NOVEL APPROACHES FOR NANOCOMPOSITES PREPARATION AND CHARACTERIZATION

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NOVEL APPROACHES FOR NANOCOMPOSITES PREPARATION AND CHARACTERIZATION

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Thesis

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ABSTRACT

In recent years, clay filled polymer nanocomposites are manufactured for a variety of advanced applications due to the abundant resource in nature, platelet structure bearing high aspect ratio, high efficiency, and promising ion-exchange capacity of clay minerals, especially Montmorillonite. To achieve a moderate level of clay dispersion, one of the most ubiquitous approaches is to modify the surface of the layered silicates by exchanging inter-gallery metal cat ions with quaternary ammonium salts. The resultant product is commonly referred to as organoclay. However, the existence of small organic molecules, such as alkyl-ammonium salt in the polymer, leads to vitiation of thermal properties and unnecessary hydrophobicity, in addition to involving tedious ion-exchange and drying process during the preparation of surfactant modified clay. To resolve these issues, in this work, we have developed an ultra-sonication assisted film casting technique to achieve well-intercalated nanostructure of polymer/clay nanocomposites.

According to the chemical structure of natural Montmorillonite, hydroxyl groups are present among the negatively charged silicate layers. These hydroxyl groups, if made accessible to the polymer chains area wise, can promote polymer-clay surface interactions for polymers with polar repeating units via hydrogen-bonding. Using ultra-sonication film casting technique, we have dispersed natural Montmorillonite in zinc-neutralized sulfonated EPDM ionomer (Zn-S-EPDM) and polycaprolactone. We also have proved that this technique is applicable to the traditional
polymer/organoclay systems through the preparation of polystyrene/Cloisite 10A nanocomposites. The morphology and properties of these composite systems are characterized using wide angle X-ray diffraction (WAXD), transmission electron microscope (TEM), tensile test, dynamic motion analysis (DMA), and strain-induced buckling instability for modulus measurements (SIBIMM). We have observed different phase behaviors at various filler volume fractions, which are consistent with the intercalation thermodynamic modeling. Because of the well-dispersed nanostructure, Halpin-Tsai model provides generally accurate prediction of the enhancement towards mechanical properties at lower levels of clay loading.
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CHAPTER I
INTRODUCTION

Hybrid polymeric materials and polymer blends define a unique family of materials, such as thermoplastics, thermosets (elastomers), and a type of filler particle of a nanometer size scale (often less than 100nm). Such materials are known as polymer nanocomposites (PNC). Polymer nanocomposites (PNC) are widely manufactured for advanced applications. Nowadays, due to the high popularity of research in synthesis, processing, and morphology control of PNC, dispersing nano-fillers into a polymer matrix has proven to be an effective and economically efficient strategy to achieve retardation of thermo degradation, superior barrier properties, and enhanced mechanical strength. Of particular interest is the study of clay filled polymer nanocomposites due to the abundant resource in nature, platelet structure bearing high aspect ratio, high efficiency, and promising ion-exchange capacity of clay minerals.

Ever since the first time Toyota introduced the concept of clay filled nylon 6 nanocomposites, enhancements towards novel preparation methods and determining the associated improvements in the characteristics of polymer/clay nanocomposites (PCN) have been widely investigated in recent decades \(^1\). The level and state of dispersion of clay layers in the polymer matrix is the key factor impacting the physical and mechanical properties of the composite material. Overall, the uniformity of dispersion can be subcategorized into four types of morphologies: aggregation of clusters, intercalation
(polymer chains sandwiched by silicate layers), flocculation (intercalated agglomerates dispersed into small tactoids), and exfoliation (complete disassociation of layers by polymer chains), shown in Figure 1.1. The first type, aggregation of clusters, is no different from the carbon black filled elastomer, in which filler particles are aggregated into micron sized clusters. In this instance, a substantially large amount of fillers have to be introduced into the host matrix in order to upgrade polymer performance. Unlike aggregation of clusters, a small amount of clay particles can yield a prominent improvement of properties if at least one of the latter three dispersion conditions can be satisfied, so the resultant composite can be called a nanocomposite.

![Figure 1.1. The most common morphologies of polymer-clay nanocomposites](image)

There is no shortage of preparation strategies and characterization techniques reported in both academic publications and industrial patents. For non-polar polymers, adding polar functional groups that have strong interactions with the coupling agent is a recently reported approach to allow one step melt mixing among the polymer, surfactant, and natural clay. Besides, a more ubiquitous first step is the chemical modification of clay by exchanging metal cations of the original clay mineral powder with organic surfactant ions (e.g. quaternary ammonium salts). The resulting product is commonly

2
referred to as organoclay, which has a great advantage over the pristine clay. This is because energy produced by high shear in the extruder or intense mixing in the solution can hardly reach the minimum energy required to overcome the electrostatic and van der waals attractions among the negatively charged layers and their metallic counter ions. The surface of silicate layers has to be modified by organophilic cations so that activation energy for polymer chains to open the inter-gallery spacing can be significantly reduced due to the hydrophobic interactions between surfactant and polymer chains. However, the existence of small organic molecules, such as alkyl-ammonium salt in the polymer, leads to vitiation of thermal properties and unnecessary hydrophobicity, in addition to involving tedious ion-exchange and a drying process during the preparation of organoclay. For polymers applied in the biomedical field, the presence of surfactant molecules can potentially cause complications in biocompatibility, leading to a higher toxicity and restrictions in clinical use.

Development of polymer/pristine clay nanocomposites is more attractive than usage of organically modified clay (organoclay) for lowering costs and additional processing steps on the clay needed for nanocomposites preparation. To achieve this, aside from the aforementioned one step melt intercalation, in-situ polymerization is a frequently used technique. Inserting catalyst into the inter-layer gaps, followed by polymerization has been reported for preparation polyolefin/clay nanocomposite, but besides the exquisite catalyst preparation process, a large amount of the clay-supported catalyst has to be used for acquiring the composite with proper clay content. In case of highly hydrophobic polymers, due to the lack of polymer-clay interaction preventing re-aggregation, high temperature in the processing equipment can inevitably compromise the intercalated nanostructure.
obtained through in-situ polymerization. In contrast, water-assisted mixing is a simpler and cheaper method because colloidal suspension of clay minerals in water can invoke the swelling of the galleries as water molecules inside the inter-gallery spacing are able to weaken the electrostatic tractions among the charged layers\textsuperscript{20}. Because of this, intense stirring and ultra-sonication can effectively lower the particle size or even exfoliate the silicate layers. Therefore, pre-dispersing clay particles in an aqueous media is applicable to host matrices that are either water-soluble or hydrophilic in nature, such as nylon\textsuperscript{6} \textsuperscript{21}, polyvinyl alcohol\textsuperscript{22}, polyamide 11\textsuperscript{23}, and starch\textsuperscript{24}, etc. Similarly, nanocomposites made from emulsion polymerized compounds have been developed through latex coagulation with the addition of proper coupling agents\textsuperscript{25-30}. In this case, water in the emulsified colloid is used as the gallery swelling agent. However, the lack of interfacial interactions is still a bottleneck that makes this strategy non-feasible to sustain the achieved morphology if the host matrix doesn’t contain polar repeating units, which is why these coagulated latex composites require the use of coupling agents.

Though extensive research has been focusing on the preparation of polymer/clay nanocomposites, the majority of the techniques reported only focus on the interaction between polymer and organoclay surfactant or coupling agent, but ignore the intrinsic chemical structure of clay. Even for polar polymers containing hydrophilic groups, such as polymer grafted with maleic anhydride, hydroxyl-containing surfactant was used to promote interactions between the polymer chains and surfactant ions.\textsuperscript{31-36} For example, during the reactive extrusion process to produce maleated cellulose/Cloisite 30B nanocomposites, grafted maleic anhydride reacts with the hydroxyl group contained in the methyl, tallow, bis-2 hydroxyethyl, and quaternary ammonium, the organic modifier of
Cloisite 30B. In this case, the intercalated nanostructure indicates that polymer chains are well combined with the organic modifier using maleic anhydride as a compatibilizer. Similarly, dielectric loss observed in the Cloisite 30B intercalated with polycaprolactone (PCL), indicating the restriction of chain motions due to effective hydrogen bonding interactions between carbonyl groups in PCL and hydroxyl groups in quaternary ammonium. In both cases, hydroxyl groups in the organic modifier play a key role in the polymer-clay interaction. In essence, so long as the polymer contains segments that have either physical or chemical bonding with hydroxyl groups contained in the surfactant, an intercalated or exfoliated nanostructure can be effectively achieved and stabilized. However, it is worthy to mention that clay minerals, such as montmorillonite and laptonite, are hydroxyl-rich substances by themselves. As illustrated in Figure 1.2, a large amount of hydroxyl groups are present within the alkali metal oxides in the two dimensional tetrahedral structure of montmorillonite layers.

![Chemical structure of the layered silicates](image)

Figure 1.2. Chemical structure of the layered silicates
Now, the only question is whether these hydroxyl groups are accessible area wise to the polar part of polymer chains so that polymers grafted with hydrophilic functional groups can intercalate non-modified clay. Although this mechanism hasn’t been investigated in detail, the possibility of accessing inter-layer hydroxyl groups has already been effectively demonstrated in water soluble polymer systems. Examples of these systems are polyvinyl alcohol and starch.\textsuperscript{22, 24, 31} Little attention has been drawn to the non-water soluble polymer systems that contain hydrophilic repeating units. Therefore, it is of great interest to broaden the use of this mechanism and develop a generally feasible technique to prepare nanocomposites with natural clay.

In this work, a novel approach to prepare polymer/pristine clay nanocomposite has been adopted by dissolving polymer into hydrocarbon solvent and mixing with pristine clay suspended in a small amount of water upon intense sonication. Common sense seems to dictate that introduction of water into water-immiscible solvent can result in precipitation of polymers. In reality, it is important to note that a small amount of water can be uniformly suspended in the solutions of polymers that contain hydrophilic groups for a sufficient amount of time before the occurrence of precipitation, which can be caused by a high local concentration of water as clay containing aqueous solution is introduced into the organic solution drop wise. To resolve this issue, intense sonication can help to disperse water drops into smaller sizes, preventing the local water concentration from surging. Therefore, we have successfully developed a novel ultrasonic assisted film casting technique, and several polymer systems with polar repeating units have been tested. First, super-hydrophobic EPDM elastomer was grafted by sulfonate groups and neutralized with zinc cations. The performance of the resulting
nanocomposite was evaluated by tensile test and dynamic motion analysis (DMA).

Secondly, the biodegradable polymer polycaprolactone (PCL), was mixed with Montmorillonite suspended in aqueous media directly assisted by probe sonication. Last but not least, we have proved that this novel technique is also effective for the traditional polymer/organoclay system through the preparation of polystyrene/Cloisite 10A nanocomposites. Both of the latter two systems (polystyrene and PCL) were examined through though strain-induced elastic buckling instability for mechanical measurements (SIEBIMM) to investigate the effect of nanoclay on thin film modulus.
CHAPTER II
LITERATURE SURVEY

2.1 Mechanisms of Intercalation

2.11 Effect of Organic Modifiers on Intercalation

Nanocomposites prepared using a variety of polymers and surfactants have been investigated extensively in recent decades. It is a no-easy-task to summarize every polymer system with all the characterization techniques in a comprehensive manner. However, regardless of preparation methods and polymer types, the process for polymer chains to penetrate through the inter-layer spacing has to be spontaneous ($\Delta F < 0$) in order to achieve a stable morphology of the resulting composite product. On the other hand, a positive free energy of gallery-opening process yields complete phase separation between polymer chains and platelet sheets. To determine the directionality of this process in a general picture, mean field theory was used to assume that the free energy of layer separation can be divided into two components, namely internal energy and conformational entropy, as shown in Equation 1. 

\[ \Delta F = F(h) - F(h_0) = \Delta E - T\Delta S \]  

Equation 1

Here, $h$ and $h_0$ stand for the height of basal spacing after intercalation and the basal spacing of the original clay, respectively.
For the entropic component, first order approximation was used to assume that the total energy gain of the system is the summation of $S_{\text{polymer}}$ and $S_{\text{chain}}$. $S_{\text{polymer}}$ is the conformational entropy loss in the polymer chain due to the constrain of chain motions after silicate layers are introduced, and $S_{\text{chain}}$ stands for entropy gain in the clay sheets due to the more chaotic inter-gallery conformation.

\[ \Delta S \approx \Delta S_{\text{chain}} + \Delta S_{\text{polymer}} \]

Equation 2

The number of statistical configurations of the organoclay was computed using Flory-Huggin Lattice model. It assumes that $n_0$ lattice sites are available for the $n_0 - i$ surfactant backbone chains (with $m_2$ backbone carbon atoms) to occupy, as shown in Figure 2.1.\textsuperscript{39,40,41}

Using the mean field theory model developed by Barrer\textsuperscript{41}, and etc, the number of statistical configurations for the $i + l$th surfactant chain with $m_2$ backbone carbon atoms follows from the expression:
Here, the parameter $c$ accounts for the number of lattice sites near the surface of the other layer unavailable to the surfactant chains. The parameter $\chi_s$ denotes the fraction of lattice sites near the surface accessible to the surfactant backbone carbon atoms. It can be envisioned that the fraction of the lattice sites available to the chains is closely related to the gallery height. As the height is increased to a value exceeding the surfactant chain length, the number of interlayer lattice sites also increases. Consequently, a fraction of these sites will become inaccessible to the surfactant chains due to the limited chain length. Assuming the distribution of surfactant chains among the interlayer lattice sites follows the Gaussian distribution, the parameter $\chi_s$ takes the following term:

$$\chi_s(h) = \frac{a_2}{h} \cos^2\left(\frac{\pi}{2} \frac{h}{h_\infty}\right)$$

Equation 4

where $a_2$ and $h_\infty$ denote the chain length of the surfactant and the height of gallery when exfoliation is achieved, respectively.\(^{39\ 42\ 43}\)

Based on the mean-field theory, the total number of configurations of all the surfactant chains combined $\Omega$ is derived by taking the statistical combination of all the single surfactant chain configurations, and the result is shown as follows:
Here, \( z \) is the coordination number of lattice sites in a Cartesian coordinate. It can be seen that the total number of surfactant chain configurations are contributed by three factors, as expressed in Equation 5. The first term accounts for the ideal mixing of the surfactant chains by assuming random walk, exclusion of volume, and absence of hydrodynamic interactions. The second term takes into account the fact that silicate layers restrict the motion of the end carbon atom located near the clay surface. The third term describes the reduction of the number of lattice sites available to the surfactant chains as

\[
\Omega = \frac{1}{n_2!} \prod_{i=1}^{n_2} \eta_i = \frac{1}{n_2!} \prod_{i=1}^{n_2} \frac{(n_0 - m_2 i)!}{(n_0 - m_2 (i + 1))!} \times \left( \frac{z - 1}{n_0} \right)^{m_2 - 1} \frac{n_2 - i}{n_0 - m i} c^{(m_2 - 1) \chi_s} \]

\[
= \frac{n_0!}{(n_0 - m_2 n_2)! n_2!} \left( \frac{z - 1}{n_0} \right)^{(m_2 - 1) n_2} \times \left( \frac{n_0 - m_2 !}{n_0 - m_2 n_2} \right) \frac{n_0}{(n_0 - m_2 n_2) m_2 n_2} c^{(m_2 - 1) \chi_s n_2}
\]
the galleries are opened to a wider height. Using Sterling’s approximation, the conformational entropy of the surfactant chain can be expressed in Equation 6:

$$\frac{\Delta S_{V}^{\text{chain}}}{N_{A}k_{B}} = \frac{1}{N_{A}k_{B}}(S_{V}^{\text{chain}}(h) - S_{V}^{\text{chain}}(h_{0})) =$$

$$\frac{-1}{m_{1}\nu_{1}} \hat{\varphi}_{1} \ln(\hat{\varphi}_{1}) + \frac{1}{\nu_{2}} \hat{\varphi}_{2} \ln(c)(\chi_{S} - \chi_{S0})$$

**Equation 6**

Here m, v, and \(\varphi\) represent the chain length, molar volume per segment, and interlayer volume fraction, respectively.  

Since the number of surfactant chains, \(m_{1}\), is a relatively large number, the first term in Equation 6 is negligible compared to the second term. Thus, the expression of surfactant chain conformational entropy becomes:

$$\Delta S_{V}^{\text{chain}}/N_{A}k_{B} \approx \frac{1}{\nu_{2}} \hat{\varphi}_{2} \ln(c)(\chi_{S}(h) - \chi_{S0})$$

**Equation 7**

All the sections above address the conformational entropy of the surfactant chains, which falls into the entropy term of Equation 2. Thus, the next critical component is the entropy loss of the polymer chains due to the restricted motion imposed by the layered silicates, which can be modeled using modified Flory-Huggin theory of polymer melt following Dolan and Edward’s method. The expression of polymer conformational entropy loss is shown as follows:
\[
\Delta S_{V}^{\text{polymer}}/N_{A}k_{B} = -\frac{\hat{\varphi}_1}{\nu_1} \pi^2 \left( \frac{a_1}{h} \right)^2 - \frac{\hat{\varphi}_1}{\nu_1} \sqrt{\frac{3}{m_1}} \frac{a_1}{h}
\]

Equation 8

Here, \( u \) is the dimensionless exclusion of volume parameter.\(^{39}\)\(^{40}\)\(^{42}\)

The combination of entropy loss of the polymer chains and organic surfactant yield the total conformational entropy of the system when polymer chains attempt to penetrate through inter-gallery spacing. Figure 2.2 shows the free energy change due to the statistical conformation change of the polymer-clay hybrid system, where the dashed lines represent the entropy of surfactant chains and polymer, and the solid line depicts the total entropy change.

![Figure 2.2. Change of intercalation free energy with increasing basal spacing\(^{39}\)](image)

\(^{39}\) To cite figure reference.
It can be seen that without accounting for the internal energy change of the system, there exists a threshold value where the total change in system entropy starts to fall into a negative regime, indicating that the gallery-opening process is unfavorable. Without the contribution of internal energy, the unfavorable regime applies to most values of gallery height. Therefore, it is exceedingly crucial to consider the effect of internal energy change on the overall directionality in order to characterize the free energy in an accurate fashion. To achieve this, it is assumed that the internal energy change is governed by the energy associated with interaction, which can be described using area approach developed by van OSS and co-workers\textsuperscript{39, 45}:

\[ \Delta E = A^f_{sp} \epsilon_{sp} + A^f_{ap} \epsilon_{ap} + (A^f_{sa} - A^i_{sa}) \epsilon_{sa} \]

Equation 9

Here, $A^f_{jk}$ and $A^i_{jk}$ are the initial and final contact area between two components during the process. Parameter $\epsilon$ denotes the total interaction energy per unit area.

Taking into account both internal energy and entropic factors, the polymer-clay hybrid system can fall into four categories, as shown in Figure 2.3, where curves (a), (b), (c) and (d) depict four different types of hybrids.\textsuperscript{39}
Figure 2.3- Four different types of polymer-organoclay hybrids.

The first type describes the scenario when all values of gallery height correspond to positive free energy of intercalation, indicating the polymer chains are incompatible to both layered surface and organic modifier. In contrast, when the polymer is compatible with the surfactant, the hybrid can exhibit intercalated nanostructure with limited gallery height. This instance falls into the second type. Sometimes, the intercalated agglomerate fall apart into smaller particles, and this situation can be described by curve (c). As a result, all the gallery height values are negative, but there exists a local minimum near the gallery height threshold. Finally, complete exfoliation of layered silicate can be depicted by curve (d), when all height values correspond to negative free energy with a prominent decreasing trend.\textsuperscript{6 39 46 47 48 49}

2.12 Effect of Polymer Functionalization on Dispersion

In the previous section, we can conclude that organic modifier can help polymer chains to penetrate through inter-gallery spacing to achieve the intercalated nanostructure.
However, from the mean field theory statistical analysis, it is apparent that the effect of surfactant chains themselves can only yield intercalated morphology if interaction between the polymer and silicate surface is weak. The reason is that a high value of gallery height renders more lattice sites unavailable to the surfactant chains. Consequently, the conformational entropy of the surfactant chains is compromised due to the reduction of $\chi_s$ value, leading to a less spontaneous or even unfavorable gallery-opening process.

To achieve a better dispersion morphology, such as exfoliation or flocculated intercalation, a feasible approach is to modify the polymer chains with functional groups that are able to facilitate polymer-silicate interactions. To numerically quantify this effect, a self-consistent field method was applied using the Scheutjens and Fleer theory.\textsuperscript{50,51,52} In essence, lattice sites have the planer, layer by layer structure, assuming a translational invariant system along the lateral direction. Each repeating monomer unit occupies one lattice site. The layers are counted from the first layer ($z = 1$) to the Mth layer ($z = M$). If the system is simplified in one dimension, the properties are only dependent on the layer parameter $z$. The probability that a monomer repeating unit $i$ is present in the layer $z$ follows from the expression:

$$G_i(z) = \exp\left(-\frac{u_i(z)}{kT}\right)$$

\textbf{Equation 10}

Here, $k$ is the Boltzmann’s constant; $u$ is the potential of the repeating monomer to be in the layer $z$, which is given as follows:
The first term ensures that every single layer of lattice sites is filled with at least one repeating monomer. The parameter \( \phi \) denotes the bulk polymer concentration, and the parameter \( \chi \) represents the Flory-Huggin interaction parameter. The term \( \langle \phi_j(z) \rangle \) describes the fraction of monomers in the layer \( z \) that have contact with chains located in the nearby layers, which follows the expression below:

\[
\langle \phi_j(z) \rangle = \lambda_{-1} \phi_j(z - 1) + \lambda_0 \phi_j(z) + \lambda_1 \phi_j(z + 1)
\]

**Equation 13**

Here, \( \lambda_{-1} \) is the fraction of segments in contact from the previous layer, \( \lambda_0 \) is the fraction of segments in contact from the same layer, and \( \lambda_1 \) is the contact fraction of the segments in the next layer.

The volume fraction of a single segment is follows from the expression:

\[
\phi_j(z, s) = C_i G_i(z, s|1) G_i(z, s|r)/G_i(z)
\]

**Equation 14**

Here, \( C \) is the normalization constant to make sure the maximum value of this fraction doesn’t exceed unity. \( S \) represents the number of repeating monomer segments. \( G \) is the probability for the segment \( s \) to be located within the layer \( z \), which is represented by the Green’s correlation computed from the recurrence function shown as follows:
The total volume fraction is obtained through adding up the volume fraction of every single segment:

\[ \phi_I(z) = \sum_s \phi_I(z, s) \]

**Equation 16**

The free energy of the system, \( F \), as a function of lattice layer location \( z \), is expressed as follows:

\[ F(z) = \sum_j \phi_j(z) \ln G_j(z) + \frac{1}{2} \sum_{jk} \chi_{j,k} \int \eta(z - z') \phi_j(z) \phi_k(z') \, dz' \]

**Equation 17**

Here, the term \( \eta(z - z') \) is the short range interaction parameter. The change in free energy as a function of gallery height is obtained by taking the difference between the free energy state when the layers are not separated and the free energy state when the gallery height is increased from the initial value to \( H \). Figures below depict the free energy behavior described by this model.\(^{50}\)
Figure 2.4 depicts different free energy curve when the functionalized segment has a length of \( N = 100 \) (with different volume fraction), and the non-functionalized segment has a length of \( P = 300 \). The interaction parameter between the functionalized chains and the surface is fixed at \( \chi = -75 \). It can be seen that the dispersion is overall favorable. As the volume fraction is increased from a lower value to a higher value, the process becomes more spontaneous. All of these three curves are consistent with the third type of dispersion behavior shown in Figure 2.3. This indicates that proper modification of polymers with functional groups compatible with the silicate layers can cause the intercalated agglomerates to fall apart, forming partial exfoliation or flocculation.
Alternatively, the length effect of both functionalized chains (Figure 6a) and non-functionalized (Figure 2.5b) chains were investigated. At a functionalized chain volume fraction of $\phi = 0.05$ and a interaction parameter value of $\chi = -75$, it is observed that the free energy decreases with an increasing non-functionalized chain length and increases with an increasing functionalized chain length. This indicates that a long chain of the functionalized chains has an adverse effect on the intercalation spontaneity. Therefore, the key factor to drive a more favorable intercalation process is the volume
fraction of the modified components instead of the length. A long chain of functionalized repeating monomers results in aggregation of functionalized components automatically because monomers are closely attached to each other since these components have strong surface interactions with the silicate surface. Aggregation of functionalized repeating units leads to aggregation of silicate particles. Consequently, the free energy becomes more positive. On the other hand, a shorter functionalized chain can cause the compatible units to be well dispersed, leading to a more spontaneous dispersion process.

![Figure 2.6. Free energy curves describing different interaction parameters. In this case, N = 100, P = 300, and ϕ = 0.05.](image)

Besides the chain length of functionalized and non-functionalized components, it is crucial to consider the interaction parameter between the functionalized chains and silicate. Figure 2.6 depicts curves with various interaction parameters between the functionalized components and silicate layers. Apparently, more negative values of this interaction parameter drive the intercalation more favorable.
2.13 Combination of Functionalized Polymer and Organic Surfactant

Polymer functionalization and the use of surfactant are both effective techniques to produce a thermodynamically stable dispersed nanostructure of the resulting composites. It is of great interest to investigate the combination of both effects. The first consideration is the compatibility between the polymer and surfactant in the absence of functional groups compatible with the layered silicate. Under this condition, the solvent quality of surfactant to the polymer system becomes a key factor. Figure 2.7 displays free energy-gallery height curves with various surfactant \( \chi \) parameters, where it can be seen that the surfactant has to be a \( \Theta \) solvent to the polymer in order to yield possible favorable intercalation process.

![Free energy curves depicting various interaction parameters between the polymer and the organic modifier.](image)

In addition to the solvent quality of the surfactant, another significant factor is the length of the surfactant chains. According to the lattice model in the mean field theory, as the inter-gallery spacing is increased, the fraction of lattice sites available to the surfactant chains are reduced leading to an entropic barrier against a favorable process.
intercalation. Therefore, a longer surfactant chain is helpful to compensate for this entropic barrier to a limited extent. Figure 2.8 shows that an increasing surfactant chain length always yields more negative free energy curves despite the poor solvent quality.
Figure 2.8 Effect of surfactant chain length on free energy curves. a) $\chi = 0$  b) $\chi = 0.01$  c) $\chi = 0.02$. 53
The next critical factor to consider is the effect of interaction between clay sheets and functionalized polymer. Figure 2.9 depicts various free energy curves based on two situations. One scenario is that clay sheets, modified by surfactant chains, have no compatibility with the polymer chains (Figure 10a). In this case, the intercalation is purely driven by the presence of organic modifiers, and curves correspond to poor solvent have positive values of free energy, indicating complete phase separation between polymer chains and layered silicates. On the other hand, functionalized polymer with a good compatibility with clay sheets can result in highly favorable states regardless of solvent quality of the surfactant (Figure 10b).
2.14 Phase Behavior of Polymer/Clay Nanocomposites

One of the advantages of using nanoclay as filler particles is the disk structure bearing a high aspect ratio. As the polymer chains and these disk-structured particles are mixed together, several scenarios can take place. As a result of weak interactions, such as poor solvent quality of the surfactant with absence of direct polymer clay interactions, the mixture will undergo complete phase separation, and polymer chains and clay disks are considered immiscible. On the other hand, as the polymer chains penetrate through the gaps between the disks to disrupt the original layer-by-layer structure, intercalated, flocculated, or exfoliated nanostructures can be achieved. In this instance, the dispersed disk can either exhibit random orientation forming isotropic phase or have a certain
degree of alignments along one direction to form a nematic-like phase. To analyze these possible phase types, a model developed by Onsager was used, which assumes the free energy of mixing takes the form shown as follows\textsuperscript{54}:

\[
F = F_{\text{conf}} + F_{\text{ster}} + F_{\text{int}} + F_{\text{transl}}
\]

\textbf{Equation 18}

Here $F_{\text{conf}}$ is the conformational entropy compensation due to the oriented disks. $F_{\text{ster}}$ is due to the steric interactions among the disks. $F_{\text{int}}$ is due to the unspecific attraction interactions among the disks. $F_{\text{transl}}$ is due to the translational entropy of the clay disks. Using this method, the free energy of mixing is developed, which takes the form shown as follows:

\[
F = n_d (\text{constant} + \ln \phi_d + \sigma - \ln(1 - \phi_d) (b/v_d)(\rho - 1) - \chi v_d \phi_d) + n_p \ln \phi_p
\]

\textbf{Equation 19}

Here, $n_p$ is the number of polymer chains. The term $v_d$ is the volume of a single disk. The term $\sigma$ is a parameter describing the entropy compensation due to the alignment of these disks. The terms $\phi_d$ and $\phi_p$ are the volume fraction of the disk and polymer, respectively. And the term $\rho$ takes the form that

\[
\rho = (4/\pi) \langle |\sin \gamma| \rangle.
\]

\textbf{Equation 20}

where $\gamma$ is the angle between any two disks. \textsuperscript{55}
Using the relationships described above, a phase diagram is generated by equating the chemical potential of the polymer and the chemical potential of the clay disks and solving the system numerically. It turns out the phase behavior follows the trend shown in Figure 2.10, where phase regions are separated by boundary lines (dashed line for rods and solid line for disks). The phase region labeled i represents the isotropic phase, and the phase region labeled n represents the nematic phase. The phase region above the phase boundary describes the scenario that polymer chains and clay sheets are immiscible.

Figure 2.10. Phase diagram of typical polymer-disk (rods) nanocomposites

It can be seen from the phase diagram that disk-like particles have similar phase behavior as rod like particles, differentiating that disk like particles have a broader region of nematic phase. As the volume fraction of clay is increased from a small value to a larger value, the morphology undergoes a transition from isotropic phase to nematic phase via an immiscible region. Besides the geometry (rod or disk), this model is also
able to quantify the effect of disk size. With an increasing disk size, the region of nematic phase becomes broader, as shown in Figure 2.11.

![Figure 2.11 Phase behavior of composites with increasing plate diameter.](image)

**2.2 Grafting Reactions to Polymers**

**2.21 Electrophilic Substitution**

In sections from 2.7 to 2.9, it has been discussed that modification of polymer with functional groups compatible with clay sheets potentially serves as a better alternative to achieve superior dispersion than the usage of organic surfactant. Generally, the functionalization of polymer doesn’t have the entropic barrier caused by the increased fraction of lattice sites unavailable to the surfactant chains. To effectively functionalize the polymer chains with polar groups compatible with the layered silicates, several types of grafting reactions can be the potential options. Generally speaking, maleic anhydride is the most practically used chemical compatibilizer for grating a carboxyl acid group on
the main chain of non-polar polymer. However, the grafting reaction involves the use of free radical initiator or strong shearing force in the mixer, which either causes undesirable degradation or crosslinking of the polymer. In addition, the excess maleic anhydride may cause the corrosion of equipment in the course of processing. Alternatively, sulfonate groups can potentially have hydrogen bonding interactions with hydroxyl groups in the silicate layers. For benzene rich polymers, such as polystyrene, electrophilic substitution is a promising technique to graft sulfonate groups to the benzene rings. It has been reported that electrophilic substitution reactions to sulfonate polystyrene, followed by neutralization of quaternary ammonium or alkyl-amine salts and addition of natural clay, can effectively achieve intercalated nanostructure through melt processing. In this instance, the neutralization agent, alkyl ammonium salts, facilitates inter-gallery ion exchange.

Figure 2.12 shows that the pristine polystyrene/natural clay composite has the characteristic peak of polystyrene left un-shifted, whereas chemically sulfonated polystyrene neutralized with tri-butyl ammine has an apparent shifted clay characteristic peak, indicating that the polymer chains have successfully penetrated through the inter-gallery spacing.
Figure 2.12 Gallery distance comparison between sulfonated polystyrene and pristine polystyrene.\textsuperscript{3}
Figure 2.13 shows the TEM images of sulfonated polystyrene/clay hybrids in comparison with that of non-functionalized polystyrene. The former has a relatively large dark area, meaning that high shear in the melt mixer did not provide the energy required for gallery-opening process to occur. The aggregation is within micron scale, which is consistent with the wide angle X-ray diffraction results. In contrast, the particle size of the functionalized samples is majorly reduced in the micron-scaled microscope images.
compared with the non-functionalized sample. In a higher magnification scale, tiny white lines sandwiched between two dark disk-shaped regions indicates that intercalation occurred during the mixing. This agrees with the shifted characteristic peak observed in the wide angle X-ray diffraction results.

The ion exchange capacity also affects the extent of intercalation. A higher volume fraction of functionalized chains results in a higher ion exchange capacity. Figure 2.14 shows the X-ray scattering patterns of samples with different IEC/CEC ratio, the ratio of ion exchange capacity of the polymer chains to the cation exchange capacity of the natural clay. It follows the trend that higher ion exchange capacity has larger opened basal spacing. As IEC/CEC ratio drops below 3.5, the gallery swelling extent becomes smaller than those of larger ICE/CEC ratios. Because a higher ion exchange capacity is an indication of a higher volume fraction of the functionalized repeating units, the results shown above approve the conclusion drawn from the free energy modeling results that a higher volume fraction of functionalized chains produce more favorable intercalation process.
The type of neutralizing agent is also a factor to the level of intercalation. Figure 2.15 compares the X-ray diffraction pattern of two different quaternary ammonium, tetrabutylammonium and tetraoctylammonium. Apparently, neutralization agent with the greater chain lengths, namely tetraoctylammonium, helps to achieve a better state of intercalation. Under this condition, the neutralization agent behaves more like organic modifier of the organoclay. The aforementioned free energy curve depicts that longer chains tend to drive the intercalation process to a lower free energy state. Moreover, solvent quality can also affect the shape of the free energy curve. In this case, tetraoctylammonium is a better solvent for polystyrene, leading to a better intercalation state.

Figure 2.14-Intercalation characteristics with various IEC/CEC ratios.  

(b)

The type of neutralizing agent is also a factor to the level of intercalation. Figure 2.15 compares the X-ray diffraction pattern of two different quaternary ammonium, tetrabutylammonium and tetraoctylammonium. Apparently, neutralization agent with the greater chain lengths, namely tetraoctylammonium, helps to achieve a better state of intercalation. Under this condition, the neutralization agent behaves more like organic modifier of the organoclay. The aforementioned free energy curve depicts that longer chains tend to drive the intercalation process to a lower free energy state. Moreover, solvent quality can also affect the shape of the free energy curve. In this case, tetraoctylammonium is a better solvent for polystyrene, leading to a better intercalation state.
A high level of intercalation achieved by tetraoctylammonium can also be confirmed by TEM images (Figure 2.16). At a low magnification scale, black lines (clay sheets) are generally well dispersed among the white background (polymer matrix). These black lines are oriented in all directions, indicating an isotropic phase morphology. At a higher magnification scale, it can be seen that two or three individual clay sheets are stacked up forming small size agglomerates. A small amount of white areas are sandwiched in between these disk-like black lines, meaning that the gaps of these agglomerates are penetrated with polymer chains. However, these agglomerates do not stack up forming a large size aggregation.
Figure 2.16- Tem Images of tetraoctylammonium neutralized samples with two different magnification scales\textsuperscript{3}
Sulfonated polystyrene not only serves as a good candidate to achieve intercalation itself, but also can be used as a compatibilizer to enable non-functionalized polystyrene to penetrate through the inter-gallery spacing. In this case, the functionalized polystyrene serves as an ultra-long chain surfactant itself. Using the long chain functionalized polymer as the organic modifier can resolve the entropic barrier small molecule surfactants have due to the reduced fraction of accessible lattice sites. Figure 2.17 shows the effect of different neutralizing ammonium on the quality of intercalated ionomer as a compatibilizer. It turns out the ionomer sample neutralized with tetraoctyl ammonium serves the best compatibilizer. With the exception of tetradecyl ammonium, chain length has a positive impact on gallery opening. Understandably, long chain surfactants have lower the $\chi$ parameter with both the sulfonated polystyrene ionomer and the non-functionalized polymer, resulting in more negative free energy of mixing. The dispersion levels shown in Figure 2.17 are consistent with TEM images (Figure 2.18), where it can be seen that aggregation is prominent without the use of ionomer compatibilizer. In contrast, samples with the presence of ionomer compatibilizer majorly reduced aggregation size.

![Figure 2.17 Wide angle X-ray diffraction pattern of composites samples using compatibilizer neutralized with different quaternary ammonium a) Natural Clay. b)Polystyrene clay hybrids without the presence of compatibilizer c) Sample with tetradecyl ammonium d)Sample with tetraoctyl ammonium](image)
Figure 2.18 TEM Images of a polystyrene homopolymer/clay composites using a) no surfactant b) tetraoctyl ammonium c) tetradecyl ammonium
2.22 Sulfonation of Diene-Containing Elastomers

In case of elastomeric materials with pi bonds containing repeating units, such as polybutadiene, EPDM (ethylene propylene diene monomer), and styrene butadiene rubber, direct addition of sulfuric acid will break the double bonds and may cause undesirable cross-linking. Therefore, the technique to have mild reaction to graft sulfonic groups to the polymer while keeping the double bonds intact has to be applied. It has been described by Makowski that acetyl sulfate is an effective sulfonation agent to chemically modify EPDM rubber. The reaction formula is shown in Figure 2.19.

Acetic anhydride reacts with sulfuric acid in a cold bath to produce acetyl sulfate, which serves as the sulfonation agent to graft sulfonate groups to the ENB blocks of EPDM. This technique is not only used to add sulfonic acid groups to the ENB unit of the un-crosslinked EPDM, but also capable of sulfonating Vulcanized network gel swollen in various solvents. The produced sulfonated polyelectrolyte is of great interest because the ionic groups added to the ENB units bring perfect physical cross-links and can be relaxed at an elevated temperature to allow further processing. More importantly, the sulfonation reaction is stoichiometric based on the ENB content of EPDM without involving free radical generation or undesirable crosslinking, ensuring that the molecular structure of the main chain of EPDM can be maintained. The only concern is that the presence of sulfonate groups in the acid form renders the polymer thermally unstable. The degradation mechanism is shown in Figure 2.20. Sulfonic acid groups accelerate the decomposition of the polymer because of the de-sulfonation reaction upon heating. This process generates free radicals, which gives rise to the further rupture of the polymer backbone. To resolve this instability issue, a base or a salt acting like a weak base has to be used in order to neutralize the product from an acid form to a metallic salt form.
The existence of sulfonate groups grafted to the ethylidene norbornene can be confirmed by FTIR (Figure 2.21). Peaks at 1161cm⁻¹ and 1033cm⁻¹ correspond to the existence of S=O bonds. A small amount of water moisture is absorbed to the final product, as a result of hydrogen bonding between sulfonate groups attached to the EPDM.
backbone and hydroxyl groups. The presence of water can be confirmed by the peaks at 3424cm\(^{-1}\) and 1704cm\(^{-1}\), which are signals of OH groups.

![FTIR spectroscopy of the sulfonated EPDM](image)

Figure 2.21- FTIR spectroscopy of the sulfonated EPDM\(^{59}\)

As a part of our work, zinc-neutralized sulfonated EPDM ionomer prepared through the Makowski method was dissolved in organic solvent at high temperature upon stirring to fully relax the ionic cross-linking between the metal cation and polymer anion. Natural clay is dispersed in a small amount of water. Assisted by intense sonication, the resulting water-clay colloid liquid was homogeneously mixed with the high temperature ionomer solution. In expectation, ENB units attached with hydrophilic sulfonic acid groups enable the surface interaction between the polymer chains and water molecules bonded to the silicate layers. The dispersion of clay layers in the composite is assessed by using wide angle X-Ray diffraction (WAXD) and transmission electron microscope (TEM). Tensile properties of the composite are assessed through comparing experimental
results with the Halpin-Tsai model. And finally, viscou-elastic properties were analyzed through Dynamic Motion Analysis (DMA).
3.1 Materials

3.11 Clay Products

All of the following clay products were used without further drying or purification:

- **Sigma Aldrich Montmorillonite K10**
  First, we used raw montmorillonite (non-refined), sodium Montmorillonite K10 powder, with surface area around 220 m$^2$/g and an average size of 100 nm (purchased from Sigma Aldrich). The cation-exchange capacity (CEC) is 92 mequiv/100g. The average inter-gallery spacing is reported to be 1.17 Å.

- **Cloisite Na+**
  Another type of natural clay used in this project is sodium Cloisite (Na MMT), which is the highly refined Montmorillonite. It has a cation-exchange capacity (CEC) of 92 mequiv/100g. According to the product information, the average inter-gallery spacing is 11.7 Å.

- **Cloisite 10A.**
  This is a type of organoclay modified from sodium montmorillonite with quaternary ammonium salt, namely dimethyl, benzyl, hydrogenated tallow, and
quaternary ammonium. The d001 spacing reported by the manufacture is 19.2Å.

The structure of the organic modifier is shown in the Figure below:

![Chemical structure of Cloisite 10A surfactant](image)

Figure 3.1- Chemical structure of Cloisite 10A surfactant, where HT stands for hydrogenated tallow.

### 3.12 Polymer Systems

- **3720 EPDM Elastomer**
  
  Nordel 3720 EPDM hydrocarbon Elastomer (C2: 69 wt%; ethylidenenorbornene (ENB): 0.5wt%; ML1+4 125°C: 20) was supplied by Dow Chem. The density of the product is 0.88g/cc.

- **Zinc Sulfonated EPDM Ionomer**
  
  Zinc-neutralized sulfonated EPDM ionomer elastomer was prepared through Makowski method from ExxonMobil Vistalon™ 2504 EPDM elastomer (C2:57 wt%; ethylidenenorbornene (ENB): 4.7wt%; ML1+4 125°C: 25).

- **Polycaprolactone**
  
  Poly (ε-caprolactone) with a number-average molar weight of ≈80 000 g/mol, was obtained from Sigma-Aldrich without further purification.
- **Polystyrene**

   Polystyrene with a number-average molar weight of $\approx 192$ 000 g/mol, was obtained from Sigma-Aldrich without further purification.

---

**3.2 Experimental Methods**

**3.21 Non-neutralized sulfonated EPDM (Nordel 3720)/K10 MMT Composites**

Sulfonated EPDM was synthesized in octane solution in a flask equipped with mechanical stirrer according to the procedures reported by Makoski. Carefully dried before dispersed in 10ml distilled water, montmorillonite/water mixture with calculated clay content was sonicated, stirred overnight, and added to the system. The resulting composites with various weight percentage of clay were precipitated from the solution with an excess amount of ethanol, washed several times with ethanol, and finally dried to constant weight in vacuum.

IR spectra were recorded on Nicolet is10 FTIR spectrophotometer. Films were cast on a KBr disc from polymer solution in CS2. Wide-angle X-ray diffraction (WAXD) measurement was performed by using a D/max 2000PC instrument with Cu-K$\alpha$ radiation. TEM observation was performed on a JEOL JSM-1230 transmission electron microscope. Specimen films with the thickness near 100nm were spin-coated from a 1wt% toluene solution. Thermal gravity analysis (TGA, Perkin-Elmer 7 series thermal analysis system) was carried out at a heating rate of 8°C/min from 30 to 600°C under a continuous nitrogen purge (20 ml/min).
3.22 Non-neutralized sulfonated EPDM (Nordel 3720)/Cloisite 10A Composites

Following the same procedure described in 3.21, the reaction was carried out using the aforementioned sulfonation agent. During the previous procedure, a trace amount of polymer precipitation could be seen as water-clay colloidal solution was introduced into the polymer solution. This is because water droplets caused a high local water concentration, which negatively affected the solvent quality, resulting in polymer precipitation. To prevent such an effect, high intensity probe sonication was applied polymer solution. The water-clay liquid system was introduced to the polymer solution drop-wise through a piping system located right next to the head of the sonication probe. It was observed that water drops leaving the piping system were dispersed into small size droplets as a result of the high intensity sonication. Because of this, no major polymer precipitation was noticeable. The resulting solution was immediately casted into film on a heating plate. This procedure can be described in Figure 3.2.
Figure 3.2 Conceptual schematic of ultrasonic assisted film casting technique: a sonication probe is placed into the polymer solution. The piping system delivers water-clay colloid liquid drop-wise to the head of the sonication probe with high intensity ultrasonication, preventing polymer precipitation caused by local accumulation of water drops. The resulting hybrid solution system was directly casted into films for further processing.

3.23 Zinc Sulfonated EPDM/Na+ Cloisite Composites

Zinc-neutralized sulfonated EPDM was dissolved in Toluene and heated to 200 degree Celsius to completely overcome the ionic interactions. Carefully dried before dispersed in 10mL distilled water, montmorillonite/water mixture with calculated clay content was stirred for an hour, sonicated, and added to the heated ionomer solution under intense probe sonication. Following the same procedure depicted in Figure 3.2, the resulting solution mixtures were casted films onto polyimide substrate with the assistance of high intensity
ultra-sonication.

Wide-angle X-ray diffraction (WAXD) measurement was carried out using a D/max 2000PC instrument with Cu-K\textsubscript{\alpha} radiation. JEOL JSM-1230 transmission electron microscope was used for microscopic analysis. Specimen films were peeled off from the substrate and were compression molded into sheets of different dimensions for DMA and mechanical property measurements. TEM samples were prepared through flow coating specimen films into 100nm thin films from 1wt% toluene solutions. Temperature-frequency sweep was carried out at a constant temperature ramping rate of 3°C/min from -80 to 60°C using Dynamic Motion Analysis (DMA TA Instrument Q50). Tensile test was done on an Instron-1121 electronic tester at a drawing speed of 50cm/min.

3.24. Polystyrene and Polycaprolactone

Polystyrene and polycaprolactone systems are also prepared into nanocomposites through the similar method described through sections 3.22 and 3.23. Polycaprolactone was mixed with natural clay following the same procedure as section 3.23. Clay was suspended in deionized water with ultra-sonication, and the polymer was dissolved in toluene. The whole process was performed at room temperature. In contrast, due to the absence of polar functional groups, polystyrene was mixed with Cloisite 10A organoclay. In this system, the organoclay was not suspended in water. Instead, the clay powder was homogeneously dissolved in Toluene. The organoclay/toluene solution was delivered to the polystyrene/toluene solution through ultrasonic-assisted film casting in a similar fashion. The dispersion morphology was characterized using WAXD and TEM. The mechanical properties were investigated through strain-induced elastic buckling instability for mechanical measurements (SIEBIMM). This metrology was initially reported by
Various studies have shown that this metrology is effective to characterize elastic modulus of ultra-thin films. Polymer films are peeled off from the ultra-sonication apparatus, re-dissolved in toluene, and coated to the silicon wafer through flow coating. The film thickness was measured using an Ultra-Violate interferometer. These thin films were transferred onto the surface of polydimethylsiloxane (PDMS) elastomer though a film floating technique, shown in Figure 3.3. The wavelength of the buckling instability was taken using snap shots with an Olympus optical microscope and translated into a digitized periodic signal using MATLAB with a script code based on Fourier Transform (FFT).

Figure 3.3 Schematics of strain-induced elastic buckling instability for mechanical measurements(SIEBIMM)

The elastic modulus of the thin film was calculated through Equation 3.24, where $E_f$ is the modulus of the thin film, $E_s$ is the elastic modulus of the substrate, while $v_f$ and
\( v_s \) are the Poisson ratio of the thin film and the substrate, respectively. The term \( d \) is the buckling wavelength; \( h \) is the film thickness.\(^{60}\)

\[
\frac{E_f}{(1-v_f^2)} = \frac{3E_s}{(1-v_s^2)} \left( \frac{d}{2\pi h} \right)^3
\]

Equation 3.24
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Non-neutralized sulfonated EPDM (Nordel 3720)/K10 MMT Composites

Sulfonated EPDM (SEPDM) has been prepared by sulfonation reaction in octane solution, as reported by Makowski. Signals at 1022 cm\(^{-1}\) and 1261 cm\(^{-1}\) assigned to sulfonic acid group in IR spectra confirm the occurrence of a modification reaction, shown in Figure 4.0. The S-EPDM solution was mixed with the pristine clay in-situ and assisted by a small amount of water, allowing the insertion of SEPDM molecular chains into the clay layers through the ion-exchange of proton of sulfoacid attached to ENB of EPDM with the metal cation in between the clay layers. By co-precipitating and a vacuum drying process, EPDM/pristine clay composites with different clay contents were prepared.

Figure 4.10 IR Spectra of sulfonated EPDM/clay composite
Figure 4.11. Wide angle X-ray diffraction patterns of (a) MMT and composite containing (b) 3wt%, (c) 5wt% and (d) 10wt% clay.
Figure 4.12. TEM images of the composites with different clay contents (a: 3wt%, b: 5wt% clay, c and d: 10wt %)

The d001 inter-gallery spacing of the pure clay was calculated via Bragg’s diffraction law ($d = \lambda / 2\sin(\theta)$), with the X-ray wave length $\lambda$ equal to 1.54Å. XRD patterns of composites (Fig. 4.11a) show that the peak at $2\theta = 9.1^\circ$ corresponds to the 001 silicate layers reflection with spacing of 0.97nm, which is consistent with the range of d001 spacing reported elsewhere. In comparison, the composite containing 3wt% clay shows diffraction peaks corresponding to the 001 spacing of 1.1, 1.5 and 2.0nm (Fig. 4.11b). Furthermore, 3 peaks with different layer spacing and all larger than that of pristine clay indicate the polymer chains have been partially intercalated between the layers. The difference in layer spacing implies clay layers are intercalated by different amount of polymer chains, possibly resulting from heterogeneity in ENB distribution along the chain of the original EPDM polymer. Similarity is noticed in the composite containing 5wt% clay (Fig. 4.11c), where 3 peaks with layer spacing of 1.1, 1.5 and 2.3nm are visible. In the case of the composite containing 10wt% clay (Fig. 4.11d), besides 3 peaks similar to that in Fig. b and c, there is a very weak peak corresponding to
layer spacing of 1.0nm almost the same as that of pure clay, suggesting the existence of a small amount of aggregated clay.

TEM images of the composites are shown in Figure 4.12. Most of the silicate layers appear to be well-dispersed in the polymer matrix as seen in all the samples. Fairly good dispersion of layered particles in EPDM matrix suggests that the insertion of EPDM molecular chains with strong hydrophilic sulfonated ENB unit into clay layers has been enabled during the in-situ mixing. The intercalation of polymer chains into the clay layers behaves similarly to the intercalation of alkyl groups of alkyl-ammonium salt into the clay layers during the preparation of organoclay, differentiating in the former through ion-exchange of protons of sulfonic acid attached to the polymer with the metal cation in between the clay layers, while the latter via exchanging the metal cation with ammonium cation. In addition, the fact that some clay layers looks exfoliated, but thicker than a single layer, indicates they are actually intercalated only in small regions or sections, consistent with the relatively low intensity of resulting XRD peaks compared to the pristine clay (Fig. 1). Moreover, the composite containing 5% clay (Fig. 2b) shows some concentrated clay areas (labeled by arrow in TEM), where clay layers show a trace amount of intercalated morphology. When the clay content further increases to 10%, besides exfoliated silicate layers in most regions (Fig. 2c), aggregates start to appear, as enlarged in Fig. 2d, probably corresponding to Fig. 1d which shows the small peak with the same layer spacing as that of pristine clay (1.0nm).
As mentioned previously, sulfonated EPDM ionomer in the acid form possess poor thermal stability. Once the proton of the sulfonic acid groups are replaced by metal cations through ion-exchange, the thermal stability can be significantly improved. However, even though the clay particles are dispersed in the ionomer matrix, the presence of these clay sheets did not render the final product thermally stable. Figure 4.13 shows that over 25% weight loss occurred during the heating from 0°C to 200°C. The weight curve plateaus from 200°C and finally underwent main chain degradation. This indicates that the interaction between the clay particles and ionomer matrix is only governed by hydrogen bonding.

Results discussed above have demonstrated that natural clay particles can achieve intercalated nanostructure through functionalizing the polymers without the presence of quaternary ammonium, meaning that hydroxyl groups existing within the basal spacing
are accessible area wise. However, this preparation technique has two major drawbacks. First, the addition of water into the hydrocarbon system, despite the slow rate, can cause a very high local water concentration, resulting in a trace amount of polymer precipitation. Secondly, the final product was separated from the solvent by washing the product with a large amount of methanol and water. During this process, it is not guaranteed that the nanoparticle can be kept in the polymer matrix. Therefore, in the next section (Section 4.2), we demonstrate an ultrasonic assisted film casting technique as discussed in the experimental section. In essence, the water drop is cut down into significantly smaller size through high intensity ultra-sonication. The resulting mixture is cast into film through vaporization of solvent instead of using the washing method, preventing the filler particles from flushing away with the washing agent. This procedure is discussed in detail in Section 3.22.
4.2 Sulfonated EPDM/Cloisite Na+ Composites

Figure 4.20 WAXD for sulfonated EPDM/Cloisite Na+ nano-composites with two different clay concentrations a) pure Cloisite Na+ b) 1wt% clay and c) 3wt% clay

According to Figure 4.20 XRD patterns of composites show that the peak at 2θ = 7.45° corresponds to the 001 silicate layers reflection with spacing of 1.18nm, which agrees with the manufacture information given by Southern Clay Products. Compared with Montmorillonite K10, bearing a basal spacing of 0.97nm. Sodium Cloisite has a broader characteristic peak and wider basal spacing. This may due to the moisture exposure during the refinery process. Figures 4.20c and 4.20d show the WAXD results of
nano-composites with two different weight fractions, 1wt% and 3wt%. Achieved by the combination of intense ultra-sonication and film casting, clay characteristic peaks are significantly shifted to smaller angles. For the 1wt%, values d001, d002, and d003 are 4.25°, 6.0°, and 6.8°. In case of the 3wt% sample, a weak peak of d001 spacing has a value of 4.25°, whereas the d002 peak (6.5°) is much stronger and closer to that of the original clay. In other words, clay particles start to have phase separation with the bulk polymer matrix. With a low ethylidene norbornene content (0.5wt %), the amount of sulfonic groups attached to the polymer backbone is low. Consequently, the lack of surface attraction caused the aggregation to occur. Figure 4.21 shows the TEM images of the resulting composites. With 1wt% clay concentration, plate-like structured tactoids are dispersed in a discrete fashion. As the concentration is increased to 3wt%, more black-colored clusters are observed. This also indicates that in the previous results with K10 powder, some fraction of clay particles is lost during the course of washing. Otherwise, more severe aggregation could be observed in the case of 5wt% and 10wt% samples.
Figure 4.21. TEM images of S-EPDM/Cloisite Na⁺ composites with 1wt %(a, b) and 3wt(c, d)

Figure 4.22. Thermal gravity analysis of sulfonated EPDM/Cloisite Na⁺ composite with 3wt% clay

As shown in Figure 4.22, a degradation behavior similar to the previous sample can be observed. From room temperature to 42.5°C, the sample undergoes a sharp weight loss,
and the second degradation occurs near 400°C. This means the highly refined
Montmorillonite, namely Cloisite Na+, does not engage in any ion exchange process with
the sulfonic acid. The achieved intercalation is purely due to the hydrogen bonding.
Therefore, in order to make the product thermally stable, weak base has to be used to
prevent degradation. In the next section, we applied ultrasonic assisted film casting
technique to the zinc-neutralized sulfonated EPDM ionomer (Zn-S-EPDM). The thermal
stability can be shown in Figure 4.23. Contrary to the acid form ionomer, the zinc
neutralized EPDM does not exhibit weight loss below 220°C, meaning the final product
can be processed in the melt in order to conduct further bulk mechanical testing.
Moreover, due to the ionic interaction, the preparation of the composite in the solution
was done at 180°C with the help of ultra-sonication to completely overcome the physical
crosslink. This time, instead of using the ionomer with low sulfonation degree, the
ionomer product has a fully sulfonated ENB content of 4.7wt%.

![Figure 4.23 Thermal gravity analysis of zinc neutralized EPDM ionomer.](image)
4.3 Zinc neutralized EPDM/Cloisite Na+ Nanocomposites

Figure 4.31 Wide Angle X-ray Diffraction of the clay containing ionomer samples in comparison to that of the pristine clay. a) Pure MMT. b) Zn-S-EPDM/1wt% clay c) Zn-S-EPDM/3wt% clay c) Zn-S-EPDM/4wt% clay d) Zn-S-EPDM/5wt% clay

XRD patterns (Figure 4.31) of composites show that the peak at 2θ = 7.45° corresponds to the 001 silicate layers reflection with spacing of 1.18nm, which agrees with the manufacture information given by Southern Clay Products. Disappearance of the clay characteristic peak in the composites in samples containing 1wt%, 3wt%, clay indicate that neither aggregate nor intercalated agglomerate of the raw clay with a specific orientation is dominant in the matrix. A weak characteristic peak shifted to 2θ = 6.1 can be observed in the samples containing 3wt%, 4wt%, and 5wt%
signify small portions of intercalated nanostructures with a basal spacing of 2.82nm. Dispersed clay tactoids in the above samples can be confirmed by TEM images with different clay contents, shown in Figure 4.32. It can be proved that the surface interactions of sulfonated ENB unit and small size clay particles dispersed in water through ultra-sonication have achieved a well-dispersed nanostructure. Such a type of interaction behaves similarly to the intercalation of alkyl group of alkyl-ammonium salt into the clay layers during the preparation of organoclay. Differentiating in the former uses the alkyl-ammonium salt as surfactant to facilitate surface interaction, while in the latter case water molecules bonded to natural clay serve as a coupling agent between clay tactoids particles and the highly hydrophilic sulfonated ENB units.

Moreover, in the case of lower clay content samples (1wt% and 3wt %), layered tactoids exhibit isotropic behavior in TEM images, whereas in higher clay content samples (4wt% and 5wt %), small aggregates start to align in one direction. This indicates that two phase behaviors are observed, isotropic phase and nematic-like phase. The two phase phenomenon occurred in this study is consistent with the modeling of phase transitions described by Yulia, etc, where it was demonstrated that with an increasing clay content, if no large aggregations, the polymer-clay composite can undergo phase transitions from isotropic phase into nematic-like phase.\textsuperscript{55} Compared with the results discussed in Sections 4.1 and 4.2, the intercalation conditions are significantly improved. This is because the current samples contain more ENB units, allowing a higher level of sulfonation. This agrees with the self-consistent model discussed in Section 2.1, where it has been concluded that a higher volume fraction of functionalized polymer chains results in a more favorable state of intercalation.
Figure 4.32. TEM images of ionomer samples containing a) and b) 1wt% Clay, c) and d) 3wt% clay, e) and f) 4wt% clay, g) and h) 5wt% clay.
The moderately dispersed nanostructure is critical for the enhanced mechanical properties. Curves depicting stress-strain behaviors are displayed in Figure 4.33, and properties of samples with different clay content are presented in Table 4.31. Due to the strong interaction between layered silicates and polymer chains, increased Young’s modulus with increasing clay concentration can be observed among all the samples. This is because the formed network structure hinders chain movements upon stretching. A critical factor affecting the Young’s modulus is the filler aspect ratios (the ratio of width and thickness), measured from TEM images using Image J and listed in Table 4.32. As shown in Figure 4.33, samples containing 1wt% and 3wt% clay exhibit tensile modulus close to the neat ionomer samples due to the low aspect ratios. In contrast, samples containing 4wt% and 5wt% exhibit significantly higher tensile modulus due to the high aspect ratios. Moreover, it can be seen from the TEM images that orientation of clay particles are relatively random at low clay concentrations (1wt% and 3wt %), indicating that the polymer clay nanocomposites are in the isotropic regime. At higher concentrations (4wt% and 5wt %), plate-structured particles start to have discrete alignment. In other words, the composites are in the nematic phase. This type of phase behavior is consistent with the phase behavior modeling discussed in Section 2.2

Table 4.31 Aspect Ratio Analysis of TEM Images Using Image J

<table>
<thead>
<tr>
<th>Measurement</th>
<th>1wt%</th>
<th>3wt%</th>
<th>4wt%</th>
<th>5wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>100.14</td>
<td>169.54</td>
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<td>4</td>
<td>72.26</td>
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<td>91.05</td>
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<td>42.98</td>
<td>45.59</td>
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<td>66.74</td>
<td>45.08</td>
<td>108.70</td>
<td>183.35</td>
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</tbody>
</table>
Figure 4.33. Overall stress-strain behavior of the composite samples with different clay concentrations.

### Table 4.32 Tabulated values of mechanical properties

<table>
<thead>
<tr>
<th>Clay Content (wt%)</th>
<th>Tensile Modulus (MPA)</th>
<th>Halpin Tsai Modulus (MPA)</th>
<th>Average Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.23</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>1.74</td>
<td>1.54</td>
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<tr>
<td>4</td>
<td>4.14</td>
<td>3.21</td>
<td>108.70</td>
</tr>
<tr>
<td>5</td>
<td>4.21</td>
<td>5.39</td>
<td>183.35</td>
</tr>
</tbody>
</table>
Figure 4.34 comparison between experimental values and empirical models

It’s worth mentioning that by assuming the clay modulus of 170GPA, a specific gravity of 2.3, and a filler aspect ratio (Table 2) tensile modulus, values with various clay concentrations obtained experimentally follow the same trend as ones predicted empirically through Halpin-Tsai model,

\[
\frac{E}{E_m} = \frac{1+\xi \eta \Phi}{1-\xi \eta}
\]

where \( E \), \( E_f \), \( E_m \), \( \Phi \), and \( \xi \) represent the modulus of the composite, filler modulus, modulus of the starting EPDM, filler aspect ratio, and volume fraction, respectively.\(^{69} \)
Figure 4.34 compares the experimental values of composite modulus and theoretical values predicted by Halpin-Tsai model. Clearly, based on the empirical model, an increasing trend of modulus can be observed as clay content increases from 1wt % to 5wt %, which is consistent with our observations.

![Graph comparing experimental values to theoretical predictions](image)

**Figure 4.34** Figure 4.34 curves depicting stress-strain behaviors at small deformation amplitude

**Figure 4.35** presents the same stress-strain curve magnified in the small strain region. It can be seen that the neat ionomer, 1wt%, and 3wt% samples have almost linear stress-strain behaviors, whereas the remaining samples with higher clay contents clearly exhibit yielding near small deformation amplitude. Probably, with higher volume fraction of the filler, polymer chains can be embedded inside of the filler network, and change of nanostructure occurs when the bulk composite undergoes deformation, causing the observed yielding behavior. This type of phenomenon was previously reported by Payne and other researchers in their works of describing carbon-black filled elastomer
composites, where a significant drop of Young’s modulus can occur during small amplitude deformation.\textsuperscript{69}

![Figure 4.36 Plot of loss factor tan\(\delta\) over a range of temperatures](image-url)

Figure 4.36 Plot of loss factor tan\(\delta\) over a range of temperatures
Figure 4.37 Effect of clay concentration on glass transition temperature

Figure 4.38 Storage modulus of different clay-containing samples
Figure 4.36 shows the plot of loss factor, tan(δ), over a range of temperatures. Clearly, clay-containing samples have lower loss factor peak values, and the peaks are narrower than the pristine ionomer. This suggests that the dispersed clay tactoids, including the intercalated nanostructure in the 4wt% and 5wt% samples, are effective at hindering the mobility of polymer chains and weaken the damping ability of the polymer.\(^7\) The temperatures at which loss factors have peak values are the glass transition temperatures, shown in Figure 4.36. There are two competing effects of clay presence on the glass transition temperature. One effect is that polymer chain motions are restricted due to the polymer-filler surface interaction\(^7\), resulting in higher glass transition temperatures. This effect is dominant in the 1wt% and 3wt% samples. With higher filler concentration, the other effect comes into play. In essence, inter-particle distance shortens under a higher volume fraction and can reach a critical value where tough-brittle transition takes place. At concentrations higher than 3wt% transition from brittle to toughness occurs due to lower inter-particle distance, causing a sharp decreases in Tg in 4wt% and 5wt% samples. Moreover, unlike 1wt% and 3wt% samples in which the characteristic peak has very small magnitude or even disappear in the wide angle X-ray diffraction, the latter two samples exhibit stronger shifted characteristic peaks, suggesting an increased amount of intercalated agglomerates. Obviously, short inter-particle distance is present in samples with higher clay concentrations, causing the brittle-toughness transition to happen. The occurrence of such type of transition can be confirmed by the decrease in storage modulus around the glass transition at temperature below Tg, shown in Figure 4.38. \(^7\)
We have demonstrated that the combination of film casting and ultra-sonication is effective to disperse clay in the polymer matrix functionalized with sulfonic groups. Thus, it is of great interest to investigate the effectiveness of this technique to polymers bearing other functional groups, such as carbonyl groups. In this case, the hydrogen can have the hydrogen bonding interaction with the hydroxyl groups in the clay sheets. In the upcoming section, we show that the technique used for the ionomer system is also effective to polycaprolactone, a polymer with a sufficient amount of carbonyl groups attached to the backbone. For the mechanical testing, we adopt strain-induced elastic buckling instability for mechanical measurements (SIEBIMM), which is only applicable to high modulus thin films that can exhibit buckling effects on the stretched elastomeric substrate. In case of zinc sulfonated EPDM, the modulus is too low to observe the buckling instability on a substrate having an elastic modulus comparable to the thin film itself.
4.4 Polycaprolactone (PCL)/Cloisite Na+ Nanocomposites

Figure 4.41 WAXD results of PCL/Cloisite Na+ nanocomposites. a) Na+ Cloisite. b) PCL/1wt% Na+ Cloisite. c) PCL/3wt% Na+ Cloisite d) PCL/5w% Na Cloisite
Figure 4.41 displays the X-ray diffraction patterns of PCL/natural clay nanocomposites with three different clay contents. In the sample with 1wt% clay, the characteristic peaks almost vanished. Low intensity peaks corresponding to d001 and d002 spacings are at 2θ = 2.75° and 2θ = 4.6°, meaning the majority of the clay sheets are exfoliated in the polymer matrix with a small amount of intercalated nanostructures. With higher clay concentrations, intercalated peaks have slightly higher intensities. In the 3wt% sample, three distinct peaks are located at 2θ = 2.75°, 2θ = 2.75°, and 2θ = 2.75°. In the 4wt% sample, d001 and d002 spacing are relatively close to each other. Though the behavior of intercalation does not exhibit a unique pattern, it is apparent that hydroxyl groups within the clay sheets are accessible to the carbonyl groups in the polycaprolactone. High quality dispersion can be confirmed by TEM images shown in Figure 4.42, where individual platelet structured sheets are widely and homogeneously spread out. Also, these individual sheets are generally aligned in one direction, indicating all the samples fall into the nematic phase. These TEM images are analyzed with Image J to calculate the average aspect ratios of the clay sheets. These values are tabulated in Table 4.4, which are used to compute empirical values of elastic modulus using Halpin-Tsai Model.

**Table 4.41 Tabulated Values of Clay Aspect Ratios**

<table>
<thead>
<tr>
<th>Measurement</th>
<th>1wt%</th>
<th>3wt%</th>
<th>5wt%</th>
</tr>
</thead>
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<td>Average</td>
<td>105.35</td>
<td>74.89</td>
<td>123.53</td>
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</table>
Figure 4.42 TEM Images of PCL/Clay nanocomposites with 1wt% Cloisite Na+(a,b), 3wt% Cloisite Na+(c,d), and 5wt% Cloisite Na+
The existence of polymer-clay interactions can be confirmed in the enhanced mechanical behavior. Strain-induced elastic buckling instability for mechanical measurements was conducted to calculate the elastic modulus of the thin films. The substrate used was polydimethylsiloxane (PDMS) elastomer prepared with a cross-link density of 1:20 weight ratio, bearing an elastic modulus of 0.7MPA and a Poisson ratio of 0.35. The thin films were coated onto the silicon wafer and transferred on to the PDMS through the film floating technique. Optical images of the buckled PCL thin films are shown in Figure 4.43. These optical images were analyzed using periodic computation MATLAB code. The statistical distributions of wavelength are shown in Figure 4.44. The correlation between these parameters and thin film elastic modulus is described by Equation 3.24.

![Optical microscope images of PCL buckling](image)

Figure 4.43 Optical microscope images of PCL buckling. a) Pure PCL; b) PCL/1wt% clay; c) PCL/3wt% clay; d) PCL/5wt% clay
Figure 4.44. Statistical distribution of buckling wavelength based on MATLAB code a) Pure PCL; b) PCL/1wt% clay; c) PCL/3wt% clay; d) PCL/5wt% clay

Without the presence of clay, PCL thin film does not only exhibit buckling upon the stretching of the PDMS substrate, but also stress-induced crystallization, as shown in Figure 4.45. Maltese cross shape crystals are observed under the optical microscope, indicating that spherulites are generated due to the elongation of the PDMS substrate. Regions with spherulites are only present in the pure PCL thin film. With the addition of clay, only buckling instability can be observed. Therefore, the nano plate particles are effective to restrict the mobility of PCL chains, resulting in the suppression of stress-induced crystallization.
Besides the suppression of crystallization, nanocomposite samples exhibit enhanced elastic modulus according to the analysis of strain-induced buckling. Values of elastic modulus calculated through the buckling analysis and Halpin Tsai Model are tabulated in Table 4.41 and plotted in Figure 4.46. The aspect ratios of clay are measured based on the digitization of a TEM image. The empirical elastic modulus was calculated based on Equation 4.31. According to the buckling analysis, the elastic modulus increased from 187MPA to 392 MPA as the clay content is raised up to 5wt%. Halpin Tsai model is relatively accurate at low clay concentrations, as depicted by Figure 4.46. However, at a higher clay concentration, the discrepancy between the empirical model and experimental results starts to occur. This agrees with the previous analysis of zinc-sulfonated EPDM ionomer, where it was shown that Halpin Tsai modulus almost overlap with the tensile test results at low clay concentrations.
### Table 4.42 Tabulated Values of Elastic Modulus

<table>
<thead>
<tr>
<th>Clay Content (wt. %)</th>
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<th>Halpin Tsai Modulus(MPA)</th>
<th>Aspect Ratio</th>
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<td>5</td>
<td>272.39</td>
<td>392.77</td>
<td>63.26</td>
</tr>
</tbody>
</table>

**Figure 4.46** Comparison between experimental measurements and Halpin-Tsai Model for PCL/Cloisite Na+ system.
4.5 Polystyrene/Cloisite 10A Films

All the results discussed in the previous sections have proven that ultrasonic assisted film casting technique is effective to achieve moderate dispersion of natural clay in polymer matrices that have polar functional groups. Using natural clay is a cost-effective alternative to produce polymer-clay nanocomposites in a convenient and rapid fashion. However, in some applications, the non-polar structure of the polymer has to be kept. Thus, the use of organoclay is necessary. In this section, we demonstrate that the ultrasonic film casting technique is also applicable for the preparation of non-polar polymer/organoclay nanocomposites. This time, instead of using water as a clay swelling agent, toluene is used to suspend clay sheets before adding to the polymer solution.

Here we use polystyrene as the host matrix to prepare composites filled with Cloisite 10A, which is a type of organoclay modified with dimethyl, benzyl, hydrogenated tallow, and quaternary ammonium. The presence of the benzene ring makes the organic surfactant a moderate solvent for the polystyrene, which is a benzene-rich polymer. Based on the simulation analysis discussed in the earlier sections, a low value of $\chi$ parameter of the surfactant to the polymer yields a more negative free energy of intercalation. This can be confirmed by our results, where highly flocculated nanostructures are observed.

Figure 4.51 shows the WAXD results of polystyrene filled with different amount of Cloisite 10A organoclay. The pure clay (Figure 4.51 a) has a d001 diffraction peak of $2\theta = 4.5^\circ$, which corresponds to an inter-gallery spacing of 1.9nm. This is consistent with the product information. With 1wt% organoclay added to the system, most clay particles are exfoliated in the matrix, with a small fraction of intercalation having d001, d002 and
d003 peaks located at $2\theta = 2.6^\circ$, $2\theta = 3.2^\circ$, and $2\theta = 4.0^\circ$. With 3wt% organoclay, the intensities of d001, d002, and d003 spacing are still low, indicating the majority of the clay sheets are exfoliated due to the good solvent quality and assistance of ultrasonication. In contrast, the sample filled with 5wt% organoclay has a d002 spacing near $2\theta = 4.3^\circ$, which is very close to the original clay sample, meaning aggregation has occurred. Probably, due to the non-polar nature of the polymer, the dispersion fundamentally relies on the use of surfactant. A higher load of clay may cause a reduced amount of lattice sites available to the surfactant chains, causing an increase in free energy and a decrease in entropy.

Figure 4.51 WAXD Results of PS/Cloisite 10A Nanocomposites. a) Cloisite 10A b) PS/1wt% clay c) Ps/3wt% clay d) PS/5wt% clay
Figure 4.52 TEM images of PS/Cloisite 10A nanocomposites with 1wt% clay(a,b), 3wt% clay(c,d), and 5wt% clay(e,f)
Figure 4.52 shows the TEM images of the composite samples achieved by the ultra-sonication assisted film casting. With lower filler loading, the dispersed nano-sheets have relatively random alignment (4.52 a, b). As the clay content is raised up to 3wt%, the clay sheets start to align along one direction, meaning the system transformed from the isotropic phase into the nematic phase. This agrees with the previous results of other polymer systems with natural clay as well as the phase behavior modeling. Despite the aggregation that occurred in the sample containing 5wt% clay, these TEM images were analyzed through Image J to calculate the average aspect ratio, as shown in Table 4.51. These values are used to fit the Halpin Tsai model as discussed previously.

Table 4.51 Aspect Ratio Measurements of PS/Cloisite 10A composites

<table>
<thead>
<tr>
<th>Measurement</th>
<th>1wt%</th>
<th>3wt%</th>
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</table>
Since polystyrene is a non-crystalline polymer, Maltese cross cannot be observed upon the elongation of the PDMS substrate. Unlike the polycaprolactone sample, only strain-induced buckling is observed in the pure polymer sample. Optical microscope images of buckling are shown in Figure 4.53. Due to the high modulus of polystyrene, the thin films deposited onto the PDMS substrate are fairly brittle but exhibit uniform buckling wavelength. These images are analyzed using the same MATLAB code used for the PCL system. The number distribution of the wavelength among the film is shown in Figure 4.54.
Figure 4.54 Buckling wavelength number distribution of PS/Closite 10A composites with a) 0wt clay; b) 1wt% clay; c) 3wt% clay; d) 5wt% clay

Table 4.52 Tabulated values of composite elastic modulus

<table>
<thead>
<tr>
<th>Clay Content (wt%)</th>
<th>Elastic Modulus (MPA)</th>
<th>Halpin Tsai Modulus (MPA)</th>
<th>Aspect Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3132.26</td>
<td>3132.26</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>3628.84</td>
<td>3539.16</td>
<td>105.35</td>
</tr>
<tr>
<td>3</td>
<td>3770.32</td>
<td>4204.84</td>
<td>74.89</td>
</tr>
<tr>
<td>5</td>
<td>4085.25</td>
<td>5250.06</td>
<td>123.53</td>
</tr>
</tbody>
</table>
Values of thin film elastic modulus calculated via buckling wavelength measurements and Halpin-Tsai model are both tabulated in Table 4.52 and plotted in Figure 4.55. The results agree with the behavior shown in other systems filled with natural clay. At low clay concentrations, such as 1wt%, the elastic modulus calculated through buckling wavelength almost overlaps with the empirical modulus predicted by the Halpin-Tsai model. In case of a 3wt% clay content, the discrepancy between the experimental results and the empirical model starts to occur, but the model still provides a moderate prediction overall. As the clay content is increased to 5wt%, the model fails to accurately describe the mechanical behavior of the composite.
CHAPTER V
CONCLUSION

This work describes the ultra-sonication assisted film casting approach to prepare polymer/clay nanocomposites. For polar polymers, natural clay nano-sheets are pre-exfoliated in the aqueous media and introduced into the polymer solution system through ultra-sonication before the film casting. We have demonstrated the effectiveness of this technique through the preparation of nanocomposites using sulfonated EPDM ionomer and polycaprolactone. This technique is also applicable to the non-polar polymer systems, such as polystyrene. In this case, organoclay modified with a surfactant bearing a moderate solvent quality is used. Unlike natural clay, organoclay nano-sheets are suspended on hydrocarbon solvent prior to contact with the polymer solution and film casting. The morphologies of the nanocomposites, characterized by wide angle X-ray diffraction (WAXD) and transmission electron microscope (TEM), not only confirmed intercalation and exfoliation behavior of the nano-sheets but also depicted the phase behavior modeled in earlier studies. Enhancement of mechanical properties have been investigated through tensile tests and strain-induced elastic buckling instability for mechanical measurements. The Halpin-Tsai model provides accurate prediction of the elastic modulus at lower levels of clay loading but fails to fit the experimental data at higher clay concentrations.
REFERENCES


66. Emerson, W., Liquid crystals of montmorillonite. 1956.


