (D \( \sim \) 200 nm) into the PS domains suggesting few interactions between the clay and the PS components, the heat deflection temperature of the composite system was chosen as the PS glass transition temperature. The samples with the highest amount of the organic titanate showed the best dimensional stability. The authors do not detail the processing history of the samples for mechanical testing which
may impart some orientation to the clay layers, and no consideration was given to the possible anisotropy of the system during tensile testing. Nevertheless, Galanti et al. [36] showed that the tensile strength possess a maximum depending on the percentage of clay and the percentage of the organophilic modifier in the clay.

By using a low molecular weight diblock Ren et al. [37] were able to blend organically modified (dimethyldioctadecylammonium cations) montmorillonite from 0 to 10wt% loading into the copolymer above the ODT (80 °C). The authors investigated the linear viscoelastic response of the 17,000 molecular weight, 44wt% styrene lamellar PS/PI diblock-clay composites at 85 °C. X-ray studies of the composites show an intercalated structure whereas the same clay dispersed in isoprene homopolymer does not show any noticeable shift in the clay gallery height and hence no intercalation takes place. Rheological studies show that while the unfilled PS/PI diblock exhibits liquid-like behavior (consistent with a disordered state above the ODT), whereas the clay filled hybrids begin to show solid-like behavior in the low frequency regime with increasing particle loading. Ren et al. attribute this to the physical jamming of the anisotropic particles, and not to the shift in the ODT of the clay-containing block copolymer hybrids.

Silva et al. [38] have studied the effect of large (layer thickness of 0.95 nm and disc diameter of 0.5 – 1 μm) layered-silicates in the ordering kinetics of polystyrene-poly(ethylene-butene-1)-polystyrene triblock (Kraton G1675) while the BCP undergoes an disorder-order transition to a body-centered cubic (BCC) structure or hexagonally packed cylinders (HPC) and an order-order transition from a BCC structure to HPC under oscillatory shear by changing the temperatures. The layered-silicates were modified with dimethyl-dioctadecyl ammonium and have a preference for polystyrene domains. A 0.1 wt% modifier leads to a dramatic 2.4x acceleration of the ordering kinetics from the
disordered state to the BCC state. In contrast, the ordering kinetics suggests a slight hindering of the development of the cylindrical morphology from the disordered state. Furthermore, the development of a BCC morphology from the HPC morphology is also greatly accelerated due to the presence of the layered-silicates. They conclude that the development of microphase separation in a block copolymer is critically dependent on a well-defined three dimensional nucleating and templating agent which persist over multiple block copolymer lattice spacings. Krishnamoorti et al. [39] have further verified the phenomenon using various size layered-silicates modified organically in the same fashion and show that the use of a small width laponite (30 nm diameter) has no significant effect in the ordering kinetics of the block copolymer domains, while larger width montmorillonites (0.5 – 1 μm diameter) dramatically accelerate the kinetics.

Lim and Park [40] have studied the effect of melt blending a small amount of organophilic clay (3-5wt%) in a 40wt% styrene 180,000 molecular weight SBS. They also studied a series of the same SBS but with the butadiene block epoxidized (5, 10, and 20wt% epoxy relative to the butadiene block). Based on increased layer spacings measured by XRD, they propose that only the styrenic blocks intercalate into the clay galleries with partial intercalation of the butadiene block only when it is epoxidized. Rheological studies show that despite the low loading content, both the storage moduli and the complex viscosities of the nanocomposite increase relative to the neat triblock copolymer, and show non-terminal behavior with increasing clay content. However, the authors do not take into consideration the morphology and orientation of the block copolymer which may develop (below the ODT) during the melt blending process and the oscillatory shear experiments in both the neat and the filled triblock copolymers.
Dumitru et al. [41] have studied the effect of adding a very large amount (60wt%) of organically modified clay in a SBS triblock containing 27.5 wt% styrene. Samples were produced by injection molding. They studied the effects of isosteric acid (ISA) and maleinized polybutadiene (MPB) compatibilized clay on the ultimate tensile properties and on the shear viscosities of the hybrid system, although any possible block copolymer and/or clay orientation development through injection molding was not considered. Furthermore, the organophilic substitution was performed in toluene, which suggests the cation exchange reaction may not occur and that only a monolayer of the modifiers are adsorbed onto the tactoid surfaces. No morphological characterization of the clay or the block copolymer was performed. Dumitru et al. find surprisingly that relative to the untreated SBS, the addition of 60wt% of ISA modified clay leads to lower melt viscosities and enhanced strain induced crystallization, and that the addition of MPB modified clay leads to decreased strain induced crystallization and hence reduced ultimate tensile properties. No explanation for these unexpected effects was provided.

Recently, Jain et al. [42] has utilized a sol-gel chemistry on PEO-PI block copolymers to create a silicate type material possessing a PI “coating” which was dispersed into PS-PI diblock copolymers. By this method, they were able to produce inorganic nanoparticles of well controlled shapes and dimensionalities which possess a coating which are completely miscible with the PI blocks of the PS-b-PI diblock copolymers. They utilize these nanoparticles to study the influence of filler shapes on the order-disorder transition behavior of the lamellar PS-b-PI diblocks (Mn = 20,800 g/mol, 18.7nm spacing). They report that the thickness of the plates, and the radius of the inorganic particles are approximately 14 nm, which makes these nanoparticles larger than the PI domain size. They mixed these nanoparticles at 0.5 wt% and used simple casting to
produce the samples. Unfortunately, TEM was not performed to verify whether there was preferential segregation of these nanoparticles into the PI domains. Nevertheless, SAXS studies show that the lamellar morphology is maintained and that the ODT is lowered by 15 °C (platelet), 18 °C (spherical), and 23 °C (cylindrical), accompanied by significant broadening of the transition temperature. They attribute the broadening to the fairly broad size distribution of the nanoparticles which induces inhomogeneous melting due to varying defect sites. They conjecture that the incorporation of platelet and spherical particles are less defect prone than the cylindrical nanoparticles which explains the lower ODT of the blend containing cylindrical nanoparticles.

1.2.2 Theoretical Treatments

The thermodynamic behavior of CBCP nanocomposites has also been modeled theoretically. Lee et al. [43] performed simulations on the intercalation kinetics of short (24 repeat units) lamellar-forming amphiphilic diblock copolymers into an organically modified clay tactoid. The authors examined the influence of various assumed interaction parameters between the clay and each of the copolymer components. They fixed the Lennard-Jones potential between the various components and varied the level of the attractive or repulsive interactions between the block components (A and B) and the clay surface (S), but not the surfactant. Nevertheless, they showed that intercalation is heavily favored in all scenarios considered. Under the assumption that the interactions between S-A and S-B are identical to the A-A and B-B interactions, with a large repulsion between the A-B components, the block copolymer will intercalate the clay even when its individual blocks (of 12 repeat units) do not intercalate as individual homopolymers. Furthermore, by estimating the approximate value of the LJ potential at the ODT, they
maintain that intercalation can occur both above and below the ODT. They maintain that the diblock apparently decreases its free energy by exchanging the weakly repulsive intrablock polymer-polymer interactions for the weakly attractive polymer-surface interactions. In another theoretical study, Groenewold and Fredrickson [44] have also performed simulations on the thermodynamic stability of fully exfoliated clay residing preferentially in one block of a lamellar diblock copolymer. Upon exfoliation and insertion into the lamellar medium, they show that the elastic interactions between particles propagate over large distances through the lamellar medium due to the large aspect ratio (~1000 which is true for larger sized layered-silicates) of the clay layers. Despite the long-range interactions, thermodynamic stability is observed in the cases of flexible and of rigid clay particles in the dilute and the semi-dilute regime, but an instability towards macrophase separation of the particles from the copolymer may develop if the long range elastic deformation forces are overcome by fluctuations due to the small elastic constants of the block copolymer melt.

1.3. Deformation Behavior of Neat Lamellar Triblock Copolymer

Thermoplastic elastomers can also be considered as a type of nanocomposite system. Triblock copolymer thermoplastic elastomers (ABA chain structure) are typically comprised of glassy and rubbery domains where the domains are intimately connected via the covalent bonds between the respective blocks. The blocks self assemble into a variety of geometries: BCC packed spheres, hexagonally packed cylinders, double gyroid, and lamellae. They can be processed into near-single-crystal texture structures and used as model systems to study the morphological evolution during deformation [45-61]. The ability to form highly textured samples using various combinations of temperature and
flow fields is critical for elucidating the detailed microstructural basis for their anisotropic mechanical properties.

Numerous deformation studies of lamellar triblock copolymers have been performed. The work by Fujimura et al. [62] appears to be the first study of the microstructural evolution of lamellar glassy-rubbery-glassy triblock copolymer during large strain deformation. They spun-cast the triblock copolymers and annealed the samples at 60 °C which probably leads to a nonequilibrium structure and an ill-defined orientation. They showed that beyond the yield point, the sample initially forms a four-point pattern in the SAXS (called the “chevron morphology” as evidenced by the appearance of thin kink boundaries in TEM images obtained through chemical crosslinking to preserve the plastic strain in the thin microtomed samples). At very large deformations, the SAXS pattern shows a diffuse scattering which was interpreted as due to broken PS domains. Indeed a chaotic morphology of broken PS domains was observed in the TEM. Suguela and Prud’homme [63] also used SAXS to study the deformation behavior of an unoriented sample prepared through simple casting. They again observed the development of a four-point diffraction pattern, in which the reflections continue to rotate away from the deformation direction with increasing strains. However, they attributed the formation of the four-point pattern to intragrain shearing of lamellae and not to chevron formation within the grains.

Allan et al. [64] studied the effect of orientation on the mechanical properties. They oriented the lamellae through shearing using a specially modified single screw extruder. TEM showed highly oriented samples and these were utilized to measure the composite moduli as a function of angle with respect to the lamellar normals. Bulk moduli of styrene and butadiene were used to extract the five elastic constants. However, no
microstructural studies of the morphology during/after deformation were carried out. Yamaoka et al. [65] studied the deformation behavior of an oriented lamellar triblock obtained by compression molding and injection molding. TEM studies were carried out on both as-processed and deformed samples along three orthogonal directions which gave indications of changes in morphology with deformation. They showed that the initial orientation greatly affects the measured mechanical properties, but no further studies were carried out to study the exact microstructural evolution during the deformation. Recently, Cohen et al. [55,56] have clearly elucidated the mechanisms of deformation using well-oriented near-single crystalline roll cast samples of a lamellar styrene-butadiene-styrene (SBS) triblock copolymer by deforming along various directions with respect to the lamellar normal and as a function of temperature. These studies provide a valuable reference for our studies of clay-filled BCP systems and will be reviewed in detail in sections 1.3.2 and 1.3.3.

1.3.1 Producing a Near Single Crystalline Thermoplastic Elastomer

The production of an oriented block copolymer has been performed through numerous methods. These methods have been reviewed in detail by Honeker and Thomas in a paper concerning the influence of structure on the mechanical properties of block copolymers [47]. The formation of the particular block copolymer orientation with various block copolymer morphologies based on various flow fields has been studied extensively. In particular, roll-casting, developed in 1993 by Dr. Ramon Albalak in the Thomas lab, permits the formation of a very large (20cm x 5cm x 1cm) near single crystalline samples [66,67]. A viscous solution of the block copolymer dissolved in a slow evaporating solvent is poured into the nip region between two counter-rotating
parallel cylinders. The evaporation of the solvent in the imposed flow field leads to microphase separation at the critical concentration with the domains aligning in the flow field. Under certain processing conditions, the orientation in lamellar block copolymers is such that the lamellar normals lie along the roll-caster cylinder axis (the neutral axis) designated in our coordinate system as $z$ (see Figure 1.7a and b) and is termed the perpendicular orientation. Roll-casting can also result in a fiber symmetric lamellar morphology instead of the near single crystalline morphology, and morphology verification must be performed after each roll-casting (see Figure 1.7c). Interestingly, under the processing conditions we employed, a novel parallel orientation, where the lamellar normals are along $y$, has not been observed in neat roll-cast lamellar triblock copolymers. This parallel orientation is frequently observed in oscillatory shear oriented (diblock copolymer) specimens [68]. In fact, depending on the frequency, temperature, and the strain amplitude, flipping transitions between the parallel and the perpendicular lamellar orientations are commonly observed in shear aligned neat diblock copolymers and are detailed in several excellent review papers [52,69,70].
Figure 1.7: (a) Schematic representation of the roll-caster. It is comprised of a stainless roller and a Teflon roller counter-rotating with respect to each other separated by a finite gap. The solution is added while rolling, and the evaporation of the solvent in the presence of a flow field leads to a near single crystalline orientation of various triblock copolymers. (b) The lamellar triblock copolymer orients its microdomains as shown with its lamellar normals pointed along z. (c) Another possible orientation that can develop during roll-casting in lamellar systems is the fiber symmetric orientation.
1.3.2 Deformation at Ambient Conditions

For a near-single crystal sample of lamellar SBS (45wt% styrene) deformed along the lamellar normal ("perpendicular deformation"), the tensile modulus is 65 ± 3 MPa and the yield strength is 3 MPa. Cohen et al. [55,56] have shown when the applied force is along the lamellar normal, the layers start to undulate near defect sites at low strains. At higher strains the undulations fold into a chevron morphology, followed by the formation of distinct kink boundaries. The deformation was affine with the macroscopic elongation, \( \lambda = \frac{\ell}{\ell_0} = \varepsilon + 1 \), and simply given by \( 1/\cos \alpha(\lambda) \), where \( \alpha \) is the angle between the force direction and the location of the lamellar peak reflection at a particular elongation also along the lamellar normal \( \hat{n} \) (see Figure 1.8). Immediately upon unloading from 300% strain (\( \varepsilon \)), the macroscopic residual strain is about 40% and the initial lamellar period returns without noticeable residual layer strains. Annealing above the \( T_g \) of PS resulted in full recovery of the lamellar spacing and ordering and the residual strain decreased to zero.
Figure 1.8: Stress-strain curve of a lamellar styrene-butadiene-styrene triblock copolymer deformed along the lamellar normal with the in-situ SAXS data superposed. Loading shows that the chevron morphology is formed at an angle $\alpha$ near 60% strain, and increases with higher strains. The unloading curve shows that the chevrons relax during unloading. Adapted from Cohen et al. [55].

Under parallel deformation, the PS layers initially take up most of the load, leading to a tensile modulus of $180 \pm 3$ MPa. Fragmentation of the PS domains leads to the necking phenomenon at a yield stress of approximately 5 MPa. The fragmentation process creates voids elongated parallel to the stretching direction, and these give rise to an anisotropic low angle scattering streak as evidenced in the SAXS patterns (see arrow in Figure 1.9).
Figure 1.9: Stress-strain curve of a lamellar styrene-butadiene-styrene triblock copolymer deformed along the roll-cast direction with the in-situ SAXS data superposed. Loading shows that the PS domains breakup leading to void formation at 200% strain. The unloading curve shows that the lamellar morphology returns albeit a poorer degree of ordering. Adapted from Cohen et al. [55].

Cohen et al. also showed that for single crystal samples oriented 45° to the deformation direction, the majority of the sample responds via the rotation of the lamellar normal away from the loading direction with increasing strain. However, due to lateral forces from Poisson contraction, small portions of the layers form narrow asymmetric kink bands, with the kink boundaries parallel to the force direction. Upon unloading, the initial 45° orientation is returned (see Figure 1.10).
Figure 1.10: Evolution of the SBS microstructure when deformed 45° to the lamellar normal. The domains respond by a rotation of the lamellar normal away from the loading direction (see arrows), followed by the formation of small asymmetric kink bands due to Poisson contraction. Upon unloading, the lamellar structure returns possessing nearly the same degree of order. Taken from Cohen et al. [55].
The comparative stress-strain curves for the three different deformation directions are illustrated in Figure 1.11. Note that due to the loading of the glassy high modulus PS domains, the parallel deformation direction shows the highest modulus while the 45° direction with its easy rotation of the lamellar domains shows the lowest modulus (43 ± 3 MPa), even lower than that of the 90° direction (65 ± 3 MPa).

![Stress-strain curves](image)

**Figure 1.11:** Superposed stress strain curves of parallel, perpendicular, and diagonal deformation showing the various initial tensile modulus differences. The parallel deformation possesses the highest modulus since the PS domains initially take up all the loading and the diagonal deformation possesses the lowest modulus as the domains initially respond by rotation of the lamellar normals away from the deformation direction. Taken from Cohen et al. [55].

### 1.3.3 Temperature Dependent Deformation Behavior

Cohen et al. [56] were the first to consider the temperature dependent deformation behavior of a thermoplastic elastomer and modify the system from a glassy/rubbery nanocomposite to a viscoelastic/rubbery and rubbery/rubbery system [71].
They focused on perpendicular deformation and showed that for room temperature deformation, due to the covalent bonding constraint of the rubbery PB layer to the glassy PS layer, no significant layer dilation is observed. They postulate that tilting of layers in the vicinity of defects leads to a yield point and that yield is not dominated by an undulation instability, as had been proposed by various theoretical models assuming an ideal defect free microdomain structure [72,73] (see Figure 1.12). Well above the glass transition temperature of the PS, the material becomes an effective rubber which leads to a pure dilation of the layers in an affine manner with respect to the macroscopic elongation. By deforming at the glass transition temperature of the PS, layer tilting returns accompanied by some lamellar dilation (see Figure 1.13).
Figure 1.12: Two different chevron formation mechanisms are illustrated. Theoretical models show that an undulation instability is the reason for the formation of chevrons as shown before and after deformation in (a) and (b), respectively. Adapted from Read et al. [73]. Cohen et al. shows that in experimental systems, tilting of layers in the vicinity of defects lead to a yield point causing chevron formations as shown in (c) and (d) before and after deformation, respectively. Adapted from Cohen et al. [56].
**Figure 1.13:** The temperature dependent behavior of when deformed along the perpendicular deformation direction. Only chevron formation occurs at ambient conditions. The lamellar layers exhibit pure dilation when deformed above the glass transition temperature of the PS domains behaving similarly to a pure rubber. At the glass transition temperature, dilation is accompanied by some tilting of the lamellar domains. Adapted from Cohen et al. [56].
1.4 Outlook

This chapter reviewed some of the important theoretical and experimental work involving polymer-clay nanocomposites. These publications clearly show the potential of these nanocomposites offer as materials systems for advanced applications of polymers. Unfortunately, much of the literature to date merely deals with reports of the processing history and the observed property enhancements or lack thereof. This is further exacerbated by the numerous shortcomings in the proper characterization of the nanocomposite leading to an inadequate and even sometimes erroneous understanding of the fundamental structure-property relationships. In reports where proper, careful, systematic measurements have been performed on well characterized materials, the apparent inability of the researchers to control the degree of exfoliation, the orientation of the layered-silicates, and the interaction of the clay layers with one or both BCP components leave the reader seeking an understanding of the fundamental role of the layered-silicates in improving the properties of the nanocomposite with a sense of disappointment. In light of this, a method for producing a well-controlled nanocomposite morphology and studying the response of the model system to various applied loads will lead to significant insights into the fundamental nature of the layered-silicates on the nanocomposite system. One possible method of production of these ideal nanocomposites would be to utilize the self-assembling nature of the block copolymer to serve as a template to organize the clay particles and lead to a more ideal, model layered-silicate BCP nanocomposite. Figure 1.14 outlines the various possible morphologies which can arise with the interaction of the layered-silicates and the block copolymer. In particular, the exfoliated layered-silicates may allow the creation of a model hierarchical nanocomposite possessing a well-defined geometry and orientation. Synthesizing a
diblock off the clay surface may lead to a pseudo-triblock copolymer like behavior where
the rubbery phase is reinforced at every domain by a layered-silicate possibly leading to
phenomenal property enhancements. However, there has been essentially no exploitation
to date of the fact that a hierarchical nanocomposite possessing a well-defined anisotropic
morphology can be created with the clay-triblock copolymer system. Jain et al. [42] used
inorganic particles that were larger than the domain size of the compatible block of the
**Figure 1.14:** Various possible layered-silicate morphology in a triblock copolymer and its possible influences on the chain architecture. In exfoliated systems, the ordering and orientation of the block copolymer can be used to produce a near single crystalline nanocomposite to study anisotropic deformation behavior.
matrix which most likely prevents ideal incorporation into the BCP domains. Most other prior systems studied focused on the rheological behavior above the ODT when the layered-silicates are incorporated and furthermore, in systems where properties were probed below the ODT, block copolymers forming PS cylindrical microdomains were selected. Given the size and shape anisotropy of the layered-silicates and the claims that the layered-silicates prefer to be located near the PS chains with microdomain diameters that are an order of magnitude smaller in size than the width of the clay particles, it is unlikely that a morphologically well-controlled system exists when combining clay platelets and PS cylinders.

In this thesis, I exploit the lamellar block copolymer morphology which should be geometrically compatible to the layered-silicates to experimentally achieve the various ideal morphologies of the CBCP envisioned in Figure 1.14. Furthermore, use of the roll-casting process to produce near-single crystal BCP domains with a very well controlled orientation of the layered-silicates will lead to understanding of the anisotropic nature of the deformation. The stress-strain behavior will be studied as a function of orientation of the lamellar normals (of both BCP and clay) relative to the deformation directions. These deformation mechanisms are studied both ex-situ via TEM of thin sections, but also in-situ via SAXS experiments to elucidate the real-time deformation of the BCP microdomains – experimental techniques which are detailed in Chapter 2 of this thesis. In the process, proper morphological characterization of the orientation of the BCP microdomains, the spacing of the layered-silicates, and the location and orientation of the layered-silicates and their importance in the overall deformation mechanisms will further elucidate structure-property relationships.
The thesis essentially tracks along the following path. The first chapters deal with organically modified layered-silicates incorporated into BCP. These chapters are necessary in order to build the understanding of the role of the layered-silicates in BCP and serve as a reference dataset. This is followed by the incorporation of PS modified clay into block copolymer domains which can lead to nearly ideal model nanocomposites. These can be used to extract principles of nanocomposite engineering and potential property enhancement factors. This thesis is then capped off by a beautiful model nanocomposite where all the possible exploitable benefits learned through these previous studies are incorporated into one final truly ideal system.

Chapter 3 will show the deformation behavior when layered-silicates are incorporated into the block copolymer matrix mainly as a tactoid material. These systems had uniaxial symmetry and possessed mainly immiscible clay particles although a small degree of intercalation and exfoliation did occur. Results show promise for significant improvements in the large strain tensile deformation behavior of these materials and significantly altered microstructural evolution as compared to neat triblocks during deformation due to the presence of the layered-silicates.

Chapter 4 discusses a purely intercalated layered-silicate in a precise orientation relative to the near single crystalline block copolymer morphology. Modest improvements are shown in the mechanical properties of the nanocomposite over that of the triblock, and the block copolymer microstructural evolution during deformation at various temperatures is shown. These block copolymer nanocomposites show a significant increase in their temperature stability as has been demonstrated in homopolymer nanocomposite systems. The suppressed dilational response of the matrix
block copolymer as compared to the neat triblock copolymer during deformation is shown to be due to the additional constraint of the clay.

In Chapter 5, I show that by selecting the lamellar BCP morphology with a correct set of compatibilizers, a nearly ideal CBCP nanocomposite system can be synthesized. The parameters of concern are enthalpic interactions (type of surfactant), entropic interactions (molecular weight of the surfactant), and the grafting density of the surfactant on the layered-silicate (graft-onto or graft-from changes the grafting density). These studies lead to a heretofore unexpected revelation of the role of the layered-silicate surfactants on not only the dispersion behavior, but the orientation of the BCP domains during roll-casting. This was manifested in a sharp flipping transition from the perpendicular to the parallel orientation depending on the layered-silicate surfactant used.

Chapter 6 summarizes the overall results and lessons learned from these studies. It summarizes some of the main results to be expected for various improvements in immiscible, intercalated, or exfoliated structures specifically as dispersed in a lamellar triblock thermoplastic elastomer. It also lists on-going work and suggestions for future studies which should lead to further insights in the fundamental role of these layered-silicates in the various properties of these nanocomposites.
1.5 References


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CHAPTER 2: Experimental Methods

2.1 Typical Nanocomposite Characterization Techniques

After the production of a sample, we are always eager to measure the resulting properties of the nanocomposite. However, careful characterization of the structure is required, including investigation of the separate components as well as the complete composite, to arrive at a full understanding of the fundamental structure-property relationships. Careful analysis of the surfactant properties on the modified layered-silicates and the morphology of the nanocomposite, on many lengths scales, are critical to perform correctly and reliably. To accomplish this, one needs a thorough understanding of the various pitfalls of each characterization techniques. As such, I will outline and discuss several key techniques which are crucial in the study of CBCP nanocomposites. The techniques to be described are appropriate for modified layered-silicates which are ready for dispersion into a matrix material. The special surface modification of the layered-silicates will be discussed in the later section 2.2.

2.1.1 Thermogravimetric Analysis

The amount of the organic modifiers relative to the inorganic content can greatly affect the number of layered-silicate particles dispersed in the matrix. In some cases, low molecular weight modifiers comprise only 10% of the total weight of the modified clay, whereas high molecular weight modifiers can account for as much as 90% of the total additive component weight. Thus, using our example above, a naive approach of simply adding 5 wt% modified clay can result in a weight fraction of the inorganic particles which could vary from 0.5 – 4.5 wt% content. This variability will have dramatically
differing reinforcing mechanisms even though the additive weight fractions are the same. In order to quantify the amount of reinforcing particles which will be added, thermogravimetric analyses (TGA) are performed prior to mixing. Essentially, TGA measures the mass lost when the sample is burned. As the organic modifiers decompose at lower temperatures, the mass loss can be used to calculate the relative amount of the organic modifier relative to the layered-silicate. The typical conditions utilizing a Perkin-Elmer TGA7 are to ramp up the temperature from ambient conditions to 900 °C at a heating rate of 20 – 40 °C and measure the weight loss. At some critical point depending on the organic modifier (typically 300 – 500 °C), the weight loss undergoes an abrupt change where the mass quickly falls off. The remaining mass can be used to calculate the weight fraction of the organic modifier to the inorganic layered-silicates. It is important that the samples are free of excess moisture or residual solvents, and thus the samples are kept in a vacuum oven at 60 – 80 °C for a few days prior to measurement. Significant lowering of the organic degradation temperatures have been observed due to the catalytic sites on the aluminosilicates and thus, the lowest possible temperatures should be used in the drying process [1]. Furthermore, natural montmorillonites, without any organic modifiers, tend to lose approximately 10% of its mass at approximately 700 – 800 °C. Thus this mass loss should be taken into account. The densities of the various unmodified layered-silicates are available (typically between 2 – 3 g/cm³) and can be used to approximate the volume fractions in the final nanocomposite. Representative TGA data of a commercially available Cloisite® 15A (C15A) is shown in Figure 2.1.
Figure 2.1: Thermogravimetric analysis (TGA) data of dimethyl dihydrogenated-tallow quaternary ammonium modified layered-silicate obtained from Southern Clay Products under the product name Cloisite® 15A (C15A). Heating rate was 20 °C/min using approximately 10 mg.

2.1.2 X-Ray Diffraction in Bragg-Brentano Parafocusing Geometry

X-ray powder diffractometer (XRD) was used to determine the layer spacings of the layered-silicates which are approximately an order of magnitude larger (1 – 5 nm) than the atomic unit cell crystal structures within the layer (0.1 – 0.3 nm). As such, the technique possesses features which are different from traditional XRD measurements due to the regime of interest at low 2θ (1.5 – 10°). Vaia and Liu [2] have recently published a thorough and excellent review article particularly focusing on the use of XRD in
polymer/layered silicate nanocomposites in a Bragg-Brentano parafocusing geometry, as shown in Figure 2.2. The details of their discussion are left for the reader to pursue, but the main important parameters will be discussed below and their effects on experimentation and data interpretation.

Figure 2.2: Schematic diagram of a Bragg-Brentano parafocusing geometry used in XRD. Taken from Vaia, R.A., Liu, W.D. [2].

Essentially, the intensity of a diffraction profile, \( I(\theta) \), is expressed by a combination of Lorentz polarization factor, \( L_p(\theta) \), (which depends on the distribution of the scatters and geometrical factors), interference function, \( \phi(\theta) \), (which depends on the distance and extent of coherency between scattering units), and a structure factor, \( F(\theta) \), (which depends on the type and position of atoms in the unit cell).

\[
I(\theta) = L_p(\theta) \phi(\theta) F^0(\theta)
\]  

(2.1)

For a layer geometry, the structure factor scales as \( q^2 \), where \( q = 4\pi\lambda^{-1}\sin(\theta) \), which causes a marked increase of the (001) reflection with increasing interlayer distances. Thus, it can be misleading to use the area of the scattering peak among
different samples at a fixed volume fraction as the relative measure of concentration of intercalated or immiscible structures since the intensities can change depending on the exact location of the peak position.

Assuming the diffracting species are simple 1D periodic stacks of layers, the interference function is affected by two main parameters; the number of diffracting layers in a stack and the degree of disorder within the stack. In regards to the number (N) of diffracting species, with higher number of scatters, the peak diffraction intensity will increase as $N^2$ while decreasing its breadth as $1/N$. This affects all the (00$\ell$) peaks. However, when disorder exists within the layer, the higher order interference maxima are reduced and broadened preferentially.

The Lorentz polarization factor essentially deals with the orientational distribution of the layered-silicates relative to the incoming x-rays. If the particle stacks are all perfectly aligned such that the layer normals ($\hat{n}$) bisect the incident and reflected beam, the scattering intensity is at a maximum and consists of a set of Bragg spots oriented along $\hat{n}$. For a random distribution of the layered-silicates, this intensity is spread over a set of spherical shells and the recorded intensity on a 2D detector is a relatively weak circular ring.

Additional experimental factors such as surface roughness, sampling depth, parasitic scattering and detector smearing, which require the correct choice of slits, complicate data acquisition and interpretation further.

For example, in the Bragg-Brentano geometry, the volume of the sample exposed stays constant, but the area increases while the penetration depth decreases as $q$ is decreased. This can have dramatic consequences if the sample has a gradient in structure in the thickness direction and also necessitates a relatively large area sample.
Furthermore, surface roughness can alter the background noise and the measured absolute intensity at low q and care is required to produce sample surfaces which will be smooth. The alignment of the sample relative to the beam is also another issue. A 500 μm location error of the sample surface can alter the measured d-spacing by as much as 1 nm at very low 2θs which can easily be misinterpreted as a sign of intercalation. Thus, use of a standard powder sprinkled onto the sample surface to calibrate d/2θ is recommended. Lastly, the ability to observe reflections at very low 2θ depends on the choice of the source slits. Smaller slits restrict the incident beam, reducing parasitic scatter from the sample holder and direct exposure to the source at low angles. This implies the use of smallest possible slits available for all slits but increasing counting times to compensate for the decreased intensities.

In a nutshell, samples preparation should be performed with the aforementioned factors in mind, and during data acquisition, the smallest possible slits should be used with sufficiently long enough counting times to accommodate the decreased intensity. Normally, a quick scan to locate the peak position followed by long counting times at various peak positions of interest will lead to rapid, high quality data. Lastly, special care needs to be taken to ensure that either the sample location is always constant or a reference powder is used to precise the correct spacing.

For the experiments performed at MIT, a Rigaku rotating anode generator using Cu Kα radiation (λ = 0.154nm) at 60 kV and 300 mA was used. The slits used were 0.5°, 0.5°, and 0.15° for divergence, scatter, and receiving slits, respectively. The 2θ scan angles ranged from 1.5 to 10° with a maximum scan speed of 0.1 °/min and a sampling interval of 0.01°, but were sometimes varied to ensure good counting statistics. A typical scan took approximately 20 minutes to an hour.
2.1.3 Transmission Electron Microscopy

Despite the power of the XRD in determining the spacing of immiscible or intercalated nanocomposites when experimentally performed correctly, the data must always be complemented in some form with a real-space imaging technique such as transmission electron microscopy (TEM). The absence of a scattering peak in the reciprocal space through XRD can only be definitely attributed to an exfoliated structure through the use of real-space images. More often however, are the scenarios where examination of a system which is thought to be intercalated or immiscible by XRD turns out to possess a mixed morphology when observed with the TEM. Furthermore, the observation or absence of a scattering peak in the XRD should not be taken as the final word on the nature and distribution of the layered-silicate throughout the sample since depending on the processing history, fluctuations of layered-silicate concentration within the sample can sometimes be observed. For example, skin-core morphology may develop during processing where there is a distribution of exfoliated, intercalated, and immiscible structure as a function of sample depth. Furthermore, depending on the flow field during processing, orientation of the layered-silicates may occur which may enhance or reduce the number of layered-silicates which possess its layer normals at the correct orientation for Bragg condition to occur. Furthermore, partial orientation of the layered-silicates relative to Bragg conditions may lead to erroneous interpretation of the relative percentage of intercalated and immiscible layered-silicates. These various aspects require the use of TEM, but capturing the overall morphology of the whole sample is also a daunting task using TEM due to the limited sample size and can only be approximated by examining various representative local areas of a given sample.
In general, the electrons which have interacted with the sample carry information in both the amplitude and phase part of their wave function [3,4]. Information from the amplitude part of the wave function, typically in the mass-thickness contrast mode, is most commonly utilized in studying the morphology of a clay nanocomposite in a homopolymer matrix. Essentially, materials which possess a higher electron density will scatter more electrons outside the objective aperture and appear dark in the bright field image. This implies that the heavy atom containing layered-silicates will appear as dark lines or plates (depending on the orientation of the layered-silicates) in the final image whereas the organic polymer matrix will typically appear as a light background when the sample is at or near its focal plane. This technique can also be utilized in the same manner in unstained clay-block copolymer nanocomposites to characterize the degree of intercalation and/or exfoliation in the sample.

However, when dealing with the layered-silicates in a block copolymer nanocomposite, it is of significant interest to observe which microphase of the BCP the clay is situated in. As the mass-thickness contrast between the two blocks of the matrix copolymer is usually not significant, this requires the use of preferential staining agents. Typically osmium tetroxide, which preferentially stains the butadiene or the isoprene chains, is utilized. However, care must be taken so that the staining agent does not also stain the clay organic modifier as this may mask the observation of the layered-silicate. Thus, the selection of appropriate staining agent is critical. Another technique which can be utilized is phase contrast imaging, where the information stored in the phase part of the electron wave function is utilized [5-7]. Essentially, changes in intensity can be induced from phase differences in the electron interacting with the sample by defocusing the objective lens. The advantage of this technique is that it does not require selective
staining, but image interpretation can be difficult since defocusing in the electron microscope shifts the phases in a complicated manner. For specific details into the theoretical treatments of TEM imaging, I will refer the reader to the following excellent references [3,4,8].

In order to prepare representative thin specimens from the bulk samples prepared for mechanical testing and XRD analysis, all samples were microtomed using a Reichert-Jung Ultracut FC 4E at −90 °C (knife) and −110 °C (sample). Typical settings were 40 – 80 nm section thickness, 1 – 3 mm/s knife speed, and 35° or 45° diamond knife. Concentrated sucrose solution was used to pick up the samples from the diamond knife and transfer them onto copper grids (400 – 800 mesh). TEM imaging was performed prior and after staining which utilized OsO₄ vapors for about 1 – 2 hours. TEM imaging was carried out on JEOL 200CX using a tungsten filament as the source. Standard operating conditions were 200 keV, condenser aperture #2 (300 μm), spot size (C1) #2, objective aperture #4 (40 μm), and magnifications which ranged from 10,000x to 50,000x. Micrographs were taken using Kodak Electron Image Film SO-163 and developed in Kodak developer at full strength for approximately 5 minutes. The developed negatives were then rinsed in flowing water for 2 minutes and subsequently placed in a fixer bath (Kodak Rapid Fixer) for 5 minutes. Prints were made using Agfa Brovira-Speed BH310RC glossy grade papers (#2,3,4), at varying projector magnifications (1 – 8x). The prints were then digitized at 600 dpi using a scanner. Lastly, digital Fourier transforms (FFT) were obtained by using a freely available program, NIH Image. Images were required to be cropped into a 512x512 or 1024x1024 pixel size prior to FFT operation. Some relevant references on FFT are included for the reader [9-12].
2.1.4 Deformation Stages for Mechanical Property Measurements

After successful preparation and morphological characterization of the nanocomposite sample, various properties are measured. One of the most actively pursued property measurements are the mechanical properties as discussed in Chapter 1. These techniques are rather straightforward and need not be discussed in too much detail.

For large strain deformation behavior, samples were loaded in two types of tensile deformation stages to probe the mechanical properties. For ex-situ measurements, an Instron 4501 equipped with a 10N load cell was used to perform tensile tests typically prior to experiments at a synchrotron beamline. Instron IX software was interfaced with a 4500 Instron controller for data acquisition and to control testing conditions. Typical testing conditions are 3 – 4 mm/min stretching rate, 5 – 20 mm gauge length with a sampling rate of 5 points per second. The grips were pneumatic grips with serrated edges at approximately 75 psi of holding pressure, and typically necking and fracture was propagated from these grip edges.

For in-situ SAXS deformation experiments, a custom tensile deformation device devised by Dr. Christian Honeker [13] was utilized in synchrotron x-ray source beamlines. The device is equipped with a 50 lb load cell and is controlled by a custom built motor control box. The output of the load is recorded on a strip chart recorder and subsequently converted to stress strain data after the experiment through digitization using an add-on program in Origin software. The key feature of the machine is the counter-rotating screws which allow symmetric stretching at the middle of the sample gauge length. Further details on the schematic and the design strategies of the device can be found in Dr. Honeker’s thesis [13]. Typical operating conditions include 3 – 4 mm/min stretching rate, 5 – 15 mm gauge length, and a sample dimension of approximately 0.1 – 0.3 mm
thickness by 2 – 3 mm width. The grips are sawtooth patterned faces which prevent sample slippage and spring loaded Bellevue washers are used to compensate for thinning of the samples at high strains.

2.1.5 Deformation Experiments at Synchrotron Sources

Synchrotron experiments were performed in three different beamlines: X12B and X27C at Brookhaven National Labs in the National Synchrotron Light Source and the D1 beamline at Cornell High Energy Synchrotron Source (CHESS). Unfortunately, the X12B beamline is no longer available for small angle x-ray scattering experiments as it has been converted over into a protein crystallography beamline. However, X27C and CHESS beamlines are still currently available. The operating conditions in these two beamlines will thus be discussed, although readers are referred to the beamline information web pages for X27C and CHESS at http://bh03.chem.sunysb.edu/X27C/ and http://www.chess.cornell.edu, respectively. Information on the X12B line can also be found in Dr. Honeker’s thesis [13].

The X27C beamline allows the simultaneous operation of wide angle x-ray scattering (WAXS) and SAXS. This is done by placing two BASF image plate detectors at appropriate locations, where the WAXS detector has a hole near the beamstop (r=0.6 cm) allowing the SAXS data to be recorded on a second detector further downstream. The image is scanned in a Fuji BAS 2500 image plate scanner and the calibration to convert pixels to q (Å⁻¹) depends on the scanning resolution, but an appropriate scanning resolution is 200 μm/pixel from the 25 cm x 20 cm image plates (leading to 1250 x 1000 pixels). Typically, silver behenate is used as the calibrant with a d-spacing of 116.72 Å. Typical operating x-ray wavelengths are 1.3 – 1.6 Å and sample-to-detector distances are
typically 40 cm and 230 cm for the WAXS and the SAXS, respectively. However, both the wavelength and the sample-to-detector distances can be varied depending on the spacings of interest in the material as is the case in all synchrotron sources. Understanding the proper placement of the detectors for the size scales of interest requires the knowledge of the geometry of the detector positions at the beamline and is shown in Figure 2.3.

![Diagram](image)

**Figure 2.3:** Schematic diagram of the X27C beamline at Brookhaven National Lab. The beamline can simultaneously measure WAXS and SAXS by using a hole cut in the center of the WAXS image plate.

In general, it is necessary to calculate the maximum spacing desired on the WAXS detector, and then calculate the smallest observable spacing in the SAXS depending on this. The largest possible spacing observable in the SAXS will be dependent on the beamstop and the beam alignment. For an explicit example of calculation of the required spacings, refer to Appendix A.
Due to the use of image plates, it is necessary to stop the deformation, take an exposure and scan sequentially. Comparisons of the morphology as a function of applied strain in other beamlines indicate that these quasi-static experiments do not significantly differ from continuous deformation and exposures using an electronic detector where data readout is much faster.

The beamline at CHESS can however perform continuous deformation experiments as it employs a charged couple detector (CCD). The CCD has a 51 μm/pixel resolution and has 1024 x 1024 pixels. Otherwise, the conditions for SAXS are similar to the beamline at BNL. The main difference is the interface which uses SPEC programming language and arises from the data acquisition from the CCD detector. Important commands required for the operation of the beamline are outlined in Appendix B.

Lastly, all of the data interpretations were performed using freely downloadable software, Fit2D, which allows a host of powerful data extraction tools [14,15]. Further details on the operation and use of the software can be found in http://www.esrf.fr/computing/expg/subgroups/data_analysis/FIT2D.

2.2 Modification of the Layered-Silicates

The importance of modifying the hydrophilicity of the layered-silicates to a hydrophobic nature has already been detailed in the previous chapter. In general, the modification can be broadly classified into either a “grafting to” or a “grafting from” process. Both procedures possess advantages and disadvantages which need to be considered prior to functionalization. I will illustrate four specific techniques used in this work among the various techniques that exist. These techniques have previously been
reported in the literature, and the results have simply been reproduced. However, rather
than outlining the experimental protocols which is already present in the literature, I will
attempt to provide an underlying principle and the reason for the experimental procedures
along the way.

Before continuing, I must digress shortly to acknowledge my collaborators in
these synthesis schemes. Dr. Younghwan Kwon, who is now Professor Kwon, has
synthesized all of the initiators used in these studies. Prof. Kwon also performed the
living free radical polymerization of PS from the clay surfaces. Dr. Thomas Breiner and
Edwin Chan worked closely to produce amino terminated polystyrene to graft onto the
clay surfaces. Lastly, Edwin’s tireless efforts at glass blowing allowed the anionic
synthesis of diblocks from clay surface possible using Prof. Kwon’s initiators. I thank
them profusely.

2.2.1 Cation-Exchange Reaction of Amino Terminated PS

As discussed in Chapter 1, the majority of the clay functionalization schemes
exploit the negatively charged surfaces on the layered-silicates. Typically, an oligomer is
functionalized with a positive endgroup and tethered to the surface of the clay. An
oligomer is used so that despite its hydrophobic nature, it can be dissolved in water due to
the strong ionic interactions with water which dominate over the large hydrophobic tail.
As such, it is sometimes desirable to use a higher molecular weight polymer to increase
the hydrophobicity of the modified layered-silicate, and various solvents of increasing
hydrophobicity are used in combination with water to prevent precipitation of the
surfactant. In our approach, we synthesized a variety of molecular weights of PS chains
and functionalized the endgroup with an amino group.
The terminating agent was synthesized by a cyclization reaction of 3-chloropropylamine with 1,1,4,4-tetramethyl-1,4-dichloro-1,4-disilabutane in methylene chloride, as described by Ueda et al. [16]. Purification of the product was carried out by fractional distillation under reduced pressure. The product was then distilled from triethyl aluminum in order to remove traces of moisture. The purified terminating reagent was kept under vacuum until further usage (see Figure 2.4). The total yield of the reaction was 35%.

\[
\begin{align*}
\text{Cl-} & \quad \text{NH}_2 \quad + \quad \text{Cl-} & \quad \text{Si-} & \quad \text{Si-} & \quad \text{Cl} \quad & \xrightarrow{\text{N(C_2H_5)_3}} \quad \text{Cl-} & \quad \text{Si-} \\
& \quad \text{Si-} & \quad \text{Si-} & \quad \text{CH}_2\text{Cl}_2 & \quad \text{Si-} & \quad \text{Si-} \\
\end{align*}
\]

**Figure 2.4:** The terminating agent reaction scheme for producing amino terminated polystyrene.

After obtaining the terminating agent, polystyrene was synthesized anionically as follows. First, the styrene was purified by adding a solution of 1M dibutyl magnesium in hexane to the degassed styrene until a yellowish color appeared [17]. After the solution was stirred in the dark for several hours, the hexane was carefully removed under reduced pressure while the solution was cooled with an ice bath. Afterwards, the styrene was condensed into an ampoule and transferred into a glove-box. The polymerization was then carried out in benzene at room temperature with sec-butyl lithium (sBuLi) as the initiator. Due to the formation of polystyryl-lithium aggregates in benzene, 20 vol% of tetrahydrofuran was added before terminating the reaction to shift the equilibrium to the side of the free ions (sites most likely for polymerization) which are in equilibrium with the contact ion pairs and solvent separated ion pairs (see Figure 2.5). This is required since the associated ion pairs do not possess a high enough reactivity to undergo a
reaction with the terminating agent even after several hours, as evidenced by the persistence of color. Subsequently, the terminating agent was added to the solution which became colorless in approximately 10 – 20 minutes, indicating the end of the reaction.

*Increasing polarity of the solvent*

\[ \text{M}^+ \quad \text{association equilibrium} \quad \text{contact ion pairs (tight)} \quad \text{solvent separated (loose) ion pairs (polar solvents)} \]

M: metal counter ion  
S: solvent  
-: carbanion of the living chain end of the polymer

**Figure 2.5:** Influence of the solvent polarity on the formation of different ion pairs during anionic polymerization

Finally, the protecting group was cleaved by precipitation of the reaction solution into methanol containing a small amount of hydrochloric acid. The reaction scheme is described in Figure 2.6.

**Figure 2.6:** Reaction scheme for synthesizing amino terminated polystyrene through anionic polymerization.

Thin layer chromatography of the final product indicates a nearly complete functionalization of the polystyrene. The GPC data reveals a unimodal distribution for all
amino functionalized polymers. Figure 2.7 shows the GPC trace for an amino functionalized polystyrene with a molecular weight of 5900 g/mol.

![GPC trace]

**Figure 2.7**: GPC trace of amino terminated polystyrenes ($M_n = 1400$ and 7000) showing a unimodal distribution and a low polydispersity. The slight tail towards lower molecular weights (higher elution volumes) is likely caused by the interaction of the amino group with the columns.

The slight tail in the GPC traces toward higher elution volumes is caused by the interaction of the amino group of the polystyrene with the column gels. This behavior is especially expressed in the sample with the lowest molecular weight. Table 2.1 summarizes the molecular weights and polydispersity for the two amino functionalized polystyrenes that have been synthesized which will be used to graft onto clay (TC) surfaces.

### 2.2.2 Surface Initiated Free Radical Polymerization of PS
The surface initiated polymerization from clay (FC) surfaces possesses an added benefit as compared to the attachment of a long chain molecule to the clay. Since the initiator will possess a far smaller exclusion volume as compared to the long chains, it is more likely that a stoichiometric amount of initiator will actually get tethered to the surface of the clay. This will lead to a higher grafting density of the chains on the clay surface at a given molecular weight which may have significant effect on the thermodynamic properties of the nanocomposite system. Thus, we have synthesized PS chains off the clay surface using a living free radical polymerization initiator as described by Puts and Sogah [18].

The initiator was synthesized exactly as described by Puts and Sogah and is restated here as it appears in the publication. Benzoyl peroxide (2.0 g, 8.3 mmol) and 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) (2.84 g, 18.2 mmol) were dissolved in 4-vinylbenzyl chloride (80mL). The mixture was heated for 24 hours at 80 °C. The reaction mixture was cooled to room temperature and the 4-vinylbenzyl chloride was evaporated with a rotary evaporator under high vacuum. The recovered 4-vinylbenzyl chloride had a reddish color due to some co-distilled TEMPO. The crude dark-colored residue was chromatographed over silica gel using a gradient elution which was started with 30% CH₂Cl₂ in hexanes and gradually increased to 100% CH₂Cl₂. The pure benzoic acid 2-(4-(Chloromethyl)phenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethyl ester (LFRP-TEMPO) was isolated as a clear oil. The LFRP-TEMPO was then mixed with trimethylamine (Me₃N) (97% grade) to obtain the final initiator as shown below.
Figure 2.8: Synthesis scheme for initiator to be used in living free radical polymerization to synthesize polystyrene off clay surfaces.

The LFRP-TEMPO was then redissolved in water, and ion-exchanged with sodium montmorillonite dispersed also in water using 10% excess LFRP-TEMPO. The clay was added dropwise into the LFRP-TEMPO solution to maintain an excess of the initiator relative to the layered-silicate. The increase in spacing from 0.97 nm to 2.2 nm clearly indicates that intercalation has occurred. Furthermore, the weight loss measured upon ignition of the organic component clearly shows that intercalation has occurred nearly stoichiometrically. Previously, Weimer et al. [19] have used the initiator modified clay to form an exfoliated high molecular weight PS nanocomposite. In our case however, we synthesized PS off the clay surface such that the number average molecular weights (Mn) were 870 and 6000 g/mol with a polydispersity index (PDI) of 1.5 and 1.2 respectively (see Table 2.1). The polymerization of the 6000 molecular weight PS was performed in bulk while the low molecular weight PS needed toluene as the amount of styrene monomers were not enough to fully wet the clay. After polymerization, the samples were dissolved in THF completely and precipitated in methanol. TGA analysis was performed on the resulting samples after completely drying in a vacuum oven for a few days at 60 °C and the measured weight loss confirms a nearly stoichiometric amount of PS chains.
<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1K TC</td>
<td>1300</td>
<td>1.12</td>
</tr>
<tr>
<td>7K TC</td>
<td>7100</td>
<td>1.04</td>
</tr>
<tr>
<td>1K FC</td>
<td>870</td>
<td>1.5</td>
</tr>
<tr>
<td>6K FC</td>
<td>6000</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Table 2.1: The molecular weight and the polydispersity index for polystyrene which will be grafted to clay (TC) or which was synthesized from clay (FC) surfaces.

2.3 Nanocomposite Sample Preparation

General methods of nanocomposite preparation have been outlined in Chapter 1. In general, there are 3 broad classes of sample preparation: in-situ polymerization, solution processing, and melt processing. Other than the in-situ polymerization of the PIB-PS from the clay surface, all other samples were prepared by solution blending the appropriate organically modified layered-silicate with a lamellar triblock copolymer. Subsequently, all the samples were roll-cast to produce oriented lamellar CBCP nanocomposites.

2.3.1 Dispersion of Nanocomposite in Solvent

In order to measure the correct weight fraction of the layered-silicates in the nanocomposite, the weight percentage of the organic component relative to the inorganic content was determined on all functionalized layered-silicates through thermogravimetric analysis (TGA) as described in a previous section.

Upon determination of the inorganic content of the functionalized nanocomposite, appropriate amounts of the dried clay were then dispersed in a THF/cumene (80/20 by weight) mixture to form a dilute 2 – 3 wt% solution. Horn sonicator was utilized for approximately 10 – 30 minutes in commercially available layered-silicates to promote
dispersion while in-house functionalized clay did not require horn sonication – a simple agitation or stirring of the flask was sufficient. In all cases, the solutions were clear with only a hint of cloudiness. Appropriate amounts of triblock copolymers were dissolved separately in the THF/cumene (80/20 by weight) mixture forming a clear 10 – 20 wt% solution. The two solutions were then subsequently combined together and allowed to stir for approximately an hour to ensure good mixing. The combined solution was then allowed to evaporate slowly on top of an agitator to prevent slow sedimentation of the layered-silicates in the absence of agitation. When the solution’s viscosity became similar to a thick viscous honey (typically a 30-45% solution), the samples were capped and were ready for roll-casting.

2.3.2 Roll-cast Films

The roll-casting technique, as briefly introduced in Chapter 1, permits the development of a well-oriented block copolymer morphology. We have found from repeated experiments that whereas the formation of a near single crystalline morphology in a cylindrical block copolymer is rather easy to obtain, the neat lamellar block copolymers is more complex: films with a fiber symmetric morphology as well as with a near single crystalline morphology in the perpendicular orientation (the parallel orientation has not been observed yet in neat triblocks) form depending on the processing conditions. Eisen [20] has shown using cylindrical triblock copolymers in cumene that orientation takes place progressively as the solvent evaporates and transfers to the stainless steel rollers. He reports that altering the stainless steel roller surface to a polyimide surface leads to transfer to take place at a slightly more dilute solution concentration and the resulting orientation is poorer than the samples obtained using
stainless steel rollers. Furthermore, from in-situ birefringence studies, he states that orientation begins to develop slightly before transfer from one roller to another and continue to progress even after transfer. From these reports, it appears that the choice of solvent is critical in obtaining the resulting morphology by controlling the evaporation rate. My observations are that typically, when a high boiling point solvent is used in combination with a cover box over the roll-caster, the lamellae prefer to orient in a near single crystalline morphology. For example, use of cumene with a cover box can result in a near single crystalline morphology with perpendicular orientation, whereas using toluene (higher evaporation rate) with a cover box can sometimes lead to a fiber symmetric morphology. This is the key reason for using a THF/cumene mixture in the preparation of our nanocomposites as the THF will provide a polar environment and help disperse the layered-silicates whereas the cumene is required to obtain a near single crystalline lamellar morphology. After the agitation/evaporation process described earlier, I believe that there is little THF left in the roll-cast ready solutions since the scent given off is predominantly of cumene. Regardless, in Chapter 3, a fiber symmetric morphology was observed due to the use of toluene as the single solvent as it was initially hoped to be a suitable compromise between the polarity and low vapor pressure without using two solvent combinations. After the results, the solvent system was changed to the THF/cumene combination described above, and they lead to a more near single crystalline orientation.

The specific details of the roll-casting will also be outlined. These procedures have been outline in other theses [13,20], but the conditions I’ve employed vary slightly. The rollers used were 19mm diameter Teflon and stainless steel cylinders. They were set at 16 rpm (30V DC when measured through voltmeter). The initial gap was set at
approximately 0.2 – 0.3 mm (each revolution of the micrometer corresponds to 0.5 mm separation distance) and clamped down to prevent a gap increase when the solution is subsequently poured. At this point, the viscous solution was slowly and evenly poured onto the gap. A bulge of the solution develops and the pouring is performed such that the size of the bulge is relatively constant throughout the rollers. The cover is then immediately placed on the roll-caster to slow down the evaporation rate. After some time, as the solvent evaporates, the bulge begins to shrink, at which point the rollers were squeezed slowly to maintain the bulge, at a rate which does not cause the solution to flow over to the side of the roll-caster (gap is closed approximately 0.02 – 0.03 mm each adjustment). Depending on the initial solution concentration and the amount of solution poured, a final tacky/solid film between 0.05 – 0.15 mm is obtained. The sample is then allowed to roll with the gaps still maintaining a pressure using the fixing screws for an additional 15 – 30 minutes, afterwards which the gap is increased so that the sample is allowed to slowly evaporate its solvent as the roller rotates without the cover. This is required so that the sample does not sag to one side during evaporation. After a few hours to overnight of rolling, a sharpened wooden or Teflon stick is wetted with a high vapor pressure solvent such as THF and a straight cut is made along the film. Subsequently, using a non-solvent such as isopropanol, the film is carefully taken off the rollers and put between two Teflon sheets which have spacers in between the sheets. The sample is then brought into a vacuum oven and pumped at ambient condition for at least 12 hours. This is followed by an increase in temperature to 60 °C and the sample is pumped for an additional day. This is to ensure that all the residual solvents have escaped from the sample. Afterwards, an annealing step is carried out at 110 – 120 °C under vacuum for at least day to promote further ordering of the microphase separated domains. These are the
typical procedures carried out to produce a roll-cast nanocomposite film and should be followed to obtain a near single crystalline sample.

2.4 Summary

This chapter outlined the various experimental techniques for synthesis and characterization of a nanocomposite. Specific emphasis was given for the correct characterization of the nanocomposite morphology as this may be the most error-prone step when trying to understand the fundamental structure property relationships. However, careful synthesis and property measurements of the nanocomposites should not be overlooked. Lastly, wherever applicable, the underlying reasons for a specific technique employed were hopefully elucidated.
2.5 References


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CHAPTER 3: Deformation Behavior of a Roll-Cast Layered-Silicate/Lamellar Triblock Copolymer Micro/Nanocomposite

3.1 Introduction

As a launching point of the study of a hierarchical nanocomposite, layered-silicate – lamellar triblock copolymer composites possessing isotropic texture were produced. Solution blending of the layered-silicate suspension with a block copolymer solution and subsequent static casting and annealing resulted in a partially immiscible and intercalated structure with only a low degree of exfoliation. These samples exhibit considerable increase in modulus, higher yield stresses, earlier onset of strain hardening, increased strain hardening rate, and higher residual strains upon unloading with increasing layered-silicate content than for the static cast pure triblock.

To further elucidate the effects of anisotropic particles upon the deformation mechanism, samples possessing a uniaxial block copolymer texture were produced through solution blending and subsequent roll-casting and annealing. Characterization shows that as before, the layered-silicates were of mixed morphology, dominantly consisting of immiscible clay tactoids along with some intercalated and exfoliated material for samples of varying (2.5 – 10wt%) clay content. The clay layer normals are parallel to the BCP layer normals and typically contain approximately 10 – 20 clay layers in a tactoid. In-situ and ex-situ deformation studies were performed along various directions on the roll-cast composite samples. Deformation parallel to the roll-cast direction shows an earlier onset of strain hardening with modest increases in the modulus for particle-loaded films compared to that of the roll-cast neat triblock. The evolution of the triblock copolymer microstructure with applied strain shows the break up of the
glassy polystyrene domains as was found for pure triblock copolymers. Upon unloading, the residual strain increases with increased clay content and the unloaded SAXS patterns show a distribution of lamellar spacings, suggesting significant effects due to the presence of the clay particles. Deformation perpendicular to the texture axis shows a dramatic increase in the tensile modulus compared to the unreinforced material. The evolution of microstructure with strain in this direction is reminiscent of a neat triblock copolymer where at high strains (~100%), the BCP layers kink to form the chevron morphology and the lamellar normals continue to rotate away from the deformation direction with increasing strain while maintaining a constant lamellar spacing. Unlike a pure triblock copolymer however, the chevron morphology remains locked in place upon unloading due to the presence of the layered-silicate particles.

3.2 Materials

Films of SIS were prepared from a commercial grade Vector 4411-D obtained from Dexco Polymers. The molecular weight of each of the PS blocks was 18,000, and the isoprene block was 44,000, giving a 45wt% styrene. The layered-silicate used in this study was a commercial organically modified grade Cloisite 10A (C10A) supplied by Southern Clay Products. The montmorillonite is organically modified by dimethyl benzyl hydrogenated-tallow ammonium with a cation exchange capacity (CEC) of 125 meq/100g. Sample preparation and characterization techniques were as discussed in Chapter 2.
3.3 Results and Discussion

3.3.1 Visualization of the Morphology

The lamellar spacing of the neat SIS triblock measured by SAXS is found to be approximately 28 nm. Since the volume fraction is 43% PS ($\rho_{PS} = 1.04$ g/cm$^3$), this approximately corresponds to PS layers of 12 nm and PI layers of 16 nm. The spacing of the neat dried C10A is approximately 1.9 nm as measured by XRD. XRD in Figure 3.1 shows the gallery height spacing of the as-received clay, clay cast after ultrasonication in toluene solution (residual toluene present), and the clay after incorporation into the SIS at 10% loading content. Note that a small amount of intercalation is suggested from the XRD measurements with a weak lower angle peak occurring at 3.4 nm in the 10wt% C10A/SIS system. The 1.7 nm peak is not the second order of the 3.4 nm peak due to its much stronger intensity and much narrower width, and corresponds to the first order peak of the immiscible clay tactoids. The observation of the weak, broad ~3.4 nm peak and the strong, narrow 1.7 nm peak in the XRD suggests that there is only a small amount of intercalation while the majority of the clay tactoids remain unchanged during the processing. The slight decrease in gallery spacing is attributed to the degradation and removal of the organic modifiers from the galleries during the sample annealing process [1]. Table 3.1 lists in detail the measured intercalated d-spacings of C10A in the various samples studied.
Figure 3.1: XRD patterns of dried C10A powder, C10A cast from toluene (residual toluene present), and C10A incorporated into SIS 4411D at 10 wt%. Smallest available slits were used to minimize parasitic scattering, and the background data collected using a glass slide was subtracted from all obtained plots. Note the increase in the peak spacings suggesting that intercalated structures are present.
<table>
<thead>
<tr>
<th></th>
<th>$d$-spacing of C10A (nm)</th>
<th>Young’s modulus (MPa)</th>
<th>Yield stress (MPa)</th>
<th>2% offset yield strain (%)</th>
<th>Rate of strain hardening (MPa)</th>
<th>Residual strain (unloaded)</th>
<th>Residual strain (annealed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dried C10A powder</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10A cast from toluene</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure SIS4411D (isotropic)</td>
<td>50 ± 5</td>
<td>2.1 ± 0.3</td>
<td>4.2 ± 1.3</td>
<td>0.7 ± 0.15</td>
<td>0.42 ± 0.1</td>
<td>0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>2.5wt% C10A/SIS (isotropic)</td>
<td>3.7</td>
<td>72 ± 8</td>
<td>3.6 ± 0.4</td>
<td>5.9 ± 1.1</td>
<td>1.3 ± 0.20</td>
<td>0.57 ± 0.1</td>
<td>0.04 ± 0.1</td>
</tr>
<tr>
<td>10wt% C10A/SIS (isotropic)</td>
<td>3.5</td>
<td>105 ± 6</td>
<td>4.6 ± 0.2</td>
<td>6.8 ± 1.0</td>
<td>3.1 ± 0.38</td>
<td>0.8 ± 0.1</td>
<td>0.32 ± 0.1</td>
</tr>
<tr>
<td>Pure SIS4411D (parallel)</td>
<td>153 ± 3</td>
<td>5.1 ± 0.2</td>
<td>4.4 ± 1.5</td>
<td>0.8 ± 0.22</td>
<td>0.4 ± 0.1</td>
<td>0.0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>2.5wt% C10A/SIS (parallel)</td>
<td>3.7</td>
<td>157 ± 3</td>
<td>4.8 ± 0.2</td>
<td>4.4 ± 1.3</td>
<td>0.9 ± 0.14</td>
<td>0.6 ± 0.1</td>
<td>0.03 ± 0.1</td>
</tr>
<tr>
<td>10wt% C10A/SIS (parallel)</td>
<td>3.4</td>
<td>165 ± 3</td>
<td>5.8 ± 0.2</td>
<td>4.7 ± 1.3</td>
<td>0.9 ± 0.10</td>
<td>0.8 ± 0.1</td>
<td>0.28 ± 0.1</td>
</tr>
<tr>
<td>Pure SIS4411D (perpendicular)</td>
<td>29 ± 2</td>
<td>1.8 ± 0.2</td>
<td>5.9 ± 0.8</td>
<td>0.7 ± 0.11</td>
<td>0.3 ± 0.1</td>
<td>0.0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>2.5wt% C10A/SIS (perpendicular)</td>
<td>3.7</td>
<td>62 ± 1</td>
<td>3 ± 0.3</td>
<td>5.5 ± 1.0</td>
<td>0.8 ± 0.10</td>
<td>0.45 ± 0.1</td>
<td>0.0 ± 0.1</td>
</tr>
<tr>
<td>10wt% C10A/SIS (perpendicular)</td>
<td>3.4</td>
<td>85 ± 3</td>
<td>3.8 ± 0.3</td>
<td>5.0 ± 0.9</td>
<td>1.0 ± 0.13</td>
<td>0.75 ± 0.1</td>
<td>0.21 ± 0.1</td>
</tr>
</tbody>
</table>

**Table 3.1:** Average clay layer spacings and mechanical properties of the various composite systems.

SAXS and the XRD measurements of simple cast 2.5 and 10wt% C10A/SIS composites show that whereas the block copolymer domain spacing is essentially unchanged, the spacing of the weak lower angle peak of C10A is now approximately 3.7 nm and 3.5 nm respectively. SAXS and WAXS measurements confirm that as expected the lamellar grains as well as the layered silicates are isotropically arranged.

Roll-casting develops a preferred orientation of the lamellae as evident in the SAXS patterns taken with the beam along $\hat{y}$ for the 0, 2.5, and 10wt% C10A filled SIS
samples as shown in Figures 3.2a-3.2c. For the incident beam along \( \hat{x} \), the SAXS pattern is almost circularly symmetric (see Figure 3.2d). These two observations demonstrate the roll-cast samples display an essentially uniaxial texture. The lamellae are thus arranged in grains whose normals lie approximately perpendicular to the flow direction (the \( x \)-direction). There is however some decrease in the quality of the alignment with increasing silicate content. Figure 3.2e also shows the WAXS pattern of a 10 wt% C10A/SIS with the x-ray beam along \( \hat{y} \) showing the preferential orientation of the silicate layers within and parallel to the lamellar morphology of the block copolymer (compare figure 3.2c and 3.2e).

![Figure 3.2](image)

**Figure 3.2:** Roll-cast samples of (a) 0, (b) 2.5, and (c) 10 wt% C10A/SIS 4411D showing the orientation of the SIS lamellae in SAXS. Note some loss of orientation with increasing amount of the layered-silicate. The lamellar spacing is constant at approximately 28 nm. (d) SAXS pattern of 2.5 wt% C10A/SIS viewed along the roll-cast direction. Note the near isotropic nature of the block copolymer domains. (e) WAXS pattern of the 10 wt% C10A/SIS 4411D showing preferential orientation of the layered silicates.
Thus, the roll cast composites of silicate and block copolymer are comprised of clay layers preferentially aligned parallel to the microdomain layers within the block copolymer matrix. The lamellae and the clay tactoids are both well oriented in the flow direction and the grains containing the SIS and clay tactoids possess a uniaxial symmetry about the flow direction.

Figure 3.3 shows a TEM micrograph of a large lamellar grain stained with osmium tetraoxide viewing along \( \hat{x} \) of the roll-cast 2.5wt% C10A/SIS. The dark periodic layers correspond to the OsO\(_4\) stained isoprene and the irregular and the elongated dark regions correspond to the aligned clay layers or tactoids. The micrograph also shows a few dark streaks suggesting individual clay layers that have fully exfoliated (arrowed regions). These individual clay layers do not contribute to a scattering peak in the XRD. The inset is a low magnification micrograph of an unstained sample (hence all the dark regions are clay tactoids) that shows the long-range orientation of the silicate bundles with a lamellar grain. It is important to note that we have selected a large lamellar grain for edge-on viewing so that nearly all of the tactoids are also edge-on resulting in good visualization of both the clay particles and the PS/PI layers. The area fraction of the clay in the particular region selected is somewhat above the 2.5% loading. This arises due to fluctuations in the local clay content from region to region and our selection of an area showing many clay particles. Micrographs of grains of different orientation, e.g. those in plan view viewed along the normal to the layers and clay particles, are of low contrast.
Figure 3.3: Bright field TEM image of a large lamellar grain in a roll-cast film of 2.5 wt% organically modified montmorillonite with 18-44-18K styrene-isoprene-styrene triblock. The clay particles are dispersed and oriented parallel to the oriented lamellae. The roll-casting direction ($\hat{x}$) is normal to the figure. The arrows indicate some fully exfoliated clay layers which are well aligned and located within individual PS layers.
Thus SAXS, WAXS, and TEM demonstrate that the roll cast composites can be treated as a hierarchical anisotropic block copolymer system that contains within the structure anisotropic fillers arranged with the same orientation as the microdomain layers within micron sized grains possessing a "fiber-like" symmetry about the roll-cast direction. A microstructural schematic of the oriented roll cast clay-BCP composite is shown in Figure 3.4.

The local chain orientation of the triblock near the clay layers merits a more detailed discussion. As shown in Figure 3.4, the system predominantly consists of nonintercalated tactoids, some intercalated material and a minor amount of exfoliated layers. There are two general possibilities for intercalation. First consider only the polystyrene chains are intercalated in between the layers to avoid the unfavorable isoprene-clay interaction ("edge intercalation"). It follows then that the two styrenic end-blocks are situated near the periphery of the clay layers with the middle isoprene block remaining outside the clay layers, and the PS end-blocks can either sit in the same gallery or in different galleries. Furthermore, assume a typical C10A particle is approximately 200 nm x 200 nm (average diameter of montmorillonite) and that the area coverage in the 'edge intercalation' is similar to the radius of gyration of the styrene end block which is approximately 2 nm. Then the relative proportion of PS intercalated edge area to the whole area is approximately 10%, suggesting only a very small amount of intercalation near the edge of the clay tactoids for this scenario.
Figure 3.4: a) Schematic diagram of the roll-cast samples showing the roll-cast directions and the deformation directions. $F_\parallel$ is referred to as the parallel direction and $F_\perp$ is referred to as the perpendicular direction. Note the uniaxial orientation of the lamellar grains. b) Magnified schematic within one grain of BCP domains, exfoliated, intercalated clay layer with possible block copolymer chain configurations, and non-intercalated clay tactoids. Block copolymer junctions are bold dots.
A second possibility is to consider that both types of blocks are incorporated into the clay layers ("full intercalation"). In fact, Ren et al. [2] and Lee et al. [3] have shown in low molecular weight styrene-isoprene diblock copolymers and for differently modified organophilic clay, the incorporation of both blocks occurs despite the unfavorable isoprene - clay interaction. If full intercalation is present, the triblock architecture also raises the possibility that locally within the clay layers, a 'shielding' effect may occur by having the styrenic chains preferentially spread against the clay surfaces allowing the isoprene block to occupy the center region and thus avoid the unfavorable interaction with the surface of the silicate layers.

3.3.2 Mechanical Properties
3.3.2.1 Isotropic Properties

The average mechanical property values are reported in Table 3.1. The tensile stress-strain behavior of the isotropic static cast samples is as shown in Figure 3.5. Whereas the neat SIS polymer showed no signs of necking, the composites containing the layered-silicates all exhibited necking behavior. The onset of strain hardening occurred at lower strains with increasing clay content, and the modulus of the composite systems increased at higher clay loadings. The yield stress, defined as $\frac{d\sigma}{d\varepsilon} = 0$ for samples which neck, is shown to increase while the yield strain, using a 2% offset criterion, is seen to decrease with increasing clay content. Furthermore, the rate of strain hardening, defined by $\left\langle \frac{d\sigma}{d\varepsilon} \right\rangle$ in the strain hardening regime, is shown to increase with increasing clay content. The undulations in the stress-strain curves arise when multiple necks formed
during deformation, with each drop in stress corresponding to the formation of a new neck.

The incorporation of clay particles results in a dramatic difference in the deformation behavior of the composites as compared to the neat triblocks. Modulus and yield stress increase, necking occurs along with an earlier onset of strain hardening, a higher strain hardening rate, and higher residual strains. The deformation observed in the isotropic case is due to the combined responses of grains deformed along various directions. A deconvolution of the observed effects may be understood by studying the deformation of the textured samples in the perpendicular and parallel directions.

![Isotropic Samples](image)

**Figure 3.5:** Stress-strain curves of static cast 0, 2.5, and 10 wt% C10A/SIS nanocomposites. Note that necking occurs in both samples containing layered-silicates. Note the increase in modulus, yield strength, and the onset of strain hardening occurs at lower strain with increasing clay content.
3.3.2.2 Parallel Loading

The tensile stress-strain behavior of the anisotropic roll-cast samples deformed along $\hat{x}$ is shown in Figures 3.6. In this direction, the onset of strain hardening occurred at lower strains for samples containing higher layered-silicates content. In this direction, there is however little effect of the clay content on the modulus, yield stress, yield strain and the rate of strain hardening. Upon unloading from 400% strain, the residual strain increases with higher clay loading. Further "healing" of the lamellar structure, measured through calipers, occurs after annealing at 120 °C in vacuum for 2 days. The final residual strain decreases to approximately 10% and to 40% for 2.5wt% and 10wt% samples, respectively.
**Figure 3.6**: Stress-strain curves of 0, 2.5, and 10 wt% C10A/SIS nanocomposites deformed in the parallel ($\hat{x}$) direction. Note that necking occurs in all the samples. The modulus is nearly constant despite increasing clay loading. However, there is an earlier onset of strain hardening with increasing clay content.

### 3.3.2.3 Perpendicular Loading

For deformation along the normal to $\hat{x}$ as shown in Figure 3.7, the tensile modulus dramatically increases (~2X for 2.5wt% loading and ~3X for 10wt% loading) whereas no significant changes in the strain hardening behavior can be observed. Furthermore, the yield stress is seen to increase with increasing loading content and the yield strain is seen to decrease with increasing loading content as is evident in the inset to Figure 3.7. Necking was observed for systems that contain clay as was observed for the
isotropic samples, whereas the neat roll-cast SIS samples did not exhibit necking when deformed along \( \varepsilon \). Furthermore, the rate of strain hardening increases with increasing clay content, and the residual strain (measured immediately after unloading from 400%) is also shown to increase. Lastly, annealing of the unloaded samples at 120 °C in vacuum for 2 days resulted in near full recovery to the initial sample dimensions, the original modulus and the initial lamellar spacing (see next section).

**Figure 3.7:** Stress-strain curves of 0, 2.5, and 10 wt% C10A/SIS nanocomposites deformed in the perpendicular direction. Note that necking occurs only in the clay containing composites and not in the neat SIS. The modulus is seen to double with only 2.5 wt% C10A.
3.3.3 In-situ Deformation Studies

In-situ SAXS deformation studies were performed for the roll-cast 2.5wt% and 10wt% C10A filled systems. Results obtained from the 2.5wt% C10A filled system are presented in Figures 3.8 and 3.9 below. Generally similar behavior was observed in the 10wt% system and is not shown.

3.3.3.1 Parallel Loading

Figure 3.8a and 3.8b correspond to SAXS patterns at 0 and 50% nominal strain, respectively with the incident beam along the \( \hat{y} \) direction. The (001) peak full width at half maximum (FWHM), which gives a measure of the variation of the normals to the grains of lamellae oriented along the \( \hat{x} \) direction, is approximately 60\(^\circ\) for the initial sample. The loss of Bragg peaks, accompanied by an elongated, diffuse streak perpendicular to the applied force, occurs in a necked region (see Figure 3.8b). The local strain at the neck can be approximated as the ratio of the initial area to the necked area, \( A_0/A_{\text{neck}} \). At 120% nominal strain, the local strain in the neck is measured to be approximately 350\%, 300\% and 200\% for 0wt%, 2.5wt% and 10wt% C10A/SIS, respectively. When the sample is unloaded from a nominal 400\% strain, the sample regains some ordering of the lamellar layers as evidenced by the reappearance of a single broad, weak Bragg peak. Furthermore, the FWHM is approximately 55\(^\circ\), and the elliptical shape of the scattering pattern suggests that the reformed lamellar morphology has a poorer degree of orientation with the lamellar spacing varying from approximately 23nm – 28nm depending on the orientation of the lamellar grain relative to the deformation direction.
Figure 3.8: In-situ synchrotron scattering of 2.5 wt% C10A/SIS 4411D deformed parallel to the roll-casting direction. a) unnecked region of the sample, b) necked region of the sample, c) unloaded sample showing a residual compressive strain of approximately 20%.

3.3.3.2 Perpendicular Loading

Figure 3.9a shows the nearly azimuthally isotropic SAXS diffraction pattern of an initial undeformed sample viewed along $\hat{x}$. Upon deformation, Figure 3.9b (50% nominal strain) shows the loss of Bragg intensity along the force (vertical) direction and along the perpendicular to the force direction, and the buildup of intensity at intermediate angles. There is some increased diffuse scattering near the equator similar to that observed in the parallel deformation experiment. With increasing strain, a well-defined four-spot diffraction pattern appears around 100% nominal strain (Figure 3.9c). The angle
\( \alpha \) between a reflection and the force direction is about 65° and the lamellar spacing is approximately 28 nm. These four-spots continually rotate away from the deformation direction at constant lamellar spacing, reaching \( \alpha = 85^\circ \) at 400% nominal strain. When the samples are unloaded, \( \alpha \) decreases to approximately 50° (Figure 3.9f). Thus as the samples are unloaded, the chevrons do not fully relax back to the initially unkinked lamellar structure as has been observed in pure triblock copolymer systems [4], but only partial relaxation occurs. Cycling the system to 400% strain and back to the unloaded state does not erase the chevron morphology in the unloaded state nor change the residual strain.

\[ \begin{align*}
\text{(a) & } 0\% \\
\text{(b) & } 50\% \\
\text{(c) & } 100\% \\
\text{(d) & } 200\% \\
\text{(e) & } 400\% \\
\text{(f) & } \text{Unloaded}
\end{align*} \]

**Figure 3.9:** In-situ deformation scattering of 2.5 wt% C10A/SIS 4411D deformed perpendicular to the roll-cast direction (along \( \hat{z} \)) viewed along \( \hat{x} \). a) initial, b) at 50% strain, c) at 100% strain, d) at 200% strain, e) at 400% strain, f) unloaded state (residual strain = 45%).
Figure 3.10 shows the TEM (edge-on view) of a large grain in an unloaded sample that was preferentially stained with OsO₄. Note the numerous chevrons that are present with $\alpha \sim 50^\circ$ as determined from the FFT in the inset. Interestingly the orientation of the clay tactoids, most of which have fallen out during the sample microtomy process, is now on average nearly perpendicular relative to their initial orientation in the undeformed state.

![TEM Image]

**Figure 3.10**: Bright field TEM image of roll-cast film of 2.5 wt% organically modified montmorillonite with 18-44-18K styrene-isoprene-styrene triblock which was stretched to 400% and unloaded (residual strain ~ 45%). The bright white regions correspond to voids where clay tactoids have fallen out during sample preparation. These are preferentially oriented perpendicular to the initial orientation direction. Inset shows fast Fourier transform (FFT) of this image area. the average value of $\alpha$ is approximately 50° in good agreement with SAXS on the unloaded samples.
3.3.4 Interpretation of the Deformation Results

3.3.4.1 Parallel Deformation

The key features of deformation along the roll-cast direction are the apparent insensitivity in modulus and strain hardening rate with respect to the clay content, but the earlier onset of strain hardening and increased residual strains with higher clay loading content. Furthermore, the distribution in the lamellar spacings also illustrates the effect of the clay particles in the unloading behavior of these composites.

Previous work by Cohen et al. [4] showed under parallel deformation, the PS layers initially take up most of the load, followed by a fragmentation of the PS domains leading to the necking phenomenon. This latter process leads to void scattering as evidenced in the SAXS patterns as shown in Figure 3.8b. The onset of strain hardening is attributed to further fragmentation of the glassy remnants.

The apparent insensitivity of the tensile modulus for deformation along the \( \hat{z} \) direction to the amount of clay loading is indicative of the fact that as in a pure triblock copolymer system, most of the initial force is taken up by the PS glassy domains. Necking occurs at relatively constant strain for the various loading contents.

Interestingly, the yield stress is slightly less at 2.5wt% loading compared to the 0% and 10% samples. This may simply be the result of surface imperfections of the clay filled tensile samples causing initiation of necking at lower stresses. At necking, diffuse scattering arises in the necked region, whereas the unnecked portions of the sample still show the original lamellar SAXS pattern, suggesting the breakup of the glassy PS layers occurs along with the formation of voids in the necked regions as has been observed in pure triblock copolymers. The earlier onset of strain hardening in parallel loading with
increasing loading content of clay indicates an earlier fragmentation of the glassy PS remnants. This suggests that the clay tactoids may induce stress concentrations in the SIS around them leading to PS fragmentation and earlier strain hardening behavior. However, the apparent insensitivity of the strain hardening rate suggests that the after the final PS fragmentation, the strain hardening is purely dominated by the stretching of the rubbery isoprene domains.

Upon unloading, the retractive forces, which are dominantly from the stretched rubber chains, are competing with not only the back stresses of the plastically deformed PS layers, but also with the clay layers that are present in the sample. This leads to a larger residual strain and a higher degree of disorder upon unloading as shown by the distribution in lamellar spacing and the elliptical shape of the SAXS scattering pattern.

3.3.4.2 Perpendicular Deformation

The key features of deformation along the normal to the roll-cast direction are significant increases in modulus, yield stress and residual strain, increased strain hardening rate, and neck formation. Furthermore, the formation and locking-in of a chevron texture as evidenced by the four-spot diffraction pattern in SAXS and the elongated kink boundaries imaged in TEM clearly elucidate how the morphology evolves during deformation.

SAXS patterns indicate the grains initially possess a uniaxial rotational symmetry about the x-axis. Thus in the perpendicular deformation, the angle between the force axis and the lamellar normal varies from 0° to 90°.

The modulus $E_\theta$ can be expressed as:
\[ \frac{1}{E_{\theta}} = S_{33} \cos^4 \theta + (2S_{13} + S_{11}) \sin^2 \theta \cos^2 \theta + S_{11} \sin^4 \theta \]  

Eq. 3.1

where \((\theta - 90)\) is the angle between the deformation direction and the lamellar normal and the \(S_{ij}\) are the 4 independent compliances. Index 3 refers to \(\theta = 0^\circ\) and indices 1 and 2 refer to any of the equivalent transverse directions [5]. Thus the modulus is maximum at \(\theta = 0^\circ\) and decreases rapidly as \(\theta\) increases reaching a shallow minimum at \(45^\circ\). The effective transverse modulus thus depends on the weighted average of the various lamellar orientations with respect to the direction of the applied force. For the isotropic static cast samples, the diffraction from the grains is uniformly distributed over the surface of a sphere, whereas for the uniaxial roll-cast samples, the normals to the layers in a grain are uniformly distributed over a circular ring where the thickness of ring is defined by the equatorial spread of the SAXS intensity pattern (for example, see Figure 3a for 2.5wt% loaded sample). The greatest contribution of a grain of lamellae occurs when the force direction is orthogonal to the lamellar normal, which occurs more often in the isotropic distribution, consistent with the 1.7x higher tensile modulus of the unfilled isotropic samples compared to that of the transverse modulus of the roll-cast sample.

Additional complexities arise due to the presence of the clay. Since the tactoids align parallel to the layers in a given lamellar grain, the clay-filled composites consist of alternating stiff PS layers and rubbery PI layers with rigid clay tactoid particles. The reinforcement due to the clay is readily apparent for the 2.5% and 10% clay filled isotropic samples and particularly for uniaxial samples in perpendicular loading where the modulus increases almost a factor of 3X over the unfilled SIS.

The SAXS and TEM data allow insight into the deformation behavior of these composites. We first discuss the deformation of a neat near-single-crystal lamellar
styrene-butadiene-styrene (SBS) triblock copolymer reported by Cohen et al. [4,6], then discuss the deformation behavior of our samples, in particular with respect to the SAXS scattering patterns.

For a near-single crystal sample deformed along the lamellar normal ("perpendicular deformation"), Cohen et al. [4,6] have shown the layers start to undulate near defect sites at low strains. At higher strains the undulations fold into a chevron morphology, followed by the formation of distinct kink boundaries. The deformation was affine with the macroscopic strain, \( \lambda \), simply given by \( 1/\cos \alpha(\lambda) \). Immediately upon unloading, the macroscopic residual strain is about 40% and the initial lamellar period returns without noticeable residual layer strains. Annealing above the Tg of PS results in full recovery.

Cohen et al. also showed that for single crystal samples oriented 45° to the deformation direction, the majority of the sample responds via the rotation of the lamellar normal away from the loading direction with increasing strain. However, due to lateral forces from Poisson contraction, small portions of the layers form narrow asymmetric kink bands aligned with the kink boundaries parallel to the force direction. Upon unloading, the initial 45° orientation is returned but with somewhat poorer ordering of the lamellae.

The scattering pattern observed in Figure 3.9b represents the contributions from lamellae deformed at various orientations with respect to the loading direction. Due to the uniaxial symmetry, only the first quadrant of the scattering pattern needs to be considered. Those grains oriented at 45° with the lowest effective modulus, respond initially to deformation by reorienting their normal toward the 0° (force) direction. After this initial response, other grains oriented in various directions respond when the critical stress to
‘activate’ these grains has been reached. In particular, the transversely loaded lamellae begin to undulate and fold leading to a decreased scattering along the loading direction. A four-point scattering pattern may already be embedded in Figure 3.9b, but the presence of strong reflections at $0^\circ$ from the parallel loaded lamellae masks this observation. This suggests that the layer fragmentation, as evidenced in the parallel deformation, has not yet occurred at this strain (50%), which is significantly higher than the strain at the onset of necking in the parallel deformation (~5% - see Figure 6). The macroscopic necking phenomenon observed near 6 – 8% strain in the perpendicular deformation is probably purely due to the presence of the clay that causes local stress concentrations around the clay tactoids as necking is an inhomogeneous yielding phenomenon observed when a maximum load is followed by nonuniform or localized deformation [7].

Upon further deformation, the critical stress to fragment those lamellae with normals at $0^\circ$ is locally exceeded and the diffuse scattering oriented principally along $0^\circ$ can be attributed to the breakup of the PS layers oriented parallel to the deformation direction. The loss of the scattering along the $90^\circ$ and $0^\circ$ directions allows easy identification of the chevron pattern with $\alpha = 65^\circ$. At higher deformation, the layer normals continually rotate away from the deformation direction without appreciable changes in the lamellar spacing as shown in Figures 3.9c-3.9e where the strain reaches 400% and $\alpha = 85^\circ$.

Our results show that the measured $\alpha$ is always somewhat larger than the value expected by assuming an affine deformation model during deformation. For example, at 100% strain $\alpha = 65^\circ$ vs. $60^\circ$, at 200% strain $\alpha = 80^\circ$ vs. $70^\circ$, and at 400% strain $\alpha = 85^\circ$ vs. $78^\circ$. The necking phenomenon can be initially attributed to the higher $\alpha$ values. However, after strain hardening, the nominal strain and the actual strain should be nearly
identical. This suggests that the presence of the clay causes the rotating layers to effectively experience a larger strain than the overall average sample strain.

The TEM micrographs suggest that during deformation at high strains, not only do the BCP lamellar normals continually rotate away from the deformation direction, but the clay layer normals also rotate away from the deformation direction. Upon unloading, the elastic restoring force of the isoprene blocks causes the lamellae to reorient back toward their initial orientations, but the clay tactoids remain aligned essentially along the initial deformation direction; restricting the relaxation of the chevrons. This ‘locking’ force induced by the presence of the clay layers accounts for the observed increases in the residual strain with increasing loading content.

3.4 Conclusion

Rollcasting has been used to produce highly oriented clay - triblock copolymer micro/nanocomposites. Observation of the microstructure with XRD and TEM shows that only a small amount of partial intercalation and exfoliation has occurred. These composites exhibit dramatic differences in mechanical behavior from that of the neat triblock copolymer. Static cast, isotropic polygranular samples exhibit increases in modulus and yield stress, necking phenomenon, earlier onset of strain hardening, higher strain hardening rate, and higher residual strains as the clay content is increased. Roll-cast samples possessing a uniaxial symmetry of the lamellar grains have the layered-silicates well oriented in the flow direction and parallel to the block copolymer layers in a given grain. These anisotropic samples were deformed in directions parallel and perpendicular to the roll cast direction. In the perpendicular deformation, modulus, yield stress, strain hardening rate, and residual strain are shown to increase with increasing clay content. The
unloading of a highly deformed sample shows the chevron morphology has been partially
locked-in due to the presence of the rigid clay particles. The parallel deformation studies
suggest that the effect of the clay particles is dominant in the higher strain deformation
and unloading regions as evidenced by earlier onset of strain hardening behavior and the
increased residual strain.

The understanding of the evolution of the anisotropic morphology during
deformation is generally applicable to many nanocomposite studies. These results
illustrate the importance of considering the symmetry of the nanocomposite system that
may be developed during processing operations. Thus, future studies should be
increasingly aware of the effects of global orientation to the mechanical properties of the
nanocomposites investigated.
3.5 References


CHAPTER 4: Temperature Dependent Deformation Behavior of a Near-Single Crystalline Intercalated Clay-Block Copolymer Nanocomposite

4.1 Introduction

The previous chapter focused on demonstrating the improvements in mechanical properties and illustrating new deformation mechanism of thermoplastic elastomers with a few weight percent of incorporated layered-silicates. The various morphological states of the layered-silicates, mainly as an immiscible component, precluded a clear understanding of the basis for the enhanced mechanical properties of the nanocomposite. Furthermore, the precise mechanisms in perpendicular deformation need further clarification due to the fiber symmetric nature of the block copolymer films tested. Thus, through further efforts, I produced a near-single crystalline nanocomposite, composed of layered-silicate and lamellar triblock copolymers. Use of a more hydrophobic organic modifier of the layered-silicate resulted in a purely intercalated system and roll-casting produced a morphology such that the clay lamellar normals are perpendicular to the block copolymer lamellar normals.

At ambient conditions, the CBCP nanocomposite shows a modest 30% increase in the tensile modulus in perpendicular deformation compared to the unreinforced material. Unlike the neat BCP which, for F_1, uniformly forms a chevron morphology throughout the sample at yield, the CBCP necks with the lamellar layers kinking to form chevrons only within a well-defined neck. This is similar to the observation of the immiscible clay-BCP sample in Chapter 3. The local strain at necking is approximately 400% as compared to 280% in the previous sample in Chapter 3. During the unloading cycle, the chevron morphology relaxes uniformly, but the presence of the layered-silicate particles retards
full recovery to its initial state. The residual strain is approximately 40% when unloaded from 500% strain which is comparable to the neat triblock copolymers ($\epsilon_r \approx 30\%$) and the immiscible system ($\epsilon_r \approx 50\%$).

Additionally, in light of the increased heat deflection temperatures observed in various exfoliated and intercalated homopolymer nanocomposites, the role of the clay on deformation mechanisms that occur at elevated temperatures is also of significant interest. The work by Cohen et al. [1] in the temperature dependent deformation behavior of near-single crystalline lamellar thermoplastic elastomers is a valuable reference for the study of our nanocomposite systems. These investigations show how the gradual decrease of mechanical contrast between the rubbery and the glassy domains due to lowering of the PS modulus with increasing test temperature finally leads to a disappearance of chevron formation for perpendicular deformations at 20°C above the glass transition temperature of the PS block. For testing at the $T_g$ of the hard domains, they find very good agreement with an affine deformation model based on a combination of dilation and rotation of the lamellae/chevrons, as discussed in Chapter 1.

CBCP nanocomposites deformed at and 20°C above the glass transition temperature of the styrenic block, (which is elevated (85 °C vs 80 °C) and broader), no longer exhibit necking behavior. Elevation of the test temperature to 105 °C indeed does erase the formation of chevrons as was observed by Cohen et al. in a neat triblock and the system dilates without any noticeable BCP tilting up to fracture. However, a significant deviation from the affine deformation model is observed (for example, $d/d_o = 1.3$ at $L/L_o = 1.6$). These results indicate that the clay induces a heterogeneous mode of deformation even at these elevated temperatures as the evolution of the SAXS patterns do not follow an affine deformation model as proposed by Cohen [1] or Kratky [2].
4.2 Materials

Films of clay-SBS nanocomposites were prepared from a commercial grade Vector 4461-D obtained from Dexco Polymers and 2wt% Cloisite 15A. The molecular weight of each of the polystyrene blocks was 18,500 g/mol, and the polybutadiene block was 45,000 g/mol, giving a 45wt% styrene which microphase separates into a lamellar structure [1]. The layered-silicate used in this study was a commercial organically modified grade Cloisite® 15A (C15A) supplied by Southern Clay Products and is reported to be the most hydrophobic of their products. The montmorillonite is organically modified by dimethyl dihydrogenated-tallow quaternary ammonium (43% organic content by weight) with a cation exchange capacity (CEC) of 125 meq/100g.

4.3 Results and Discussion

In the following, the morphology of the nanocomposite will be discussed first. Secondly, the deformation mechanism of the perpendicular deformation will be illustrated followed by the discussion of temperature dependent deformation studies.

4.3.1 Visualization of the Morphology

The lamellar spacing of the SBS triblock measured by SAXS is approximately 26.0 nm, which corresponds to PS layers of 12 nm and PB layers of 14 nm. XRD in Figure 4.1 shows the gallery height spacing of the C15A clay after vacuum drying at 80 °C for 4 days and the clay after incorporation into the SBS at 2wt% inorganic content loading. The layer spacing of the dried C15A powder is 3.11 nm as measured by XRD. Note that intercalation has occurred in the roll-cast film with the clay layer spacing...
increased from 3.11 nm to 3.44 nm without any XRD evidence of immiscible clay layers. TEM will also show that these CBCP samples do not have any exfoliated layered-silicates.

![XRD curve](image)

**Figure 4.1:** XRD showing intercalation of the C15A layered-silicates when roll-cast. The initial layer spacing of 3.11 nm increases to 3.44 nm when mixed with SBS4461.

Roll-casting develops a near single crystal BCP texture with the lamellar normal oriented along \( \hat{z} \) (the so-called “perpendicular orientation”) as evident in the SAXS patterns taken with the beam along \( \hat{y} \) and \( \hat{x} \) as shown in Figures 4.2a and 4.2b, respectively. The weaker scattering peaks at lowest \( q \) values in Figure 4.2a correspond to the first order SAXS peak due to the second harmonic of the non-monochromatic x-ray beam and should be ignored. Figure 4.2b shows the SAXS pattern taken at a smaller sample-to-detector distance with the x-ray beam along \( \hat{x} \), thereby showing the
preferential orientation of the intercalated silicate layers at 90° to the BCP layers due to roll-casting. The Hermans orientation function, $-0.5 \leq P_2 = \frac{1}{2} (3\cos^2 \phi - 1) \leq 1$, was used to measured the distribution of the two component orientations from this pattern and was evaluated following the techniques outlined by Mitchell and Windle [3,4]. The orientation function is measured to be $+0.94 \pm 0.05$ for the PS/PB layers and $-0.30 \pm 0.03$ for the clay layers.

![Diagram](image)

(a)

![Diagram](image)

(b)

**Figure 4.2:** 2D SAXS patterns illustrating the near single-crystalline nature of the BCP viewed along the neutral axis (a) and along the roll-cast direction (b). The sample-to-detector distance has been adjusted in (b) allowing the determination of the orientation of the layered-silicates which are clearly perpendicular to the orientation of the BCP layers.

Figure 4.3 shows a TEM micrograph of a large lamellar grain of the roll-cast 2wt% C15A/SBS stained with osmium tetraoxide viewed along $\hat{x}$. The dark periodic
layers correspond to the OsO$_4$ stained butadiene domains. The high magnification inset in Figure 4.3 shows the intercalated clay layers in a clay particle. Note that the lamellar normals of the BCP domains are on average perpendicular to the clay lamellar normals. However, in the vicinity of the clay layers, some of the BCP lamellae rotate to lie parallel to the clay layer normals. TEM observations on many microtomed sections also suggest little or no exfoliation has occurred as individual clay layers were not present. We thus conclude that the system consists of purely intercalated system without any immiscible or exfoliated layered-silicates.

Thus, XRD, SAXS, and TEM all demonstrate that this roll-cast CBCP nanocomposite is comprised of intercalated clay particles (approximately 10 – 20 layers per particle) preferentially aligned in the parallel orientation. Furthermore, these layered-silicate normals are perpendicular to the near single crystalline BCP microdomain layer normals which are in the perpendicular orientation. A microstructural schematic of the oriented roll cast clay-BCP composite is shown in Figure 4.4.
Figure 4.3: Bright field TEM of 2% C15A/SBS4461 stained for 2 hours with OsO₄ viewed along the roll-cast direction. The orientation of the clay layers is perpendicular to the orientation of the BCP as has been observed in the SAXS patterns. The high magnification inset shows the intercalated bundles of the layered-silicates which have approximately 10 – 20 layers and some preferential templating of the BCP domains to be parallel with the layered-silicates.
Figure 4.4: Schematic illustration of the orientation developed in the CBCP nanocomposite during roll-casting. (a) The block copolymer domains lie in a perpendicular orientation with the lamellar normals pointing in the z-direction relative to the flow field (x-direction). This is similar to the orientation developed in a neat triblock copolymer. (b) The intercalated layered-silicates are aligned perpendicular with respect to the neat block copolymer domains. A few lamellae adjacent to the clay particles are parallel to the clay layers.
4.3.2 Deformation at Ambient Conditions

4.3.2.1 Macroscopic Mechanical Properties

The tensile stress-strain behavior of the anisotropic roll-cast samples deformed parallel and perpendicular to the roll-cast axis is shown in Figure 4.5. For all mechanical property studies in this chapter, the gauge length was 5 mm and the strain rate was 3.14 mm/min. For ambient conditions, when deformed along \( \hat{x} \) (parallel deformation), the modulus of the nanocomposite system is 160 ± 10 MPa showing little effect of the clay (180 MPa for the neat triblock copolymer). The slight drop can be expected from the slightly higher azimuthal spread of the CBCP sample lamellar normals (FWHM = 15° vs 10° for the neat triblock). The yield stress is approximately the same as that of the neat triblock copolymer, both measured to be approximately 5 MPa. Upon necking, the strain needed to achieve a steady stress plateau during neck propagation is significantly increased from that of the neat block copolymer. The onset of strain hardening for the nanocomposite system occurs at 330 ± 20% which is similar to the neat triblock copolymer (300% strain). Upon unloading from 500% strain, the residual strain is 80 ± 5% as compared to 40% strain for the neat triblock copolymer.

For deformation along \( \hat{z} \) at ambient conditions (perpendicular deformation), the tensile modulus increases to 90 ± 3 MPa relative to the neat triblock copolymer (65 ± 3 MPa). Furthermore, necking was observed for systems that contain clay, whereas the neat roll-cast SBS samples did not exhibit necking when deformed along \( \hat{z} \) with the yield stress both approximately 3 MPa. The onset of strain hardening is 420 ± 30% which is larger than the neat triblock copolymer (300% strain) and the residual strain upon unloading from 500% strain is approximately 40 ± 10% which is approximately the measured value for the neat triblock copolymer. These data are summarized in Table 4.1.
**Figure 4.5:** (a) Stress-strain curves of the 2% C15A/SBS4461 roll-cast film deformed parallel and perpendicular to the roll-cast direction at ambient conditions are shown. The perpendicular deformation for 85 °C and 105 °C are also shown. Note that necking occurs in perpendicular deformation at ambient conditions, but not at elevated temperatures. (b) Comparative stress-strain curves of neat and 2% C15A/SBS4461 roll-cast films deformed parallel and perpendicular to the roll-cast direction at ambient conditions are shown. The modulus is shown to increase approximately 40% in the perpendicular orientation at ambient conditions, but exhibit little or no change in the other conditions studied.
<table>
<thead>
<tr>
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<th>Neat Triblock Copolymer</th>
<th>Intercalated Nanocomposite</th>
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<tr>
<td></td>
<td>10°</td>
<td>15°</td>
</tr>
<tr>
<td></td>
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<td>Perpendicular</td>
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<tr>
<td><strong>FWHM</strong></td>
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<td>65</td>
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<tr>
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<tr>
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<td>3</td>
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<tr>
<td>(MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Onset of strain hardening</strong></td>
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<td>300%</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Residual strain</strong></td>
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<td>40%</td>
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<td></td>
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<tr>
<td><strong>FWHM</strong></td>
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Table 4.1: Comparison of mechanical properties for SBS neat triblock copolymer and 2wt% intercalated nanocomposite. Data for the neat triblock are taken from Cohen et al. [5].

From these results, the necking phenomenon observed in perpendicular deformation in the near single crystal nanocomposite system can now, unlike the uniaxially textured sample in Chapter 3, be unequivocally attributed to the presence of the clay layers. These tactoids most likely lead to local stress concentrations which in turn lead to neck formation.

These findings are however also somewhat surprising since in Chapter 3, I have shown a nearly two-fold improvement in the modulus (29 MPa vs 62 MPa) during perpendicular deformation in a uniaxial SIS triblock copolymer with 2.5wt% clay, incorporated predominantly as an immiscible microcomposite with some intercalated and exfoliated sheets. The relatively smaller increase in the modulus in the current sample may be due to two factors; intercalated clay nanocomposites do not significantly increase modulus, and/or the orientation of the clay normals relative to the deformation direction and to the BCP layers are important in property enhancements. Simple measurements on
isotropic cast samples of C15A/SBS4461 also possessing an intercalated morphology however disprove the second postulate since the modulus enhancements observed are again only approximately 40% higher than the neat isotropic triblock copolymer. This indicates that pure intercalation does not significantly enhance tensile modulus which is consistent with various other studies on intercalated homopolymer nanocomposites [6-8].

4.3.2.2 In-situ SAXS Deformation Studies

In-situ SAXS deformation studies were performed for the roll-cast 2wt% filled systems. Results obtained for deformation along $\hat{x}$ ($F_h$) are reminiscent of the results obtained previously [9] and are not discussed further. Namely, BCP lamellae break up in the necked regions creating void scattering (streaks along $\hat{z}$ in SAXS patterns), and upon unloading, the lamellar peaks return.

Figure 4.6a shows the near single crystalline SAXS diffraction pattern of an initial undeformed sample viewed along $\hat{x}$. Upon deformation along $\hat{z}$ ($F_\perp$) and after yielding, the regions outside the neck continue to exhibit a single crystalline nature, whereas the necked regions of the sample show the formation of a distinct chevron morphology (Figure 4.6c). Figure 4.6b shows the SAXS scattering patterns near the neck region where the onset of chevron formation is distinctly evident. The angle $\alpha$ between the (001) reflection and the force direction in Figure 4.6c is approximately 70° and the lamellar spacing is approximately 26 nm. These four-spots remain at nearly constant angle until onset of strain hardening reaching $\alpha = 75°$ and a lamellar spacing of 27 nm at 500% nominal strain. Note however that very small changes in $\alpha$ at these high strains account for a very large increment in deformation.
Figure 4.6: In-situ synchrotron scattering patterns of the roll-cast film deformed perpendicular to the roll-cast direction at ambient condition and viewed along the roll-cast direction: (a) initial, (b) near the necking region, (c) 250% strain in the neck, and (d) unloaded from 500% strain. Upon loading, $\alpha$ does not change until approximately 400% strain which is the measured local strain within the neck, but it decreases continually during unloading until it reaches a residual strain of approximately 30%.

As discussed in Chapter 3, the necking phenomenon does not allow for an affine deformation model. The SAXS pattern obtained in the neck is reminiscent of the SAXS pattern obtained in a neat triblock copolymer at 400% strain [5]. The measured local strain within the neck, approximated by the ratio of the cross-sectional area before and after necking ($A_o/A_{neck}$), is also about 400%. These results again confirm that there is a significant amount of stress localization near the layered-silicates as discussed in Chapter 3.

The unloading cycle is reminiscent of a pure triblock copolymer system, where the chevrons are relaxed uniformly throughout the sample with decreasing strain. Namely, $\alpha$ decreases while the lamellar spacing remains approximately constant. As shown earlier in the fiber symmetric clay-filled nanocomposite system in Chapter 3, the chevrons are evident even when the applied load has reached zero (in-situ azimuthal intensity integrations). However, after a period of a few hours, the original lamellar orientation returns whereas the sample from the previous chapter showed chevrons in the TEM after approximately 3 weeks of relaxation at ambient conditions. The TEM (Figure 4.7) of the
2% C15A/SBS4461 clearly demonstrates full relaxation of the structure does indeed occur. This is to be expected since for the 90° oriented clay particles the loading direction will not cause any rotation of the layered-silicates during chevron formation. Thus, the clay particles do not hinder the back-rotation of the chevrons. However, relaxation times are prolonged over that of the neat triblock since the chevrons must move the layered-silicates laterally during relaxation.

![Image of bright field TEM image](image)

**Figure 4.7:** Bright field TEM image of a roll-cast film stretched to 400% strain and unloaded. The sample shows the regions where the chevrons were present, but has relaxed near to its original orientation during sample preparation. Note the BCP lamellar normals are again approximately orthogonal to the layered-silicate (circled) normals.

Thus, for intercalated BCP nanocomposites, modest mechanical property improvements are observed. While much of the morphological response in the parallel deformation is similar to those of neat triblock and immiscible microcomposites, in the perpendicular deformation, necking occurs due to the presence of the clay and the necked regions exhibit chevron formation. Upon full propagation of the neck throughout the
sample, strain hardening takes place at approximately 400% strain which causes a slight tilting of the chevrons. Upon unloading, the chevrons are temporarily hindered due to the presence of the oriented layered-silicates but eventually relax.

4.3.3 Deformation at Elevated Temperatures

SBS possesses a mechanical and a chemical contrast at room temperature. One can effectively create a homogeneously rubbery material still possessing a chemical contrast by increasing the temperature. Cohen et al. [1] have shown using an SBS triblock tested above the PS $T_g$, the unentangled nature of the melt of the styrenic endblocks. As a result of the softening of the PS, the modulus and the ultimate tensile strain are significantly reduced at elevated temperatures. However, there have been numerous reports of increased thermal stability of nanocomposites in homopolymer-clay systems. So if we combine clay in a SBS material, there is a possibility for enhanced mechanical properties of the nanocomposite at elevated temperatures which needs investigation. Furthermore the heterogeneous deformation observed at room temperature may disappear at elevated temperature as the glassy-rubbery BCP nanocomposite essentially behaves as a rubbery material further elucidating the role of the layered-silicates in the deformation behavior of these nanocomposites.

Results for the perpendicular deformation, as shown in Figure 4.5, however show that the moduli and the ultimate tensile strains of the nanocomposite at the various temperatures are similar to that of the neat triblock copolymer system (see Table 4.2). In other words, the layered-silicates do not appreciably affect the deformation behavior of these particular nanocomposites at elevated temperatures. Additionally, there is no macroscopically observable necking phenomenon occurring at these elevated
temperatures suggesting that the presence of the layered-silicates do not significantly affect the deformation behavior at elevated temperatures. However, these particular mechanical property measurements may simply not be a sensitive enough tool to gauge the effect of the layered-silicates in the deformation behavior. The ensuing sections show a study of the microstructural evolution during deformation as a function of temperature is insightful.

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<th>Neat Triblock Copolymer</th>
<th>Intercalated Nanocomposite</th>
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<tbody>
<tr>
<td></td>
<td>At $T_g$ (80 °C)</td>
<td>At $T_g$ (85 °C)</td>
</tr>
<tr>
<td></td>
<td>Above $T_g$ (100 °C)</td>
<td>Above $T_g$ (105 °C)</td>
</tr>
<tr>
<td>Modulus (MPa)</td>
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<td>10</td>
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<tr>
<td>Strain at fracture</td>
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<td>120%</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1</td>
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<tr>
<td></td>
<td>50%</td>
<td>60%</td>
</tr>
</tbody>
</table>

Table 4.2: Comparative mechanical properties of the neat triblock and intercalated nanocomposite at $T_g$ and 20 °C above $T_g$ of the PS block. Data for the neat triblock are taken from Cohen et al. [1].

Since there is no visually observed necking of the nanocomposite samples at these elevated temperatures, this permits us to use the affine deformation model to compare and contrast the deformation in these nanocomposites with the neat triblock. Cohen et al. [1] most recently described the affine deformation model, which takes into account both the dilation and tilting of the lamellae, as follows:

$$\frac{d}{d_o \cos(\alpha)} = \frac{L}{L_o}$$

They showed that neat triblocks exhibit a nearly affine deformation and a plot of the macroscopic elongation, $\lambda = \frac{L}{L_o} (= \varepsilon + 1)$ vs $\frac{d}{d_o \cos(\alpha)}$ yields a slope which is unity.

Before further discussion, I first mention the origin of the elliptical shaped SAXS pattern which develops during deformation at elevated temperatures. The effect is purely geometrical [2,10,11]. The concept is illustrated in Figure 4.8, where a homogeneous
curved material is uniformly dilated. Note how the "lamellar markings" as shown in Figure 4.8a transform. The deformation effectively dilates the lamellae in the "b" location much more than those in the "a" location (see Figure 4.8c). This will cause the SAXS intensity to form an ellipse as schematically shown next to the real space images. In fact, Kratky [2] quantitatively states that the scattering pattern should evolve as follows:

\[ I_\alpha = \frac{\lambda^3}{(\lambda^3 \sin(90-\alpha)^2 + \cos(90-\alpha)^2)^{\frac{3}{2}}} \]  

(4.2)

where \( I_\alpha \) describes the normalized scattering intensity, 
\( \lambda (= L / L_\alpha) \) is the macroscopic elongation, and 
\( \alpha \) is the angle between the force direction and a SAXS intensity.

**Figure 4.8:** Schematic representation of the affine deformation of curved lamellae following model by Kratky [2]. The evolution of a circular diffraction pattern evolves into an elliptical pattern with increasing strain. Note also that the d-spacing obtained in location "b" is higher than the d-spacing obtained in "a".
4.3.3.1 Deformation at the Glass Transition Temperature

Figure 4.9 shows the microstructural evolution of the near single crystalline BCP nanocomposite morphology at 85 °C as observed using SAXS. Figure 4.9a shows the SAXS pattern of initially undeformed sample viewed along \( \hat{x} \) where the lamellar spacing is approximately 26 nm. Note the initial oriented diffraction pattern can be overlaid on a circular ring. Increased strains however cause the diffraction peaks to lie on a slight ellipse (see Figure 4.9b at 50% strain) as discussed above. This translates to some ambiguity in determining the spacing from an elliptical diffraction pattern as discussed by Cohen et al. [1]. Following their suggestion, the dilation of the layer spacing is determined using the d-spacing obtained using the central peak of the arc at low strains and from the distinct off-axis chevron reflections at high strains. Using this criterion, the lamellar spacing increases slightly (about 26.5 nm) up to 60% strain. Increasing the strain to 70% (Figure 4.9c) shows the clear development of a chevron morphology (\( \alpha \approx 37^\circ \)) as confirmed through azimuthal integrations. The spacing of the chevrons is determined by integration through selected azimuths. The chevrons possess a spacing of 27 nm at 70% strain. Upon further deformation, \( \alpha \) continually increases to 48° at 110% strain (Figure 4.9d) and the sample maintains a constant lamellar spacing of approximately 27 nm.
Figure 4.9: In-situ synchrotron scattering patterns of the 2wt% CBCP roll-cast film deformed perpendicular to the roll-cast direction at 85 °C (Tg of PS in the nanocomposite) and viewed along the roll-cast direction. Arcing of the reflections is observed up to (b) 50% strain. Note the evolution of the chevron pattern at (c) 70% strain. However, dilation is significantly repressed at this temperature and is accompanied by a rotation of the chevrons until fracture at (d) 110% strain.

Fitting these results to the affine deformation model shows a significant deviation as shown in Figure 4.11, the data at this temperature represented in circles (open circles indicate chevron formation). It is clearly evident that a significantly lower value of the slope from unity is observed as opposed to the neat triblock copolymer. Although tilting may contribute to the suppression of dilation, the layered-silicates appear to contribute significantly to the observed discrepancy with the dilation/tilt affine deformation model (especially evident at lower strains). This trend is observed even in the deformation performed above the glass transition temperature of the PS and is discussed in the next section.
4.3.3.2 Deformation above the Glass Transition Temperature

At 105°C, chevron formation is not observed up to fracture. The sample dilates and evolves into an elliptical pattern possessing a Gaussian distribution of the intensity. Figure 4.10a and b shows the initial and pre-fracture SAXS patterns, respectively. Applying again the same criterion as Cohen et al of taking the spacing obtained using the central peak of the arc, the lamellar spacing gradually increases from the initial 26 nm to 34 nm at fracture.

![Figure 4.10](image)

**Figure 4.10:** In-situ synchrotron scattering patterns of the roll-cast film deformed perpendicular to the roll-cast direction at 105 °C and viewed along the roll-cast direction: (a) initial and (b) prior to fracture at 60% strain. Note no observable chevrons are present up to fracture at 60% strain.

Even at these elevated temperatures, dilation seems to be repressed due to the presence of the layered-silicates (see Figure 4.11, shown in filled squares). The slope in Figure 4.11 is 0.5 which is significantly lower than unity. It should be noted that our choice of d-spacing determination leads to the highest possible dilation at each strain, and yet, the data deviates significantly from the affine deformation model.
Figure 4.11: Evaluation of the affine dilation/tilting model for perpendicular deformation at 85 °C (●, ○), and 105 °C (■). The filled symbols represent data taken without the observation of chevrons, and the open symbols represent data taken with the observation of chevrons. Note that the samples deviate significantly from the affine deformation model at both temperatures studied.

Effectively, although the sample has been macroscopically deformed to 60% strain, the affine deformation model indicates that there is only approximately 30% strain in the sample. Furthermore, since there is no distinct α evident, kinking/chevron formation is suppressed. This additional 30% strain must be experienced by the sample somehow which suggests heterogeneous deformation of the sample. As this elevated temperature leads to a homogeneous rubber, the observed heterogeneous deformation can suggests the formation of an anisotropic rubber. Namely, the rubber where the lamellae
are at $\alpha=0^\circ$ possesses a higher modulus. For dilation to occur, this must be accompanied by a Poisson contraction which the clay opposes due to its orientation. However, when the clay is tilted (as are the BCP lamellae) with respect to the applied force direction, the lateral contraction allows the rotation of the clay as this does not involve any axial compression of the layered-silicates. This is observed in the scattering pattern since the lamellae which have its normals along the force direction experience a slightly smaller dilation, the lamellae which have its normals off the force direction experience a higher strain. Fitting the elliptical scattering pattern which Kratky has derived, as discussed above, clearly elucidate this. For clarification, the fitting will be done with the maximum strain achieved (deformation observed by Cohen at 50% strain and the current sample at 60% strain as shown in Figure 4.12). The SAXS peaks at higher $\alpha$ show a higher deviation towards lower $q$ from the theoretical elliptical pattern. The results clearly indicate that whereas the neat triblock experiences a uniform affine deformation throughout the sample, there is significant heterogeneous deformation occurring in the nanocomposite which accounts for the additional 30% strain.
Figure 4.12: Elliptical pattern fitting of (a) a neat triblock copolymer at 100 °C to 50% strain and (b) 2wt% intercalated C15A/SBS4461 at 105 °C at 60% strain. Both samples are deformed 20°C above the $T_g$ of PS. Note the good agreement between Cohen’s data and Kratky’s elliptical diffraction pattern for the neat triblock. The CBCP nanocomposite exhibits deviations towards higher q with increasing $\alpha$ (see arrows). Neat triblock copolymer SAXS pattern taken from Cohen et al. [1].

4.4 Conclusion

Roll-casting has been used to produce near single crystalline intercalated clay -
triblock copolymer nanocomposites which have the layered-silicate and BCP lamellar norms orthogonal to each other. These nanocomposites exhibit modest differences in mechanical behavior from that of the neat triblock copolymer at ambient conditions. The presence of the layered-silicates causes necking at room temperature suggesting that the layered-silicates act as sites of heterogeneous deformation. Most importantly, however, the relatively modest improvements in the mechanical properties indicate that the intercalated morphology is not a desirable morphology for significant modulus or other mechanical property enhancements. Increasing the testing temperature leads to no observable improvements in the mechanical properties of the nanocomposite relative to the neat triblock copolymer. However, neck formation is not observed, as well as significant deviation from Cohen’s affine deformation model and Kratky’s affine deformation model. This is explained in terms of heterogeneous deformation which is still occurring at these elevated temperatures despite no macroscopically observable necking process. This study shows the various heterogeneous strain fields which may be present in the nanocomposite due to the presence of the layered-silicate despite macroscopic suggestion of a uniform affine deformation. This elucidation was possible since we are able to exploit the chemical contrast of the BCP morphology inside a mechanically (nearly) homogeneous rubber. It illustrates the potential for these BCP to be utilized in elucidating the role of the layered-silicates during deformation.
4.5 References


(2) Kratky, O. "The deformation mechanism of fibrous substances. I" Kolloid Zeitschrift 1933, 64(2), 213-222.


CHAPTER 5: Towards an Ideal Layered Nanocomposite: PS-Grafted Clay in SBS Lamellar Triblock Copolymer

5.1 Introduction

The previous two chapters dealt with exploring the deformation behavior of oriented block copolymer domains with the presence of a mix of predominantly immiscible, (with some intercalated and exfoliated) clay (Chapter 3) or essentially all intercalated layered-silicates (Chapter 4). In Chapter 4, deformation experiments performed along various roll-cast directions and on isotropic samples indicated that modest property enhancements are to be expected for an intercalated structure. This arises as the interaction between the reinforcing agent and the matrix block copolymer has not been maximized since the number of layers in the nanocomposite and their surface to volume ratio is 5 – 30 times less than if exfoliated. We are thus still left with the question whether further enhancements in the mechanical properties can be expected if the nanocomposites were to possess a fully exfoliated structure? In planning the sets of experiments to investigate a truly exfoliated layered-silicate dispersed within a lamellar BCP, it is imperative to consider the chain architecture of the BCP chains as differing approaches to property enhancements can be targeted.

Most thermoplastic elastomers possess a glassy-rubbery-glassy (ABA) type structure where the A blocks are typically below their entanglement molecular weight while the B blocks are well above their entanglement molecular weight. The mechanical property improvements in these triblocks over diblocks principally come from the bridging and intercatenated looping chains. Specifically it is the B blocks which can bridge across two
glassy domains or can form intercated loops that lead to tremendous improvements in the strain at fracture of these materials. Thus, in order to maintain the benefits of improved strain at fracture, the layered-silicate particles will need to be placed in the A domains to preserve the desired B chain topology. However, in order to maximize the modulus of the thermoplastic elastomer, insertion of the layered-silicates into the rubbery B domains is expected to be required. This however will cause loss of the fraction of looping intercated B chains and also forbid bridging of B chains near the layered-silicate. For example, in a SBS (d = 26nm) filled with fully exfoliated 1 vol% MMT (200nm lateral dimension with 1 nm thickness), the area fraction of the layered-silicate would be

\[
\frac{200^2}{392^2} \sim 0.26 \quad \text{since the volume fraction of clay is given by } \frac{t \cdot \text{Area}}{L \cdot \text{Area}} = 0.01 \quad \text{or}
\]

\[
\frac{1\text{nm} \times (200\text{nm})^2}{26\text{nm} \times (392\text{nm})^2} = 0.01 \quad \text{leading to approximately 25% tiling coverage of an average layer. The tiling of all the PB layers by single exfoliated clay sheets will thus approach 100% at only 4 vol% of layered-silicate assuming one non-overlapping clay layers in every PB domain. Hence at 1 vol% exfoliated clay, there is a 50% decrease in intercated loops and bridging chains relative to the neat triblock. This could translate to 50% lower ultimate tensile strains (assuming ultimate tensile strain is a linear function of loop and bridge content) which in turn may adversely affect toughness of the material. Placing the clay layers in the PS regions may be the better strategy. The main challenge is to experimentally achieve a fully exfoliated well oriented clay-BCP nanocomposite system to test these hypotheses.}

Our previous efforts using commercially modified layered-silicates resulted in a
predominantly immiscible clay-BCP system (Chapter 3) or in purely intercalated clay-BCP system (Chapter 4). This is a consequence of the enthalpic interactions between the block copolymer and the organic modifiers. Although the differences in $\chi$ between the matrix polymer and the clay have been dramatically reduced through organic modification of the clay, $\chi$ is nevertheless still somewhat positive (repulsive). Thus, to enable the insertion of individual clay layer into the A type (polystyrene) domains, we have functionalized the layered-silicates with PS chains to change the enthalpic interaction between the clay layers and the PS blocks in the SBS to be neutral ($\chi = 0$). In fact, that the effective $\chi$ of the modified clay can be lowered towards zero by increasing the molecular weight of the surfactant as well as the grafting density of the PS chains. We show that these PS-modified clay layers preferentially sequester to the PS domains in the triblock copolymer, consistent with various other nanoparticle sequestration [1-9] and homopolymer – block copolymer phase behavior studies [10-20]. In fact, as the widths of these PS-grafted nanoparticles are quite large, it appears from TEM images of the CBCP nanocomposites that the BCP domains actually template around the modified clay sheets.

Additionally, we show that the grafting density is critical in controlling the curvature of these individual flexible sheet layered-silicates. This is verified by varying the grafting density of the PS chain on clay by utilizing two different methods of PS attachment ("grafting-to" vs "grafting-from") while keeping the molecular weights approximately constant. A high density of PS chains using a high molecular weight PS leads to relatively flat layered-silicates of low curvature. These relatively flat exfoliated particles lead to a flipping transition from the perpendicular to the parallel orientation of the BCP resulting in
a parallel/parallel clay/BCP morphology (see Figure 5.1 to recall the relative orientations that may arise during roll-casting).

![Diagram](image)

**Figure 5.1:** (a) Schematic representation of the roll-caster and the convention used to label the coordinate axes. (b) The lamellar triblock copolymer orients its microdomains as shown with its lamellar normals pointed along z (perpendicular orientation) during roll-casting. (c) The lamellar triblock copolymer is schematically oriented in the parallel orientation. This orientation has not yet been observed in roll-cast neat triblocks.
These novel single-crystal CBCP nanocomposite samples can be utilized to study the anisotropy of various material properties. In particular, mechanical properties, including large strain deformation behavior as well as barrier properties were investigated. The mechanical studies show that the modulus is somewhat lower than that from the neat triblock copolymer (FWHM ~ 10°) presumably due to higher distribution of BCP lamellae (FWHM ~ 15°) and the yield stress remains nearly constant. However, the onset of strain hardening occurs at significantly lower strains which leads to an approximately 25% tougher material as compared to the neat triblock copolymers. Lastly, the initial residual strains in unloaded samples are significantly higher as compared to the neat triblock copolymer.

5.2 Materials

The layered-silicate used was a natural sodium montmorillonite which was chemically modified to tether a PS shell around the inorganic layer. Clay modified through surface initiated polymerization ("grafting-from") are denoted as FC (from-clay) and samples modified through cation exchange reaction ("grafting-to") are denoted as TC (to-clay). The molecular weight and the polydispersity index are as shown in Table 5.1 as verified through GPC (see Chapter 2 for details of synthesis and characterization).
<table>
<thead>
<tr>
<th>Tethered PS Chains</th>
<th>MW (g/mol)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1K TC</td>
<td>1400</td>
<td>1.12</td>
</tr>
<tr>
<td>7K TC</td>
<td>7100</td>
<td>1.04</td>
</tr>
<tr>
<td>1K FC</td>
<td>900</td>
<td>1.48</td>
</tr>
<tr>
<td>6K FC</td>
<td>6000</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Table 5.1: Molecular weight and polydispersity index for the four classes of PS chains tethered on montmorillonite.

The triblock used was the same Vector 4461-D (SBS) as used in Chapter 4. The molecular weight of each of the polystyrene blocks was 18,500 g/mol, and the polybutadiene block was 45,000 g/mol, giving a 45wt% styrene which microphase separates into a lamellar structure where PS and PB domains are approximately 12nm and 14nm thick, respectively, giving a lamellar repeat spacing of 26 nm.

All samples were mixed in appropriate amounts to result in a 2 wt% (~1 vol%) inorganic content nanocomposite. The relative PS: PS/PB/PS organic content varied due to the various PS molecular weights employed. However, in all scenarios studied, the lamellar morphology was maintained.

5.3 Morphological Characterization

5.3.1 Characterization of the PS-Modified Layered-Silicates

After tethering of PS onto clay surfaces as described in Chapter 2 and the previous section, the resulting samples were precipitated in THF/methanol (ratios were changed depending on the molecular weight of PS) to rid of excess untethered PS. Subsequently, XRD and TGA analyses were carried out on the PS-clay.

The XRD data in Figure 5.2 illustrates the influence of the “grafting-to” process on
the clay.

Figure 5.2: XRD patterns of natural sodium montmorillonite, montmorillonite exchanged with 1400 g/mol amino terminated polystyrene (1K TC), and 2wt% 1K TC/SBS4461. Note the increased spacing from approximately 1 nm to 5 nm after functionalization of the clay and subsequent intercalation when incorporated with SBS4461 as the basal spacing increases to 5.5 nm. The intensities have been vertically shifted by an arbitrary amount. Due to a low number of scatterers, there is a significant amount of background noise when the clay is incorporated in the SBS4461.

The layered-silicate spacing of natural sodium montmorillonite (MMT) is increased from 1 nm to 5 nm for 1K TC. Data for 7K TC is omitted to clarify the plot, but shows the
(003), (004), and (005) peaks which can be used to obtain the (001) spacing of 11 nm. Figure 5.3 illustrates the data from the “grafting-from” process and shows that tethering of the TEMPO initiator to the MMT increased the spacing \( (d_{001} = 2.2 \, \text{nm}) \) from the natural clay \( (2\theta \approx 9^\circ) \) as shown in Figure 5.2.

\[\text{Figure 5.3: XRD patterns of TEMPO initiator grafted onto natural sodium montmorillonite which shows an increased layer spacing of 2.2 nm. Subsequent living free radical polymerization of PS to 6000 g/mol molecular weight results in a further increase in the layer spacing to 12.6 nm which can be deduced from the (003), (004), and (005) peaks. Incorporation of 2wt% 6K FC in SBS4461 resulted in no observable Bragg scattering suggesting exfoliation.}\]
After subsequent polymerization of a 6000 molecular weight PS, the layer spacing increased further to \( d_{001} = 12.6 \) nm. The data for the 1K FC modified clay is omitted for clarity, but XRD shows a layer spacing of 4.2 nm (see Table 5.2).

The grafting densities were determined for all the PS-modified layered-silicates using TGA. TGA analyses were performed to calculate the percentage of organic content after final purification of the PS tethered clay particles. By comparing the measured organic content relative to the theoretical organic content, calculated based on the PS molecular weights and the cation exchange capacity (95meq/100g), the percentage of tethered sites relative to the total allowable sites can be calculated and these results are tabulated in Table 5.2. (See Appendix C for an example calculation of ideal grafting density based on molecular weight and cation exchange capacity).

<table>
<thead>
<tr>
<th></th>
<th>Theoretical Weight</th>
<th>Measured Weight</th>
<th>Percent PS Tethered</th>
<th>XRD spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat clay</td>
<td>Percent of PS</td>
<td>Percent of PS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1K TC</td>
<td>58%</td>
<td>60%</td>
<td>103%</td>
<td>1.0</td>
</tr>
<tr>
<td>7K TC</td>
<td>88%</td>
<td>66%</td>
<td>75%</td>
<td>5.0</td>
</tr>
<tr>
<td>1K FC</td>
<td>45%</td>
<td>43%</td>
<td>96%</td>
<td>11.0</td>
</tr>
<tr>
<td>6K FC</td>
<td>83%</td>
<td>80%</td>
<td>96%</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table 5.2: TC represents PS chains being grafted to clay and FC represents PS being synthesized from clay. The grafting density is reported by taking the ratio of the measured amount of organic content relative to the theoretical amount it should possess at the molecular weights measured and CEC reported (95meq/100g). Various of d-spacing of the PS modified layered-silicates is also reported.
These results show that the layer spacing of the 6K FC is higher than the 7K TC. This can be attributed to the lower grafting density with increasing molecular weights in the TC samples (see section 5.4).

5.3.2 Characterization of the Nanocomposite Morphology

Subsequently, samples of various PS modified clays were blended with the SBS triblock copolymer and roll-cast as described above and in Chapter 2. The morphology was studied using a combination of XRD, SAXS, and TEM along various roll-cast directions. Recall that \( \hat{x} \) is the flow direction, \( \hat{y} \) is perpendicular to the rollers, and \( \hat{z} \) is the neutral axis as shown previously in Figure 1.7 and shown again in Figure 5.1.

The samples, using clay where the PS chains were grafted onto the layered-silicate surface (TC samples), are discussed first. Figure 5.4a and b show the SAXS patterns taken with the incident beam along \( \hat{x} \) and \( \hat{y} \), respectively, of the 2wt% 1K TC/SBS4461.
Figure 5.4: SAXS patterns taken of 2 wt% 1K TC/SBS4461 viewed along (a) x and (b) y. The BCP lamellae are oriented in a perpendicular orientation as shown in (c). (d) TEM viewed along x of the nanocomposite showing layered-silicates oriented orthogonally to the BCP lamellae. The high magnification inset shows the intercalated nature of the layered-silicates surrounded by the PS which appear white due to OsO₄ staining.
The (001) arcs show the preferred orientation of the BCP lamellar normals along \( \hat{z} \) as summarized in Figure 5.4c. The TEM image in Figure 5.4d viewed along \( \hat{x} \) confirms the SAXS data and also shows the orthogonally oriented layered-silicate normals relative to the BCP lamellar normals. Note that the large white regions are the PS-modified layered-silicates which are bright since the samples were stained using OsO\(_4\). The layered-silicates appear to possess an intercalated morphology. Typically there are approximately 5 to 10 layers of clay bundled together in most of the large white regions. The high magnification inset shows a bundle of clay sheets (circled region in the low magnification image). As the width of this particular white region is approximately 50 nm and it contains 9 clay layers, the average clay layer spacing is 5.5 nm. Knowing the global orientation of the clay allows XRD, with the incident and reflected beam bisecting the y-axis, to probe the layer spacing. The results nicely confirm the TEM image giving a clay layer spacing of 5.4 nm as shown by the position of the (002) reflection at 2.7 nm in Figure 5.2. Furthermore, although the BCP is principally in the perpendicular orientation, TEM shows that near most clay bundles, the BCP domains locally rearrange to maximize the PS content around the clay bundles. Thus the 1K TC/SBS sample exhibits a perpendicular orientation of the BCP with a parallel orientation of intercalated clay particles. This result is consistent with the morphology observed in Chapter 4 on another purely intercalated CBCP system.

Figure 5.5a and b show the SAXS pattern taken with the incident beam along \( \hat{x} \) and \( \hat{y} \) of 2wt\% 7K TC/SBS4461, respectively.
Figure 5.5: SAXS patterns taken of 2 wt% 7K TC/SBS4461 viewed along x and y. Large regions of the sample are now oriented in either a perpendicular or parallel orientation as shown in (c). (d) TEM viewed along x of the nanocomposite showing layered-silicates oriented parallel to the BCP lamellae. In each of the larger curved white PS domain are individual exfoliated layered-silicates.
The two patterns in Figure 5.5a are different regions of the sample separated by a few millimeters. The top pattern shows the sample to be in the parallel orientation while the bottom pattern shows a perpendicular orientation. Not shown are diffraction patterns which sometimes exhibit a circular ring suggesting uniaxial orientation. When the incident beam is along $\hat{y}$, those lamellae in the parallel orientation will not show a diffraction peak while the perpendicular and parallel lamellae will show a diffraction peak similar to the one observed in Figure 5.5b. Thus, the SAXS data indicate that there are fairly large regions of the sample which are either in parallel, perpendicular, or sometimes a uniaxial orientation (see Figure 5.5c). TEM data in Figure 5.5d show a somewhat chaotic distribution of the BCP layer normals possibly capturing a section as the morphology is changing from one orientation to another. Furthermore TEM shows that the oversized white regions (circled in Figure 5.5d) are generally thinner than the clay sheet regions in Figure 5.4d. There is a larger number of these white areas and on average they are closer to one another. Careful scrutiny of high magnification images of the individual white areas shows that there are on average only 1 – 3 clay layers encapsulated in these regions. One other noticeable feature is the shape of the layered-silicates observed in Figure 5.5d. The layered-silicates have a significant amount of curvature associated with each nanoparticle. Lastly, observation of the BCP near the PS modified clay suggests that templating also occurs which lead to many orientational defects due to meeting of nonparallel lamellae and leads to a “chaotic” texture.

A similar set of morphological studies were performed on the FC samples. SAXS data, with the incident beam along $\hat{x}$ and $\hat{y}$ in Figure 5.6a and b respectively, show that roll-casting of the 2wt% 1K FC/SBS4461 once again leads to a perpendicular BCP
roll-casting of the 2wt% 1K FC/SBS4461 once again leads to a perpendicular BCP orientation where the lamellar normals are pointed along $\hat{z}$ (see Figure 5.6c).

Figure 5.6: SAXS patterns taken of 2 wt% 1K FC/SBS4461 viewed along (a) x and (b) y. The BCP lamellae are again oriented in a perpendicular orientation as shown in (c). (d) TEM viewed along x of the nanocomposite showing intercalated layered-silicates oriented orthogonally to the BCP lamellae.
These results are similar to the observations on the 1K TC samples and are not discussed further. In the 2wt% 6K FC/SBS4461 sample, SAXS data viewed along \( \hat{x} \) and \( \hat{y} \) in Figure 5.7a and b respectively clearly demonstrate a \textit{parallel} orientation of the BCP arises (see Figure 5.7c).
Figure 5.7: SAXS patterns taken of 2 wt% 6K FC/SBS4461 viewed along (a) x and (b) y. The BCP lamellae are now oriented in a parallel orientation as shown in (c). Note little or no scattering peak in (b) which is outside the Bragg condition. (d) TEM viewed along x of the nanocomposite showing layered-silicates oriented parallel to the BCP lamellae. The high magnification inset shows the exfoliated nature of the layered-silicates surrounded by the PS which appear white due to OsO₄ staining.
The lamellar layer orientational order parameter, \(-0.5 \leq P_2 \leq 1\), as defined in Chapter 4, yields a value of \(-0.34 \pm 0.05\). The absence of higher order peaks is due to the loss of long range periodicity of the BCP as the presence of each clay sheets results in a thicker PS domain, thus disrupting the long range layer periodicity. As discussed previously, a parallel orientation of the layers should not lead to any Bragg scattering when the incident beam is along \(\hat{y}\) as confirmed in Figure 5.7b. The TEM image in Figure 5.7d shows that there are numerous elongated white regions which are approximately 2 – 3 times as thick as the adjacent BCP PS domains. In each of these thick PS domains reside single (or sometimes double) dark lines which represent exfoliated clay sheets as can be seen in the high magnification inset. This interpretation can be quantitatively checked. Since the BCP PS domains are approximately 12 nm thick, and the layer spacing of the 6K FC clay was measured to be 12.6 nm, the approximate 2x thickness increase observed in the TEM verifies that almost every oversized white domain contains only 1 clay sheet (see schematic Figure 5.8a and b).
Figure 5.8: Schematic illustration of the preferential local layer thickening observed in the PS domains. (a) As measured from XRD, the layer spacing is 12.6 nm when the 6K FC are stacked together. (b) After exfoliation, the thickness of the PS domains will increase by 12 + n12.6 nm. For example, if one clay sheet is inserted into the PS domain, the local thickness of the PS domains will increase to approximately 25 nm.

In fact, the total thickness (in nm) of the oversized white domains should be directly proportional to the number of clay layers, n, as follows: $t_{ps}^{\text{total}} = 12 + 12.6n$. The
exfoliation is further confirmed through XRD studies, with the incident and reflected beams bisecting \( \hat{y} \), as shown in Figure 5.3 where no noticeable scattering peaks exist over the q range studied. These results show that a flipping transition of the BCP domains has occurred from the normally observed perpendicular orientation. Furthermore, both the BCP layers and the individual layered-silicates are significantly straighter and much better aligned than those observed in Figure 5.5d

5.4 The Effect of Enthalpy, Entropy, and Grafting Density on Clay Dispersion

Understanding the underlying reasons for the exfoliation of the layered-silicate in the block copolymer necessitates the scrutiny free energy of the system, \( \Delta G = \Delta H - T \Delta S \). Namely, \( \Delta G \) can be minimized by lowering the enthalpic interactions and by increasing the entropic interaction. Therefore, outlining the possible enthalpic and entropic parameters will help reveal whether the exfoliated system is in a true thermodynamic equilibrium or captured in a metastable equilibrium. In particular for layered-silicate polymer thermodynamics, Vaia et al. [21,22], using a modified lattice model, and Balazs et al. [23,24], using a self-consistent field theory, have outlined several important variable in determining the thermodynamic state of the layered-silicate morphology (modeled as hard rigid plates in both theories). Namely, they are as follows:

- molecular weight of the host polymer,
- the type of surfactant used,
- the density of the surfactant on the layered-silicate, and
- the length of the surfactant used.
First, the discussions according to Vaia and Giannelis utilizing a mean field statistical lattice model will be detailed [21]. They first discuss the contributions of entropy and separate out the contributions into two components. \[ \Delta S = \Delta S_{\text{surfactant}} + \Delta S_{\text{polymer}}. \]

The entropy of the surfactant composes of three main factors which are the ideal combinatorial mixing (traditional Flory lattice model contribution), the constraints imposed by the tethering of the chain, and the conformation of the surfactant chains (which is affected by the presence of the layered-silicate surface). Of these, they show that the last factor is the dominant term. For the entropy from the polymer, they argue that two contributions to consider are the configurational entropy loss associated with intercalation into confined slits and a weak dependence on the molecular weight of the polymer (excluded volume arguments which shows that higher molecular weight surprisingly favors intercalation thermodynamically). The analysis of the entropic terms shows that whereas the surfactant increases its entropy by finding more conformations without the presence of confining layered-silicates surfaces, the polymer loses its entropy by the loss of its configurational entropy. This leads to an overall entropy change where initially, the loss of configurational entropy is offset by the increase in conformational entropy (no contribution to layer separation), but becomes thermodynamically unfavorable at higher separation distances. These various terms are plotted and shown by Vaia and Giannelis (see Figure 5.9). This suggests that enthalpic interactions must be high enough to compensate for the overall loss in the entropy of the system.
Figure 5.9: Entropic contributions from the surfactant (octadecylammonium group) and an arbitrary polymer as taken from Vaia and Giannelis [21].

The enthalpic contributions arise from the interactions occurring among the layered-silicate surface, the surfactant chains, and the polymer. It should be noted that their analysis is concentrated more heavily on commercially available very short surfactants (alkylammonium chains). As a result, they point out that important interactions arise between the polymer and the silicate layers from possible electron donating/accepting groups on the polymer repeat units. Furthermore, they maintain that the interaction between the polymer chains and the alkyl surfactants are apolar and thus repulsive. Of course, this essentially boils down to an assumption the polymer chains are more polar than the surfactants and thus is a very specific scenario. Nevertheless, they show that under these
conditions, the enthalpic contributions may be lowered to allow intercalation or exfoliation to occur (see Figure 5.10). They further mention that grafting density may be altered to maximize number of surface sites, which implies a lower grafting density is preferred for the given conditions.

![Graph](image)

**Figure 5.10:** Enthalpy change with the interaction between surfactant and polymer set to zero. The interactions between surface to polymer and surface to surfactant are set at (a) 0, (b) –4, (c) –8, and (d) –12. Taken from Vaia and Giannelis [21]

These results show that depending on the enthalpic and entropic interactions provided the system, there may be a thermodynamic driving force for exfoliation and/or intercalation to occur. These interactions can be affected by the chemistry of the surfactant and polymer, the grafting density of the surfactant, and the molecular weight of the polymer.
Nevertheless, there are some limitations to the theory which can be refined. First, the surfactants are very short and the polymers are necessarily more polar than the surfactant used. Also, the polymer is monodisperse. Furthermore, the conformation of these polymers and the surfactants are not coupled into each other which lead to independent configurations of the surfactants and the polymers. Lastly, the enthalpic and entropic contributions to the free energy are also decoupled which does not allow the effect of intermolecular interactions on the surfactant and polymer conformations to be directly taken into account.

Thus, Balazs et al. [24,25] uses a numerical self-consistent field theory to address these limitations and further brings out another variable – the effect of the molecular weight of the surfactant itself. The details of the SCF model will be left for the reader to pursue, but the specific variables of the simulation will be outlined. Two parallel surfaces immersed in a polymer melt are considered. These surfaces are covered with monodisperse surfactants with a grafting density $\rho$. The interaction parameter between the surface and the surfactants are taken to be zero (neutral which may not be correct as Vaia points out), and treat the surfactant-polymer interaction with the Flory-Huggins parameter $\chi$. Furthermore, $\chi_{\text{surface}}$ is defined as the interaction parameter between the polymer and the layered-silicate surface which the simulations essentially assume to be zero as they allow the surfactants to fully saturate the gallery layers. This essentially reduces to a relatively high molecular weight surfactant as opposed to Vaia’s theories of short surfactant chains. Finally, the repeat units of the polymer ($N_p$) and the surfactants ($N_{gr}$) are allowed to vary. One major mistake in the simulations is to assume that the $\chi$ between the surface and the surfactants is zero which is
not true in almost any circumstances. Nevertheless, the simulations vary the value of these various parameters and outlines the conditions where thermodynamic exfoliation or intercalation is observed.

First, the results show that without any grafting density (but with $\chi_{\text{surface}} = 0$), intercalation is not preferred. However, intercalation is preferred for $\chi \leq 0$ when a surfactant is present on the clay surface for $\rho = 0.04$, $N_{gr} = 25$ and $N_p = 100$ (see Figure 5.11). These illustrate the importance of the enthalpic interactions between the surfactant chains and the polymer chains and illustrate that exfoliation is possible by lowering $\Delta H$.

![Figure 5.11](image)

**Figure 5.11:** The free energy per unit area, $\Delta F/A$, as a function of separation distance, $H$, are shown. (a) A bare surface with $\chi_{\text{surface}} = 0$ in the melt of $N_p = 100$ (polymer repeat unit) is immiscible. (b) However, a surfactant of repeat unit, $N_{gr} = 25$, and grafting density $\rho = 0.04$, allows intercalation and exfoliation when $\chi \leq 0$. Taken from from Balazs et al. [24].

Furthermore, contrary to the results of Vaia and Giannelis [21], the SCF model shows that increasing $N_p$ will not lead to an intercalated morphology. Rather, increasing the $N_{gr}$ to a molecular weight similar to the polymer will further lower the overall free energy when $\chi = 0$ although $\chi = 0.02$ increases the energy for exfoliation as shown in Figure 4.12.
Figure 5.12: The effect of varying molecular weight is shown. (a) When the molecular weight of the polymer is increased, there is an increase in the overall free energy of the system. (b) At $\chi=0$, increasing the surfactant molecular weight lowers the overall free energy of the system toward exfoliation. (c) At $\chi=0.02$, increasing the surfactant molecular weight increases the overall free energy of the system for exfoliation but lowers the free energy for intercalation to occur. Taken from Balazs et al. [24].
Lastly, the grafting density is varied and the results show that increasing the grafting density increases the overall free energy of the system. However, the fact that intercalation is not possible without surfactants suggests that there is an optimum amount of surfactant grafting density which is required for exfoliation to occur (see Figure 4.13).

![Figure 5.13: The free energy for separation for \( \rho = 0.12 \) for different \( \chi \) parameters. Other parameters are as same as in Figure 4.11b. Taken from Balazs et al. [24].](image)

These results suggest that the \( \chi \) parameter between the surfactant and the polymer is a very important factor and achieving the lowest possible value is important. Secondly, the effect of the molecular weight is due to the increase in conformational entropy of the polymer and surfactant chains as the density profile of the chains is broader when \( N_{gr} \) is comparable to \( N_p \), allowing greater freedom of chain conformation. This is analogous to the
so-called “wet brush” regime as described by Borukhov and Leibler [26,27]. It is important to note that the entropy of *mixing* is not increasing. In fact, since $\Delta S_{\text{mix}} \propto \frac{\ln \phi_i}{MW_i}$ where $\phi_i$ is the volume fraction of the components and $MW_i$ is the molecular weight of the components, $\Delta S_{\text{mix}}$ is negligible since the MW is huge, especially for the PS-grafted clay particles.

The grafted density is also a byproduct of the conformational entropy in these simulations as the polymer chains cannot penetrate to intermix with the surfactant layer, the conformational entropy decreases. On the other extreme, bare surface also lowers the conformational entropy.

Somewhat overlooked in these two theories, but important experimentally, is that the grafted density can serve two additional roles. If the grafted density is not sufficiently high enough, the *hydrophilic* nature of the clay may simply not be fully masked which leads to a $\chi_{\text{surface}}$ of the modified clay which is not zero. In fact, the hydrophilic nature of the clay as opposed to the hydrophobic nature of the polymer may alter $\chi_{\text{surface}}$ to be *positive* (not negative as effectively stated by Vaia and Giannelis) despite using PS surfactants. Secondly, although they have modeled these individual layered-silicates as rigid layers, in actuality, there is considerable amount of conformational entropy to be gained by shape changes of the layered-silicate sheets [28,29]. This is analogous to linear coils with a persistence length and we introduce the term “persistence area” for these layered materials. (It should be noted that the energetics for shape curvature decreases rapidly with increasing number of layers in a stack, i.e. immiscible/intercalated clay are nearly straight regardless.) Thus, as the functionalization of the surfactant leads to an individual layer of exfoliated
sheets in solution, a higher grafting density (in addition to the higher molecular weights) leads to overlap of PS chains in the concave regions of the crumpled layered-silicates which is unfavorable. This will inevitably lead to a higher persistence area of the 2D layered-silicate whereas a lower grafting density can tolerate larger sheet curvatures and lead to a smaller persistence area.

It should be noted, that as usual, it is very difficult to prove equilibrium structures in a polymeric system. Added to the complexity is the fact that we have a solvent present which is evaporating at a finite rate and may lead to a metastable or a kinetically trapped exfoliated structure from the initial dilute suspension. Nevertheless, the degree to which these predictions are observed experimentally in our systems is remarkable. When PS is grafted onto the clay surface, we postulate that $\chi = 0$ between the PS surfactant and the BCP PS domain chains. With shorter chains, as both theories describe (although due to slightly different reasons), intercalation is observed. As the PS surfactant molecular weight is increased, an exfoliated structure is observed as described by Balazs’ theory. It appears that the experimentally obtained $\sim 100\%$ grafting density still allows exfoliation and intercalation. This does not allow us to confirm or contradict either theories: it allows us to only state that conditions were appropriate for intercalation or exfoliation to occur. Furthermore, the grafting density seems to affect the curvature of the clay layers exactly as described above as the curvature of the clay is significantly lower in the highly grafted 6K FC as opposed to the 7K FC. (The lower molecular weights exhibit an intercalated structure with increased number of layers which leads to an energetically unfavorable state for crumpling to occur.)
Additionally, another very interesting phenomenon observed due to the use of a block copolymer is the flipping transition. It appears that the layered-silicates can dictate the orientation of the BCP morphology when the surface to volume ratio of the filler is increased through exfoliation. This can be verified through numerous TEM micrographs where regardless of the global orientation of the BCP, near the layered-silicates, the BCP is shown to template around the particle. Furthermore, the various systems studied indicate that the energetically favored state of the layered-silicate in the flow field of the roll-casting apparatus is in the parallel orientation. These observations then suggest the following mechanism for the observed flipping transition. As the solvent is evaporating during roll-casting, the BCP undergoes microphase separation at which point the BCP is aware of the nanoparticles which are present and the BCP template around them. If exfoliation has occurred (leading to high surface to volume ratio), most of the BCP template around the layered-silicates in the parallel orientation and the global orientation of the BCP is forced to be in-plane (parallel orientation). However, when the layered-silicates are intercalated (and therefore there are many fewer, more sparsely spaced particles), the system minimizes its overall energy by orienting the BCP in the perpendicular orientation and templating only the BCP near the clay to the parallel orientation. This further explains the rather mixed orientation observed in the 7K TC where the high curvature of the individual clay sheets causes a chaotic BCP texture during flow orientation and subsequent templating. It should be noted that this is to my knowledge, the first observed flipping transition of the block copolymer morphology through the use of nanoparticles.

More importantly however, is the striking morphology of a near single crystalline
exfoliated nanocomposite which possesses layered-silicates preferentially confined to the PS BCP domains (see Figure 5.7d) that allows the study of a nearly model system of exfoliated anisotropic hierarchical nanocomposite. It is the first model hierarchical, exfoliated layered-silicate nanocomposite and should yield further insights into the role of the layered-silicates in the deformation behavior of the nanocomposite. Furthermore, by comparing and contrasting the various property enhancements observed in the earlier chapters of the thesis with the current nanocomposite, fundamental structure-property relationships should be garnered.

5.5 Mechanical Properties of Exfoliated Near Single Crystalline Hierarchical Nanocomposite

The observation of a near single crystalline exfoliated hierarchical nanocomposite in the parallel orientation is an exciting observation which can be utilized to study the anisotropic mechanical properties of these nanocomposites to further elucidate the role of the PS covered clay sheets on the overall properties of the nanocomposite.

5.5.1 Macroscopic Properties

The mechanical properties of the nanocomposite deformed along the parallel and perpendicular direction are shown in Figure 5.14.
Figure 5.14: Stress-strain curves of the 2% 6K FC/SBS deformed along and orthogonal to the lamellar normals. Various differences in yield stress, onset of strain hardening, and residual stress are observed between the neat SBS triblock copolymer and the 2% FC/SBS exfoliated nanocomposite.

For parallel deformation, samples were deformed along $\hat{z}$ and for perpendicular deformation, samples were deformed along $\hat{y}$. The latter required the samples to be stacked and bonded using a solvent which lead to some difficulties in property determination mainly due to debonding problems. This was visually observed during deformation as the sample which is initially homogeneously deforming, usually debonds at various places in a given cross-section. Another important factor is that stacking causes the
sample to possess slightly irregular sample dimensions as the stacking leads to jagged edges. However, stacking of the thin roll-cast sheet (0.1mm) was the only possible route to obtain data for perpendicular deformation in these samples.

The parallel deformation shows only a slightly different deformation behavior as compared to the neat triblock copolymers as reported by Cohen et al. [30]. The current system possesses a significantly higher lamellar distribution. The full-width at half maximum is approximately 20° in the nanocomposite as opposed to approximately 10° in the neat triblock copolymer, as determined through azimuthal integration. Hence the modulus is approximately 20% lower (150 ± 5 MPa) compared to the neat triblock copolymer (180 MPa). However, the yield stress is approximately the same (5 ± 0.3 MPa) as the neat triblock. The major distinction is the difference in the onset and magnitude of strain hardening. The onset of strain hardening is observed to occur at approximately 300% strain in the neat triblock whereas the exfoliated nanocomposite exhibits strain hardening behavior much earlier at approximately 100% strain. The earlier onset of strain hardening leads to a nanocomposite that is approximately 25% tougher (33 ± 2 MPa) (toughness defined as the area under the stress-strain curve) than the neat triblock copolymer (26 MPa). Lastly, the residual strain is significantly higher (100% strain) as compared to the neat triblock copolymer (40% strain) when both types of samples are relaxed from 500% strain.

In the perpendicular deformation, the modulus is approximately 40% smaller (43 ± 26 MPa) than the neat triblock copolymer (68 MPa) possibly due to the lower overall lamellar orientation. Necking occurs as opposed to the neat triblock copolymers which do not neck, and the yield stress is observed to increase by 25% (4 ± 2 MPa vs 3 MPa). The
onset of strain hardening is similar (250%) and the toughness is comparable to the neat triblock copolymer (12 ± 5 vs 10 MPa). Unfortunately, due to premature fracture of these samples (debonding problems), residual strains when unloading from 500% strain could not be determined. Comparative results of intercalated and exfoliated nanocomposites studied thus far with the neat triblock copolymer are tabulated in Table 5.4.

<table>
<thead>
<tr>
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<th>Perpendicular</th>
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<td></td>
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<tr>
<td><strong>Samples</strong></td>
<td>Neat SBS</td>
<td>Intercalated</td>
<td>Exfoliated</td>
<td>Neat SBS</td>
<td>Intercalated</td>
</tr>
<tr>
<td></td>
<td>(Cohen)²⁵</td>
<td>C15A/SBS (Chpt 4)</td>
<td>6KFC/SBS (Chpt 5)</td>
<td>(Cohen)²⁵</td>
<td>C15A/SBS (Chpt 4)</td>
</tr>
<tr>
<td><strong>Modulus (MPa)</strong></td>
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<td>90</td>
<td>55</td>
<td>180</td>
<td>160</td>
</tr>
<tr>
<td><strong>Yield Stress (MPa)</strong></td>
<td>3</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td><strong>Strain hardening onset</strong></td>
<td>300%</td>
<td>400%</td>
<td>200%</td>
<td>300%</td>
<td>300%</td>
</tr>
<tr>
<td><strong>Residual strain</strong></td>
<td>40%</td>
<td>40%</td>
<td>NA</td>
<td>40%</td>
<td>70%</td>
</tr>
<tr>
<td><strong>Toughness (MPa)</strong></td>
<td>10</td>
<td>8</td>
<td>12</td>
<td>26</td>
<td>22</td>
</tr>
<tr>
<td><strong>FWHM</strong></td>
<td>-</td>
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<td>10°</td>
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</table>

Table 5.4: Comparison of the mechanical properties for intercalated and exfoliated nanocomposites with the neat triblock copolymer. Note that due to premature fracture in perpendicular deformation of the exfoliated sample, the toughness was calculated using the area under the stress-strain curve only up to 300% strain in all samples. In the parallel deformation, 500% strain was used as the cutoff for toughness calculation.
5.5.2 Discussion of Mechanical Properties

The little to no modulus improvements in these hierarchical nanocomposites containing exfoliated clay particles may come initially as a surprise. An effect which was discussed earlier is the somewhat wider distribution of the lamellar normals (20° FWHM compared to 10° in Cohen’s neat triblock) which lower the measured parallel modulus. Additionally, as individual layers of the clay are situated in the already stiff PS domain, the relative modulus improvement of these glassy domains may not be dramatic, as has been reviewed in Chapter 1 for various glassy homopolymer nanocomposites. If this is the case, the hierarchical nanocomposite’s overall modulus should show even a less dramatic improvement as those observed in homopolymers, as the BCP is already a nanocomposite with a very soft butadiene phase. This suggests that to dramatically improve the modulus of these nanocomposites, the PB phase needs reinforcement, and not the glassy PS phase which may be carried out by the insertion of individual layered-silicates into the soft rubbery phase as described earlier in the chapter.

Secondly, the earlier onset of strain hardening in the parallel deformation merits discussion. I have reviewed in Chapter 1 that in parallel deformation, the neck forms at a very well defined location followed by a quick saturation of the stress. At this point, the neck propagates, which occurs by breakup of the PS domains, at constant stress until the neck propagates all the way to the grips. Beyond this point, strain hardening is observed to occur. In the exfoliated nanocomposite, however, as the yield stress is reached and the neck tries to propagate by further breaking up PS domains, the neighboring PS domains may contain individual layered-silicates which will impede the propagation, and as such, more
stress is needed to break up the reinforced PS domain, or the increase in load triggers deformation in another region without layered-silicates. This scenario explains the rather broad unsaturated region (in terms of stress) after the yield stress. Meanwhile, at other non-clay filled PS domain regions, styrene break up is continually occurring. But the numerous layered-silicate filled PS domains observed in the TEM translate to a quick depletion of the unreinforced regions possible for PS breakup, and strain hardening takes place at a much lower strain. Effectively, the sample recognizes that other areas of the PS domains are reinforced with clay, and work hardening ensues. This leads to an increased toughness which may be even further enhanced with higher number of exfoliated layered-silicates.

In regards to the perpendicular deformation, it should be noted that due to debonding problems, the exact property determinations were very difficult and lead to very large statistical errors during property determination. However, it should also be noted that these values turn out to be a conservative estimate of the actual properties as these debonding effects will inevitably lead to poorer materials property. Thus, the highest measured values were utilized when reporting these measurements with error bars representing the lower bounds measured. Despite these uncertainties, these deformation experiments demonstrate the role of these layered-silicates during deformation. Most importantly, as observed in all samples studied, the presence of these layered-silicates leads to necking behavior unlike in the neat triblock. Thus, even in the exfoliated state, significant stress concentrations exist around the layered-silicates to cause necking. Secondly, the lower modulus values measured may simply be due to difficulties in measuring the true cross-sectional area. If the load taken up by the sample is shared only in
certain localized regions of the cross sectional area measured, the actual modulus would be significantly higher. However, another suggestion may be that the modulus enhancements of the layered-silicates in glassy domains are not dramatic as discussed previously. Furthermore, the samples suggest that a somewhat higher yield stress is to be expected as the presence of the layered-silicates allows the PS to be somewhat stiffer and resist buckling to form a chevron structure. However, unlike the parallel deformation, the onset of strain hardening is comparable to the neat triblock as the probability of lamellar domain rotation is not drastically altered. I have shown in Chapter 4 that there is a sudden formation of chevrons at the point where neck is propagating, and the exfoliated clay should not impede this initiation of kinks in the nearby unfilled PS domains. However, it may be possible that the wavelengths of the chevrons are altered due to the presence of the exfoliated clay. These results illustrate difference in the deformation behavior of the exfoliated nanocomposite relative to the neat triblock copolymers at different loading conditions.

To approach the role of the layered-silicates in a broader view point, Table 5.4 compares the various measured properties of the intercalated and exfoliated nanocomposites to the neat triblock measured by Cohen et al. First, it appears that the presence of the layered-silicates leads to a somewhat poorer global orientation of the BCP morphology which leads to slightly lower measured moduli. However, these results also seems to indicate that the presence of the layered-silicates in the rubbery domains is important to improve the modulus properties as the exfoliated clay in PS shows little improvement in the modulus while the intercalated structure leads to modest improvements.
Thirdly, in order to increase the toughness of the system, increasing the surface-to-volume ratio of the layered-silicates is essential. Namely, exfoliated structure in the PS domains (A domains in an ABA triblock) is required to improve the toughness of the material. These various understanding of the mechanical properties which are affected by the layered-silicate morphology should lead to potentially well-designed nanocomposite which does not sacrifice modulus for toughness and vice versa. In fact, Chapter 6 will highlight a new hierarchical nanocomposite morphology which will utilize the lessons learned here to achieve an increase in both the modulus and the toughness.

5.5.3 Morphological Evolution during Deformation

The morphological evolution during deformation in the CBCP exfoliated system is markedly similar to previously studied systems. Namely, the parallel deformation leads to breakup of the glassy domains while the perpendicular deformation leads to the formation of chevrons which remain in place when unloaded.

Whereas the stress-strain behavior of the parallel deformation is markedly different from the neat triblock copolymer, the SAXS patterns do not deviate from the previously observed void formation after the yield stress until unloading whereby the lamellar period returns. Thus as was done in Chapter 4, the parallel deformation will not be discussed further to save redundancy, and the perpendicular deformation studies will be shown briefly.

As these results are again very similar to those obtained in Chapter 3 and 4, minimal discussion follows. Figure 5.15a shows the initial SAXS pattern of the stacked undeformed sample. Since the beam size was approximately 150 microns, it is quite likely
that the beam straddles about two stacked layers. As discussed previously, the lamellar orientation parameter, $P_2 = -0.3$. Figure 5.10b shows the SAXS pattern in the necked region of the sample ($\varepsilon_{\text{neck}} \approx 200\%$). Much of the diffraction intensity is lost due to uniaxial folding of the chevrons, much like an egg board, due to the sample size (1mm x 1.5mm) and leads to many lamellae which leave the Bragg condition. The $\alpha$ measured in the neck is approximately 68°. Upon unloading, $\alpha$ returns to approximately 17° with d spacing of approximately 26nm again. An exposure taken an hour later did not show the chevrons to disappear with no appreciable change in $\alpha$. Thus, the sample necks and within the neck, chevron formation occurs. When unloaded, chevrons persist. These results are analogous to the other perpendicular deformation studies shown previously and will not be discussed further.
Figure 5.15: (a) SAXS pattern taken of 2 wt% 6K FC/SBS viewed along x after the samples have been stacked for perpendicular deformation. Note the slight loss in orientation due to film bonding. (b) SAXS pattern taken in the necked region which shows chevron formation. However, note the decreased intensity due to sample dimensions which cause chevrons to fold uniaxially in the x-z plane. (c) SAXS pattern taken of a sample after fracture from approximately 200% strain. Note the persistence of the chevron morphology.
5.6 Conclusions

I have shown in this chapter that the routes for exfoliation of the nanocomposite are dependent on the enthalpic interaction of the grafted chains on the layered-silicate, the molecular weight of the grafted chains, and finally the grafting density. These experimentally observed results closely follow the theoretically results of Balazs et al. with the added notion that the grafting density can also control the curvature of the layered-silicates when they have been exfoliated. The BCPs appear to strongly template around the PS covered layered-silicates, and the increased surface-to-volume ratio during exfoliation leads to a flipping transition during roll-casting. I believe this is the first experimental proof that nanoparticles can dictate the orientational behavior of a block copolymer.

These near single crystalline exfoliated nanocomposites show that the mechanical property enhancements are to be expected in terms of toughness increase although the modulus may not be significantly impacted as the clay is reinforcing the glassy domains. This toughness increase is evidenced in parallel deformation by the earlier onset of strain hardening. Despite difficulties in experimentation with perpendicular deformation, results show that some modest improvements may be expected although to dramatically improve the modulus, insertion of the layered-silicate in the soft rubbery domains is to be desired.

Most importantly however is the experimental proof of a guiding principle in producing an exfoliated nanocomposite which was offered in this study. This may be applied to many generalized scenarios of nanocomposite formation and should lead to the ability to tailor and design the formation of a desired nanocomposite morphology.
5.7 References

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Chapter 6: Conclusions and Suggestions for Future Work

6.1 Conclusions

The primary goal of this research was to understand the role of the layered-silicates in a triblock copolymer as a function of the layered-silicate dispersion. The three types of layered-silicate morphologies are classified as immiscible, intercalated, and exfoliated. Initial efforts using commercially available organically modified layered-silicates resulted in a primarily immiscible morphology (Chapter 3) or in an intercalated nanocomposite (Chapter 4). The attainment of a fully exfoliated hierarchical nanocomposite proved very elusive until collaborations with chemists opened up the possibility of sufficiently controlling the enthalpic and the entropic interactions of the clay with the block copolymer domains. As a result, a fully exfoliated, near single crystalline hierarchical nanocomposite was finally achieved (Chapter 5). A near single crystalline texture of the BCP domains is made possible by the use of a roll-caster. Previous work has shown that the neat lamellar triblock copolymer orients in a perpendicular orientation. Interestingly, the exfoliated clay-BCP nanocomposites exhibit an in-plane (parallel) lamellar orientation due to a flipping transition.

Deformation studies were carried out on these various samples and in general, the results show that a significant alteration of the deformation behavior arises due to the incorporation of a few weight percent clay in various states of dispersion (immiscible, intercalated, exfoliated). Chapter 3 provided the initial proof that the presence of layered-silicates dramatically alters the mechanical properties and the BCP deformation behavior. In general, modulus, yield stress, and toughness are observed to increase with increasing clay content. In-situ deformation studies probing the microdomain structure reveals that
due to the presence of clay, significant local stress concentrations arise leading to necking behavior and a higher residual strain after unloading. Chevrons are observed to form only within the neck and the chevrons are locked-in after unloading unlike the neat triblock copolymers. However, a clear understanding of the nature of the reinforcement was not afforded due to fiber symmetric orientation of the BCP as well as the predominantly immiscible layered-silicate morphology.

Using a more hydrophobic organically modified clay (Cloisite® 15A), which was commercially available, led to a purely intercalated morphology. Better understanding of the issues associated with the roll-casting led to a near single crystalline morphology where anisotropic property studies were possible. The mechanical property enhancements observed were however rather modest. The modulus, in the perpendicular direction, improved modestly, but other properties exhibited little increase due to the presence of the clay. Furthermore, when the deformation was performed at various elevated temperatures (at T_g of PS and 20 °C above the PS T_g), which makes the triblock effectively behave mechanically as a homogeneous material, the results show that unlike the neat triblock, there is significant heterogeneous deformation occurring even at these elevated temperatures.

The exfoliated morphology comprised of individual layered-silicates preferentially dispersed in one BCP domain proved to be continually elusive with the commercially modified layered-silicates. In fact, there is no experimental proof in the literature that such a system has been achieved. However, previous theoretical simulations of exfoliation suggested that given the correct surface modification of the layered-silicate, exfoliation should be possible. Collaboration with several great chemists, Prof. Younghwan Kwon, Dr. Thomas Breiner, and Edwin P. Chan, arose to pursue this
goal. Discussions with Kwon, Breiner, and Chan plus review of the literature pointed to the fact that modifying layered-silicates with PS brushes would be the possible where both the grafting density and the molecular weight of the grafted chains can be varied. In another words, control of both the enthalpic interactions via coverage of the clay surface as well as the entropic interactions via chain conformation were possible. Controlling the grafting density is done by surface initiated polymerization off the clay surface. This approach achieved a near single crystalline hierarchical nanocomposite, employing a clay modified to a 100% grafting density, with PS brushes of approximately 6000 g/mol molecular weight. The mechanical properties were highly anisotropic but comparison to a similar neat triblock showed that the modulus changes were small (as was expected due to the reinforcement of the PS domain). However there was an increase in the toughness afforded by the presence of the exfoliated clay as the clay filled PS domains suppress void formation and strain hardening occurs much earlier.

This thesis explored the various responses of triblock copolymers combined with the layered-silicates and showed that, regardless of the clay morphology, significant local stress concentrations arise (necking occurs) and the presence of clay significantly retards relaxation of the BCP domains during unloading (residual strains increase and in perpendicular loading, chevrons are observed after unloading). Different clay morphologies are shown to alter various aspects of the mechanical properties and the presence of clay does not simply imply an increase in all the mechanical properties. It appears that modulus can be dramatically increased by reinforcing the rubbery domains and not the glassy component (as shown in Chapter 5). However, the presence of exfoliated clay in the glassy domain improves the toughness. Effectively, the results allude to the possibility of obtaining an increase in both the modulus and toughness,
which has been elusive in any composite systems. This is an ongoing work which unfortunately will not be finished in time for this thesis, but will be included in the future works section.

6.2 Suggestions for Future Work

6.2.1 Effect of the Nanoparticles
6.2.1.1 Material Properties of the Nanoparticle

A frustration in extracting out the precise effects of the clay sheets in the behavior of the nanocomposite is due to the lack of the knowledge of the properties of these nanoparticles. While such properties can be speculated, none of the exact properties of these clay particles at different morphologies (exfoliated, intercalated, or immiscible) are unknown. For example, it may be postulated that individual sheets of clay do not significantly enhance mechanical modulus due to their flexibility and that perhaps a certain number of layers stacked together are possibly the most desired clay state. Furthermore, in terms of barrier properties, although exfoliation will dramatically increase the surface volume ratio of the nanoparticles in the material, it is still unclear how the barrier properties will change as a function of layer stacking and number of layers in a stack. Additionally, would the inherent “waviness” of the individual clay sheets induce almost little or no reinforcements until the individual sheets are flattened, much like a crumpled paper will not provide resistance to deformation until the sheet is fully flattened out? These questions are only a sampling of the host of questions which may be raised in terms of the materials properties of individual nanoparticles. Until these properties can be satisfactorily assigned, much deductive reasoning will accompany the
interpretation of the measured properties.

6.2.1.2 Particle Size and Shape

In Chapter 1, I had mentioned the variety of sizes of these layered-silicates that are currently employed. This leads to the natural question of the influence of the nanoparticle size on the resulting nanocomposite properties. For example, the small laponite clay will probably have dramatically different barrier properties as compared to the larger fluorohectorite clay due to the surface to volume ratio of these particles. Other properties such as those discussed in Chapter 1 may also be dramatically affected by the particle size. The whole of this thesis has focused on the montmorillonites, but turning attention to different clays of different sizes will also shed deeper insight into the role of the layered-silicates in the nanocomposite properties.

Previously unmentioned is the fact that layered-silicates can also have variety of shapes (sometimes not layered!). Some examples of various clays that have non-layered structure will be discussed below.

First, halloysites are elongated hollow tubular clay which tends to roll-up with each other. Bates et al. [1] showed that the outside diameters were approximately 70 nm (ranging from 40 to 200 nm) and the inside diameters were approximately 40 nm (ranging from 20 to 100 nm). The average wall thickness was approximately 20 nm and their length ranges from approximately 100 nm to 1 \( \mu \text{m} \) (see Figure 6.1). Interestingly, dehydrated samples are not always tubular, but some have split ends or even partially unrolled tubes. A semi-hydrated sample exhibits sometimes angular tubes suggesting that the level of hydration is very important in controlling the particle shape.
Figure 6.1: TEM of a hydrated halloysite from Utah. Not the hollow "doughnut" shapes at the ends of some of the tubes which are viewed along their long axes. Taken from Grim [2].

Another interesting shape is the elongated lath-shaped bundle. Such examples are attapulgite and sepiolite. These laths are typically many microns in length and approximately 50 – 100 nm in width. There is no evidence of the tubular structure as found in the halloysites and high magnification images exhibit a "gutter and channel" like morphology (see Figure 6.2). These lath fibers are typically found in the tangled form much like the texture of a paper.

Figure 6.2: TEM images of (a) sepiolite in transmission mode and (b) attapulgite as a replica. Note the lath-like form of the bundles without any evidence of tubular structures and the paper-like texture of the replica. Taken from Grim [2].
Finally, it should be mentioned that some clays are not even crystalline at all. Clays such as allophone exhibit an amorphous texture with little or no structural organization (see Figure 6.3). Electron diffraction data also confirm the amorphous nature of these particles. Interestingly, the occurrence of allophanes and halloysites together in clays are not uncommon and some researchers postulate that allophone may be a transition form from halloysite or vice versa.

![Figure 6.3: Replica image of allophone as shown in Grim [2]. Note the fluffy aggregate texture of the particles. Electron diffraction data confirm the amorphous nature of allophane.](image)

The various questions regarding the size, shape, and individual properties of these nanoparticles will be of crucial importance for the fundamental understanding of the role of these nanoparticles in the overall nanocomposite behavior. Despite the experimental difficulties associated with performing experiments, derivation of novel and creative test methods is imperative.
6.2.2 Novel Microstructure for Dramatic Property Improvements

Despite the previously outlined shortcomings in the understanding of the layered-silicate properties, the various results from this thesis shed light on possibly improving both the modulus and the toughness of the nanocomposite. I have alluded earlier in Chapter 5 the possible downside of incorporating clay inside the rubbery domains to improve the modulus. However, rather than placing a clay inside a triblock morphology, the production of a triblock which contain clay as the component of the triblock should lead to dramatic modulus enhancements without sacrificing much of the fracture properties. This can be achieved possibly by either of the two methods listed below.

6.2.2.1 Surface Initiated Polymerization of BCP

The concept of surface initiated polymerization can be extended to that of a diblock copolymer off the clay surface which the rubbery domain is first polymerized followed by a glass domain. Although the chemistry indicates a diblock copolymer, in actuality, due to the nature of clay, this turns into a pseudo-pentablock ABclayBA copolymer material with an individual layered-silicate acting as a hard central block surrounded by the soft rubbery domain. In this embodiment, there is 100% bridging chains between the glassy domains which should lead to a material with high modulus and high toughness (see Figure 6.4).

**Figure 6.4:** Schematic showing a diblock which was anionically polymerized from the clay surface. The chain architecture effectively behaves like a pentablock copolymer with 100% bridging chains. The soft rubbery domains are reinforced with a single exfoliated silicate layer.

In addition to the potential property enhancements, fundamental polymer physics may also be addressed in this “ideal nanocomposite” as the phase behavior of the block copolymers will be drastically affected due to the presence of the layered-silicates. In another words, how the block copolymer domain morphology changes as a function of the volume fraction of one component is a question which will most likely baffle the best theoreticians and will likely only be settled by careful experimentation. For example, what happens if the rubbery component is the minority component at 10, 20, or 30 volume percent? These are answers which will probably be affected not only on the volume fraction, but the molecular weight of the polymer as well as the size of the layered-silicate used. The layered-silicate may simply force the BCP domains to be a lamellar domain, but until experimentally shown, nothing can be concluded.

This pentablock approach is an on-going project. I outline the details of the synthesis here. The synthesis of the surface initiated anionic polymerization off clay surfaces has first been performed by Fan et al. [3] and we have closely followed their
synthesis scheme. First Prof. Younghwan Kwon synthesized an initiator similar to the method described in their paper. The reaction scheme is shown in Figure 6.5.

![Chemical Reaction Scheme](image)

**Figure 6.5:** Schematic diagram of the reaction scheme for synthesizing cationic 1,1-diphenylene ethylene (DPE) derivative initiator for use in anionic synthesis.

First the 4-hydroxybenzophenone, 1,12-dibromododecane, and potassium carbonate were dissolved in acetone and refluxed overnight. The mixture was then poured into water, extracted with ether, and dried over magnesium sulfate. Once the solvent has evaporated, the remnants were recrystallized using methanol which yielded white crystals. The crystals were redissolved in THF. Next, methyltriphenylphosphine bromide was dispersed in THF and methylolithium was added and stirred for an hour. At this point, the previous solution was cooled to −80 °C and the solution of 4-(12-bromododecyloxy)benzophenone was dropwise added. After addition, the solution was brought back to ambient conditions and stirred overnight. The 4-(12-bromododecyloxy)diphenylethylene was then recrystallized into colorless crystals following the same previous scheme. The final step consisted of dissolving the obtained crystals in trimethylamine/methanol solution (10 wt%) for approximately 3 days. The
methanol was evaporated, and the residue was redissolved in cold methanol and filtered using a Buchner funnel. The filtrate was the final desired Trimethyl-[12-[4-(1-phenylvinyl)phenoxy]-dodecyl]ammonium bromide (DPE).

After obtaining the DPE initiator, cation exchange reaction is performed by dispersing the Na⁺ montmorillonite in water and the DPE initiator water/THF solution (50vol%) at approximately 1 wt% solution concentration. The amounts of DPE and clay were adjusted according to the CEC of Cloisite Na⁺ (95 meq/100 g) and the molecular weight of the initiator (442.67 g/mol) so that a 10% excess (in moles) of the initiator is present. This solution is stirred vigorously as the clay solution is dropwise added. This is again performed so that there is ideally always an excess of the surfactant relative to the clay to drive the reaction. This causes the negative clay layers to attract the positively charged DPE initiator and they subsequently precipitate. Nevertheless, the solution was stirred for an additional 24 hours to ensure full exchange has occurred. The solution is then centrifuged at 3400 rpm in a benchtop centrifuge for approximately 20 minutes and the supernatant which possessed excess initiator was discarded. This step was repeated a few times. The resulting clay was then dried at ambient condition for two days and subsequently dried at 60°C for one day to ensure all water is fully evaporated.

A closed high vacuum reactor vessel was prepared by Edwin Chan through glass blowing where a filter was inserted between two flasks as shown in Figure 2.14. The dry clay was placed in one of the flask ends with significant excess amounts of sBuLi at which point the clay turned dark red indicating the initiation of the DPE on clay surfaces. Excess sBuLi was used to rid of possible impurities in clay which may kill the living anions. The vessel was then frozen using liquid nitrogen and evacuated down further to rid of all gases. After the vessel was fully evacuated, benzene was distilled into the
reaction vessel. The benzene was then frozen using liquid nitrogen and the reactor vessel was pulled down further and the chamber was sealed off to maintain a high vacuum. The benzene was stirred for several days to fully disperse the clay. After full dispersion, the solution was then allowed to move across the filter which traps the clay but the solvent and the excess initiators are passed into the other second flask. Subsequently, benzene was redistilled into the original flask leaving the excess sBuLi in the second flask. This purification was performed three times to ensure that no free sBuLi remains in the polymerization flask at which point the flasks were then separated and carried into a nitrogen purged glove box for anionic polymerization.

![Diagram of reactor](image)

**Figure 6.6:** Schematic diagram of the reactor built for anionic synthesis. After distillation of the benzene from the collection flask back into the main reactor chamber, the reactor is sealed at the constriction and brought into the glove box, where the breakseal is broken and monomers were subsequently added for polymerization.

The isoprene monomers were then added corresponding to the amount of living anion sites present (calculated by weighing the clay and measuring the percentage of organic components on the clay through TGA) for the desired molecular weight. The color of the solution then turns to a yellowish orange which is typical of isoprene anionic
polymerization. The polymerization is allowed to be carried out for a week(!) at which point an aliquot of the sample is taken and precipitated in methanol to measure the molecular weight of the isoprene chains. In the polymerization flask, styrene monomer is then added. The change in the color is slight but can be seen to shift to a deeper orange color. The solution is stirred again overnight, and the growing chains are then terminated by adding in methanol and a clear solution is formed. The solution is taken out of the glove box and the excess solvents are then taken off using a rotary evaporator to minimize the use of methanol in the subsequent precipitation step. After precipitation, the polymer is collected and dried under vacuum for one day, and subsequently dried in a 60 °C vacuum oven for another day to ensure complete removal of solvents.

To do a GPC of the finished diblock, the corresponding aliquots and excess LiBr were dissolved in THF and refluxed at 70 °C for two days which cleaves the bonds off the clay surface. The solution was then used precipitated in methanol and the precipitates were redissolved in toluene to perform GPC.

6.2.2.2 Crosslinked Surfactants in the Rubbery Domains

One other possibility to achieve such a similar structure would be to first arrive at the understanding to obtain fully exfoliated layered-silicate preferentially inside the rubbery domains analogous to the results I have obtained in Chapter 5. However, during the surfactant chemistry, if reactive groups were present on the surfactants that are possible to preferentially crosslink to the nearby matrix rubbery chains (without crosslinking the whole rubbery matrix domains), this would lead to the desired effect of covalent bonds between the clay tethered surfactant and the matrix polymer. This would in effect lead to very similar phenomenon as the afore-mentioned surfaced initiated
diblock off the clay surface. In fact, this may be an easier route for achieving the desired effect of modulus increase with little or no sacrifice in the high tensile strain behavior of the triblock copolymer.

6.2.3 Thermodynamics of Exfoliation

In my opinion, the highlight of this thesis is based upon the successful proof that a hierarchical exfoliated nanocomposite can be synthesized by appropriately tuning the energetics of the system. This was done by considering the $\chi$ interactions between the matrix polymer chains and the grafted polymer chains, the entropic interactions through a change in the molecular weight of the surfactant chains, and lastly the grafting density which can affect the entropic interactions, the enthalpic interactions, and also the shape of the layered-silicates. However, there are far deeper studies to be performed. A noble goal would be to quantitatively predict the energetics of exfoliation and derive a map of the various energetics required for exfoliation. While it is true that much of theoretical treatments have dealt with describing the various possible variables to consider, nevertheless these results are only a very qualitative explanation of the energetics at hand. No quantifiable numbers are given. Furthermore, the variables listed in these various theoretical studies may not be complete and more considerations may exist. If we were to assume that the three variables utilized in this study are the dominant variables to consider, then a systematic change in $\chi$ from positive to a negative value accompanied by the determination of the critical molecular weight necessary to induce exfoliation would be a highly valuable tool for the nanocomposites field in general. Essentially, the required critical molecular weight may decrease as $\chi$ is decreased. As an example, using polyphenylene oxide (PPO) as the grafting chains dispersed in PS ($\chi_{\text{PPO-PS}} < 0$) may
require only short grafted chains to induced exfoliation whereas the use of alkylammonium ions may never drive exfoliation regardless of the molecular weight. These are questions which all need to be answered for the successful rational preparation of exfoliated nanocomposites. Additionally, controlling the grafting density of the grafted chains at the various molecular weights and χ’s will lead to a 3D map of the required interactions for exfoliation. And analogously, adding further variables will lead to higher dimensionality maps for exfoliation. For example, possible other variables may be the weight fraction of layered-silicates incorporated which may at high loadings lead to solubility problems, influence of processing history which may utilize various temperatures or solvents for processing, influence of flow fields in the nanocomposite during formation or after formation, role of the “other” block in the BCP chains in terms of its χ and molecular weight, and the influence of the size, shape, and stiffness of the layered-silicate used. Through the process, successful elimination of unimportant variables will allow uncluttered view of the important thermodynamic parameters and possibly eureka of very important variables may also result. Undoubtedly different variables affect the change in free energy of the system from the initial state to the final state and correspondingly can affect the exfoliation map. Granted it is a daunting task, it would however be a noble task to arrive at the quantitative guiding principle for exfoliated nanocomposite formation.

6.2.4 Rheological Behavior

We have observed a flipping transition in lamellar orientation to occur due to exfoliation of PS grafted layered-silicates. This is envisioned to occur as the numerous layered-silicates in the parallel orientation force the PS domains to adjacent to maximize
the contact area as the solvent evaporates and the BCP undergoes a order-disorder concentration. As additional solvent evaporates, the PS domains become glassy and the structure is locked in. However, whether the same parallel orientation will develop during roll-casting if the rubbery chain modified clay was exfoliated is currently unknown. Furthermore, increase of the layered-silicate content on the rheological properties is not known either.

In general, the rheological response of these complex fluids with nanoparticles is an interesting subject. The rheological response for exfoliated structures in the melt state is also an area which has not been understood as of yet. Krishnamoorti's group focused on these aspects of an intercalated structure on the ODT (see Chapter 1), but no studies were done on exfoliated structures as of yet. And as the solution's rheological behavior seems to be drastically altered, it may be possible to observe new phenomenon in the melt state of an exfoliated nanocomposite as well. Hopefully, these new insights may lead to innovative processing techniques for the production of nanocomposites.

6.3 Final Thoughts

Much of the stellar mechanical property improvements in nylon 6 nanocomposites have not been observed in most glassy material nanocomposites. In fact, the reason for nylon 6's improvement is due to the modification of the crystalline regions which has a much more profound effect on the mechanical properties as opposed to the "local" dynamics of confined amorphous glassy phases. Hence, perhaps it is naïve and overly optimistic to be touting and hoping for dramatic improvements in the mechanical properties of all nanocomposites. However, keeping a multifunctional viewpoint to the nanocomposites will be crucial in future successful development, understanding, and
commercialization of these nanocomposites. Barrier properties, increased heat deflection temperatures (allowing not just higher serviceable temperatures but faster cycle times during processing), optical transparency, ablative properties, and reduced overall composite weight should all be kept in mind as the multifunctionality of these materials may be their key attractive asset. Furthermore, there is one key point not lose track of: while the comparison to the neat materials is critical and important, the true comparison should be comparison of the properties to traditional composite systems. The painstaking efforts to make a nanocomposite may not be justified if similar or better enhancements are to be expected from simple microcomposites. And lastly, while fundamental academic understanding and knowledge is crucial, it should be kept in perspective that ultimately we want these nanocomposites to help and enhance our daily lives. As such, efforts at understanding the fundamental reasons of nanocomposite behavior or formation should ultimately have the goal of improving materials properties. Granted the importance to uncover when certain enhancements are not to be expected, a blind eyed approach of simply testing an experimental variable without purpose or reason will only add to the many non-innovative clutter currently being produced in this field.
6.4 References


Appendices

Appendix A: Calculation of detector positions at X27C beamline

Recall the schematic diagram of the X27C beamline for simultaneous WAXS and SAXS.

We will work through the example using the X-ray wavelength: 1.307 Å

First, calculate the maximum spacing desired on the WAXS detector.

Let’s say that we want to observe at maximum a 4 nm spacing in the WAXS plate. Bragg’s law simply states that $\lambda = 2d \sin \theta$. This implies that $\sin \theta = \frac{1.307}{2 * 40}$ which gives $\theta = 0.936^\circ$ which we can substitute into our schematic diagram above and calculate the position ($L_w$) of the WAXS detector. But assuming a slight non-centering of the beam relative to the hole and any other experimental errors which may cause slight deviations, let’s calculate the maximum spacing using 0.7 cm as the resolvable spacing instead of the
0.6 cm hole radius.

Thus, \( \tan 2\theta = \frac{0.7}{L_{\text{WAXS}}} \) which gives \( L_{\text{WAXS}} = 21.4 \) cm. Calculating the smallest resolvable spacing is analogous by simply measuring the outer dimension of the image plate and compensating for slight deviation from beam center.

**Calculate the smallest resolvable spacing in the SAXS**

Due to the slight small diameter flight path after the WAXS plate, the smallest resolvable spacing in the SAXS is typically slightly larger than the smallest resolvable d-spacing simply based on the image plate. The largest \( \theta \) possible is calculated as follows.

\[
\tan 2\theta = \frac{0.6}{L_{\text{WAXS}} + 3.5}
\]

which for our example gives \( \theta = 0.690^\circ \). Then using our Bragg’s Law again, \( d = \frac{\lambda}{2\sin\theta} \), the smallest resolvable spacing is calculated to be 54 Å.

The WAXS allows resolution of 40Å and smaller.

The SAXS allows resolution of 54Å and higher which depends on the beamstop.

This leads a “blind-spot” between 40Å and 54Å which simply cannot be resolved by these two detectors in the positions selected.
Appendix B: Useful Commands for Operations of CHESS D1 Beamline

These are notes taken over the course of a few CHESS D1 beamline experiments which shows the operation of the software which is used in the beamline. In the last part of the appendix is the protocol for the alignment of the beamline. However, this should be used as a guideline, and any inquiries which may arise should be directed to the beamline operator to prevent damage to equipment and user.

If you have your own computer, set your windows workgroup to CHESS – this allow access to all CHESS computers under “Computers Near Me”

Login for all CHESS computers are:
username: specuser
passwd: BeamMeUp

SPEC commands
we – write everything
mv samx 5 – move motor called “samx” 5 mm to the right
mv samz 5 – move motor called “samz” up 5 mm
tw samz 1 – tweak movement of motor “samz” slightly in either + or – by 1 mm

TV6 Program Commands

hbin=vbin=1 gives 2MB file (1024x1024)
hbin=vbin=2 gives ~500KB file (512x512) – use this if you want to do quick data collection as it will considerably reduce transfer time from the electronic detector to the file

exit – exits from dos shell to TV6 program

isose 1 1 – opens the shutter
isose 1 0 – closes the shutter
**expt=1** – exposure time to 1 sec  
**move im0=ime** – move image 0 to CCD image i.e. take picture  
**disp im0** – display the image 0  
**disp 200 0** – first number the low level  
**disp 200 -1** – move the bits over by one

**imagepath h:/Thomas** – set a default directory where images will be saved  
**autoname MIT** - makes files save as MIT0.tif with number incrementing for every new file  
**move ima=im0** – saves the current file

**typeheader MIT0.TIF** – outputs information on the MIT0.TIF file  
**disp MIT0.TIF** – displays MIT0.TIF in a linear intensity scale  
**disp MIT0.TIF 512 3000** - first number gives background second number changes other parameter  
**pwrsee filename #1 #2 #3** - log scale display bg, contrast(bigger than #1), power setting

Loop code

```plaintext
define doit="auto move im1=ime; move ima=im1"
extpt=10
for (i=1; i<51; i++) {doit; wait 50}
```

*COSMIC RAY CORRECTION (Fit2D can usually do this later so not critical)*

Basically take 2 data files, 2 background, compare the data, compare the background (to remove the zingers) and subtract data – background.

**expt=30s**  
**auto move im1=ime; move im2=ime; move im3=imb; move im4=imb; move im5=im1:im2; move im6=im3:im4; move im7=im5-im6;**  
**pwrsee im7 0 1000 0.3**  
**setint** – enter in c:\perm\1kbin1.tif for intensity correction  
**setdist** – enter in c:\perm\x1kbin1.tif for x distortion correction  
\[c:\perm\y1kbin1.tif\] for y distortion correction

*Calibration (using silver behenate or lamellar BCP samples)*  
**dens**
left mouse get center
right mouse direction of integration
a toggles between line vs circle (need to be in line mode to integrate)
i integrates
r returns to the * prompt

**peak**

x to enter in wavelength
l for lamellar mode
-1, 1 -2, 2, -3, 3 indexing using the peaks and left mouse button
c for calibrate
d for d-spacing fit

Enter in the correct d-spacing for your calibrant
f to get an idea of how good your fit is (straight if lamellar)

Spec-to-phos number multiplied by 0.051 gives actual sample to detector distance

see – brings back to image

**INTEGRATION TECHNIQUE**

**Dens**

t toggle area of integration
Right mouse click to change direction
p to turn on perpixel normalization (no V-shaped curve)
i to integrate
r to return to * prompt

**Peak**

Left hold mouse button
a to get d spacing

Left mouse
Right mouse
And make a box
e to zoom into a peak of interest
Aligning the beam

1. Find the beam position at slit1 (motors s1x and s1z and detector I0)
   * counters
     monitor – don’t change
     detector – choose I0
   * dscan s1x –2 (left (absolute) position in mm) 2 (right position in mm) 40
     (numpoints) 0.1 (time at each point)

   if slit is not wide enough, open slit using the micrometers and repeat

   * mv s1z –0.2 (if –0.2 happens to be your center position)
   * set s1z 0 (resets –0.2 to the new zero)

   Set the slit size to your desired size – one full rotation of the micrometer is 500
   microns. Usually close everything off and increase until the desired slit size.

   Do this for both s1x and s1z

2. Repeat the above procedure for second slit (s2x and s2z and I1)
   BEFORE OPENING THE CCD SHUTTER, MAKE SURE THE GARAGE DOOR IS DOWN!!!!!!!

   The slit sizes of s1 and s2 should be approximately equal.
   One full rotation of the micrometer is 500 microns
   The shutter is in place between I1 and s2, so need to open from here on out
   * isoset 1 1

   In the dscan, FWHM is twice your beam size; i.e. 300 micron FWHM is 150
   micron size slit

3. Center the sample holder using burn paper roughly. Then fine tune by using dscan on
   motors samx and samz and I2.
4. Place the tube and make sure He is flowing through using the right most flow meter on the wall since He flow will cause the Kapton tape to slightly bulge a little. So do not change flow rate after setting your beamstop.

Use a burn paper on the end of the tube (near the garage door) and poke a hole in the beam center only on the burn paper!!! Then mark the Kapton tape with a pen through the hole. Use a regular glue to place the beamstop on the Kapton tape

isoret 1 0 – close the shutter since move im0=ime command will automatically open and close the shutter.

Raise the garage door.

Set exposure time to 0.1s as you don’t want to burn the CCD detector!
  * expt=0.1
Center the beamstop
  * mv flux 0.2
  * mv ftuz 0.1 etc...

6. Remove the edge flares using slit 3.
   Carefully close down the slit3 so that the edge flares from slit2 is gone. If you close down too much, you will see sharp flare coming from slit3, so this is a delicate process. Close down SYMMETRICALLY from both sides if you know the center of the slit3 already and do it little by little. This takes time....

7. Once you get flares away sufficiently
   close garage door
   isoret 1 1
   dscan s3x -1 1 40 0.1
   dscan s3z -1 1 40 0.1
   the FWHM should give you the beam size - adjust according to the size you want.

8. You are almost ready for measurement. Close the shutter
   isoret 1 0

9. Run a calibration – Silver behenate is usually a good choice.
Appendix C: Example Calculation of Grafting Density of PS on Clay

For a given molecular weight of PS, the theoretical grafting density can be calculated given that the cation exchange capacity (CEC) of the clay is known. This section will detail an example to calculate the percentage of 6000 molecular weight PS tethered on clay relative to the theoretical amount possible.

Theoretical Grafting Density Calculations

The sodium montmorillonite used in this study possesses a CEC of 95 meq/100 g which essentially states the maximum amount of charge per gram the clay can hold. This corresponds to 91.675 C/g.

In an amino terminated polystyrene (PS), there is exactly one positive endgroup which is available for attachment to the clay surface. Of course, depending on the actual functional group on the end of the polymer, this ratio must be appropriately adjusted.

Since the PS possesses a molecular weight of 6000 g/mol, each gram of PS contains a total charge of 16.14 C as shown below.

\[
\frac{1 \text{ g of PS}}{6000 \text{ g/mole}} \times \frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mole}} \times \frac{1 \text{ charge}}{\text{molecule}} \times \frac{1.609 \times 10^{-19} \text{ C}}{\text{charge}} = 16.14 \text{ C}
\]

Then from the CEC which is supplied from the clay supplier, for each gram of 6K PS, exactly 0.176 g of clay is required.

\[
\frac{16.14 \text{ C}}{91.675 \text{ C/g}} = 0.176 \text{ g}
\]
This leads to a theoretical mass ratio of 85% in the 6K PS functionalized clay

\[
\frac{1\text{ g}}{1\text{ g} + 0.176\text{ g}} = 0.850
\]

**Percent Actually Grafted**

By measuring the mass lost upon ignition in the TGA, the relative mass fraction of the organic content can be determined. Thus, if 80% of the sample is measured to be the organic component, then there would be approximately \(0.8/0.85 \sim 94\%\) actual coverage.