EXPERIMENTAL AND MODELING STUDIES OF
CLAY/POLYDICYCLOPENTADIENE
RESIN NANOCOMPOSITES

By

Mitra Yoonessi

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EXPERIMENTAL AND MODELING STUDIES OF
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By
Mitra Yoonessi

Approved:

Hossein Toghiani
Associate Professor of Chemical Engineering
(Major Professor and Co-director of Dissertation)

Charles U. Pittman, Jr.
Professor of Chemistry
(Co-director of Dissertation)

Kirk H. Schulz
Earnest W. Deavenport Jr., Chair, Professor and Director of the Dave C. Swalm School of Chemical Engineering
(Committee Member)

Rebecca K. Toghiani
Associate Professor of Chemical Engineering
(Committee Member)

Irvin A. Jefcoat
Henry Chair Professor of Chemical Engineering
(Committee Member)

Clifford E. George
Professor of Chemical Engineering
(Committee Member)

Mark E. Zappi
Texas Olefins Professor of Chemical Engineering and Graduate Coordinator of Dave C. Swalm School of Chemical Engineering

Robert P. Taylor
Interim Dean of James Worth Bagley College of Engineering
Hybrid organic-inorganic nanocomposites have received considerable attention during the last five years due to their unexpected properties. This work incorporated nanodispersed organically modified montmorillonite clay into polydicyclopentadiene resin matrices. Montmorillonite consists of 1 nm platelet sheets with a 2:1 structure, consisting of an alumina octahedral layer sandwiched between two silica tetrahedral layers. The relative weak forces between platelets allow small molecules like water, solvents and monomers as well as polymers, to enter into the interlayer spacings between the platelet sheets.

In-situ polymerization of highly delaminated clay/dicyclopentadiene (DCPD) dispersions was used to prepare clay/polydicyclopentadiene (polyDCPD) nanocomposites. Highly delaminated composites were characterized using X-ray
diffraction, X-ray scattering and high resolution TEM. Composites with 0.5-1 weight percent of clay had higher Tg values and flexural moduli.

The flow properties of the organically-modified montmorillonite/DCPD liquid dispersions were examined using a co-rotating viscometer. The dispersions with clay concentrations higher than 0.5wt% clay in DCPD showed thixotropic flow behavior. Small angle neutron scattering (SANS) experiments were performed to obtain anisotropic scattering of highly delaminated clay in DCPD due to the orientation of clay platelets and tactoids in the shear field. No anisotropic scattering was observed. The reason for this unexpected result is not yet understood.

Highly delaminated organically-modified clay composites were examined using small angle neutron scattering (SANS) and ultra small angle neutron scattering (USANS). The SANS data from 0.5, 1 and 2wt% clay/polyDCPD composites with 2 different types of clay were fitted to the stacked disk model. The average number of clay layers per tactoid was predicted by fitting the experimental data to the stacked disk model. Extensive high-resolution TEM analyses were performed on the same samples to obtain the average numbers of clay layers per tactoid.

Two finite element models, one for the intercalated clay/polyDCPD nanocomposite and one for the exfoliated clay/polyDCPD nanocomposite, were developed. The effects of these different dispersion geometries for seven platelets in the polyDCPD matrix on the stress distributions were examined. The exfoliated platelet model showed reduced deformations and uniform stress distributions. The highest stress concentrations were found on the platelets’ surfaces and where platelets were in close proximity.
DEDICATION

I would like to dedicate this Dissertation to my father, Dr. Mohammad Yoonessi, who has been my best teacher, leader, and guide in my life, my light in the darkness and my support when I was down. I also dedicate this work to my mother, Dr. Mina Emam, who has always inspired me with her encouragement, believing in me, and loving me. I am very thankful for everything they have taught me and everything they have done for me and for all their love.

I would like to dedicate this dissertation to my son, Amir Hossein Tadayon, who is the hope and the meaning of life for me.
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CHAPTER I

INTRODUCTION

Composites

The progress of engineering through the centuries has been dependent on the discovery and availability of new structural materials. As new materials were developed, their limitations became evident and new natural or manufactured resources were examined. Each material had advantages and limitations. Wood was light and tough, but it would burn. Ceramics and metals were strong, but heavy [1].

The idea of combining two or more different materials to form a new material with higher properties goes back many centuries. Humans discovered long time ago that composite materials could offer the advantage of superior performance compared to each individual constituent material. Humans have been putting fibers into a binder or matrix body for more than 3000 years. The Pharaohs of Egypt in Biblical times and the ancient Incan and Mayan societies knew that plant fibers helped strengthen and prevent bricks and pottery from cracking [1-3]. Later, Eskimos found that moss strengthens ice [1]. Mediaeval armor and swords were made by laminating several
different layers of metals together. The multi-layered metal composite swords were estimated to have up to 8,000,000 layers of steel due to the repeated folding and reshaping [1]. Today, concrete is used, which is a mixture of sand, gravel, and cement. Structural parts with superior properties have been made using steel reinforcing bars with high tensile strength and toughness combined with a concrete matrix for rigidity and compressive strength [1-3].

Composites are materials consisting of two or more distinct components. Bone (collagen and apatite), bamboo (cellulose and silica), and wood (cellulose cells and fiber bounded by lignin) are examples of natural composites. Composites are divided into two categories: 1) Composite materials and 2) Composite structures. Composite materials are composed of a reinforcing structure, surrounded by a continuous matrix. The material should be capable of arbitrary variation of volume fraction and constituents to be considered a composite material. Composite structures exhibit a continuous matrix, which includes reinforcing agents that are dissimilar materials. Wood veneer is an example of composite structure. In this material, an adhesive matrix may act synergistically to improve physical properties. In both forms, components (reinforcements and matrix) do not dissolve into one another, but do contribute in a synergistic manner to change a material’s properties [1-3].

In principle, any combination of two or more materials, whether metallic, organic, or inorganic, could result in construction of composites. The material combinations in composites are almost unlimited, but the constituent forms are more restricted. Fibers, particles, laminaes or layers, flakes, or fillers are major reinforcing
forms used in composite materials (Figure 1.1). The matrix is the body constituent, which encloses the reinforcing constituent and provides the bulk form of composite. The fibers, particles, laminae, flakes, and fillers are structural reinforcing constituents. They are generally the additive phases, which determine the internal structure of the composite [1-3].

![Diagram of reinforcing agents](image1.png)

Figure 1.1. Some common shapes of reinforcing agents.
Interfaces and Interphases

Because the different constituents are intermixed or combined, a contiguous region always exists. The common boundary of the constituents could be simply an interface. An interface is the same as a grain boundary in monolithic materials. In some cases, an interphase exists in a contiguous region, which is a distinct added phase (Figure 1.2). The coatings on glass fibers in reinforced plastics and the adhesive that bonds the layers of the laminate together are two examples. When such an interphase is present, two interfaces are present, one between each surface of the interphase and the adjoining reinforcing and continuous matrix constituents. Generally, the surfaces of the dissimilar constituents act to produce the interphase [1-3].

Figure 1.2. Makeup of interface between fiber and matrix.
**Distribution of Reinforcing Agents**

The distribution of constituents in a composite can be in two general ways. The reinforcing agent can be present in an ordered and repetitive pattern. Matrix/particle and matrix/fiber composites are of this type of composite and the particles or fibers are evenly dispersed. Alternatively, a variable pattern can exist where the reinforcing agent is non-uniformly dispersed. These types of materials are called graded, or gradient, composites. Laminated composites made of several different types of layers are considered graded composites. The structural constituents (fibers or flakes) can be arranged in either an oriented or a random fashion in both homogenous and gradient composites [1-3].

**Nanocomposites**

Nanocomposites have property advantages that nanomaterial additives bring compared to their conventional filler counterparts and the pure polymer [4-14]. The definition of a nano-composite material has expanded significantly in recent years. Nanocomposites comprise of a large variety of 1-, 2-, and 3-dimensional and amorphous materials, made of distinctly dissimilar components, but mixed at the nanometer scale [10-14]. One fast growing area of research is the general class of organic/inorganic nanocomposite materials [4-16]. The control of the nanoscale structure in the polymer media has remained a challenge and significant efforts have been focused on the ability to control the structure via innovative synthesis techniques [4-8]. Nano-composite material properties depend not only on the properties of their individual constituent parts, but also on their morphology and interfacial
characteristics [4-8]. This rapidly expanding field is generating many new materials with unique properties [4-16]. The latter are obtained by combining properties from the parent constituents into a single material. New properties are possible, which are not exhibited by the parent constituent materials. Nanocomposite property enhancements can be more than those simply predicted by the rule of mixtures [4-12].

The inorganic components can form three-dimensional frameworks. These include: zeolites, polyhedral oligomeric silsesquioxanes (POSS), two-dimensional layered materials such as clays, carbon nanofibers, carbon nanotubes, metal oxides, and metal phosphates [4-7]. One-dimensional and zero-dimensional materials such as \((\text{Mo}_3\text{Se}_3^-)_n\) chains and clusters are also included. All types and classes of nanocomposite materials can result in new materials with improved properties when compared to their macrocomposite counterparts. Therefore, nanocomposites promise new applications, such as mechanically reinforced lightweight components, non-linear optics, battery cathodes, nano-wires, sensors and other systems [4-8].

Organic/inorganic nanocomposites are relevant in bio-ceramics and biomineralization where \textit{in-situ} growth and polymerization of biopolymer and inorganic matrix is occurring. Many organic/inorganic composite protective structures are generated by organisms. Many possess exceptional strength, up to 300 times greater than the inorganic phase itself [13]. Finally, lamellar nanocomposites have the largest interfacial area and the maximum interaction between two phases. Since the properties of conventional composites depend on interface interactions, it is important to examine such interactions using conventional bulk sampling techniques instead of
surface techniques. Nanocomposites may be produced with a broad range of properties by controlled engineering of the polymer-host interactions [4-8].

Inorganic layered materials exist in different forms. They have well-defined, ordered intra-lamellar spacing, accessible by small molecules such as monomers, solvents as well as polymers. This structure enables them to act as matrices or hosts for polymers, with resulting interesting hybrid nano-composite materials. Significant improvements in the physical and mechanical properties of alumina silicate layered polymers have been reported [10-16].

Some of the properties that undergo substantial improvements due to adding nanophases are:

- Mechanical properties, e.g., strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardance and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

The relationship between the morphology of alumina silicates within the polymer and the final properties of the polymer is still not well understood. Further
studies will be necessary to develop a better understanding of formulation/structure/property relationships, and better methods of platelet exfoliation and dispersion.

The most common types of nanoreinforcements are layered natural silicates such as mica [17, 18], montmorillonite [14-16, 19, 20], hectorite [20, 21], and saponite [22, 23]. However, synthetic clays like laponite [24, 25], synthetic mica [26, 27] and hectorite [28, 29] have also been used.

**Montmorillonite**

Montmorillonite is the most common type of smectite clay. It has a 2:1 structure. It consists of stacks of platelet sheets. Its crystalline structure is continuous in the \( a \) and \( b \) directions and stacked in the \( c \) direction. Each platelet sheet consists of an alumina octahedral sheet sandwiched between two silica tetrahedral sheets (Figure 1.3) [30]. This construction allows sharing of the oxygen between Al and Si. There are hydroxyl groups at the edges of each clay platelet. In smectite clays, there can be isomorphous substitution by ions of lesser charge, Si\(^{4+}\) by Al\(^{3+}\) in the tetrahedral positions, and Al\(^{3+}\) or Fe\(^{3+}\) by Mg\(^{2+}\) or Fe\(^{2+}\) in the octahedral positions. This type of smectite is called montmorillonite when this substitution occurs in the octahedral sheets, with Al commonly replaced by Mg. The substitution causes a charge imbalance, in the form of negative charges on the surface of the layers. These negative charges in naturally occurring clays have been balanced by interlayer counter-ions, M\(^+\) and M\(^{++}\). The cation is most often a univalent ion like sodium, but it could be a
bivalent ion such as calcium, magnesium, or iron [30]. A variety of other molecules, including organic molecules, can be introduced between layers by cation exchange reactions. In most cases, clay is hydrated with interlayer water molecules. The general formula for montmorillonite clay is [30]:

$$\left(M_{2y}^{2+},nH_2O\right)(Al_{2-y}Mg_y)Si_4O_{10}(OH)_2$$

(1.1)

The structure of montmorillonite is shown in Figure 1.3.

![Figure 1.3](www.nanocor.com)

Figure 1.3. A single layer of montmorillonite clay: alumina octahedral sheet between two silica tetrahedral sheets. (www.nanocor.com)

The negative charges on the surface of interplatelets are not constant and change from one platelet to another. An average measure of these negative charges is reported as the cation exchange capacity (CEC). The cation exchange capacity (CEC)
is expressed in units of milliequivalents per 100 grams of clay (meq/100g). It is a measure of the amount of positively charged exchangeable cations a clay can hold (Mg\(^{2+}\), Ca\(^{2+}\), Na\(^{+}\), K\(^{+}\)).

Montmorillonite platelets have a high aspect ratio. They exhibit a thickness of 1 nm and lateral dimensions of 200 nm to 1 micron, resulting in aspect ratios ranging from 1000 to 2000. There are spacings between the platelet sheets of montmorillonite that allow small molecules, water, solvents, and monomer as well as polymer, to enter into these galleries. A value of \(d\)-spacing is reported for each type of montmorillonite [30]. The \(d\)-spacing is the repeat unit in the crystalline structure including the 1 nm thick platelet and the spacing in between the platelet sheets [30].

Montmorillonite is a hydrophilic, inorganic material. Dispersion within the polymer matrix is required to form the inorganic/organic composite. In order to make montmorillonite compatible with the organic matrix, a cation exchange reaction is used to replace the sodium, potassium and/or calcium ions with an alkyl ammonium long chain (Figure 1.4) [12-16, 19, 20]. This results in expansion between the clay galleries due to the larger molecules inserted between the layers. The reaction also changes the clay from hydrophilic to hydrophobic, making it more compatible with the organic matrix. Currently, there are two producers of organically modified montmorillonite in the United States: Nanocor, Inc., and Southern Clay Products, Inc. The clay types offered by Nanocor are called Nanomer® and the ones produced by Southern Clay Products are called Cloisite®.
Figure 1.4. Hydrophilic montmorillonite clay becomes hydrophobic when it undergoes cation exchange with organic ammonium ions.
Carbon nanotubes and carbon nanofibers have been used to enhance the mechanical properties, electrical properties and thermal stability of composites [31-36].

**Carbon Nanofibers**

Vapor grown carbon nanofibers are produced from the catalytic reaction of a hydrocarbon gas, such as ethane, methane, or benzene, in the presence of hydrogen at temperatures around 1100-1300°C [36-38]. An aqueous metal salt, such as iron, is sprayed into the reactor at high temperatures, producing aerosol. At this stage, \( \text{Fe}^{++} \) is reduced to iron nanoparticles. These particles serve as the catalyst sites and the fibers start to grow from these particle [31, 33, 37, 38]. The high activity of carbon in the gas phase drives carbon to dissolve in the catalyst particles. The particle may then easily become saturated with carbon atoms arising from decomposition of vapor phase molecules containing carbon within the iron particle. As more carbon atoms become dissolved than are allowed by carbon’s solubility, precipitation into a graphite phase begins. This lowers the chemical potential (Figure 1.5) [39]. It is important to maintain the diameter of iron nanoparticles below 15 nm to avoid decreasing the activity of the catalyst (floating catalyst method) [40, 41]. Depending on the preparation conditions, carbon nanofibers can have diameters from tens of nanometers to microns and lengths from 1 micron to a few centimeters.
Figure 1.5. A metallic particle (iron) M saturated with carbon, formed by dehydrogenation of methane, is converted to a carbide phase. This phase precipitates a layer of carbon. This grows into a filament with the stacked cup morphology.

These fibers have been characterized as having outer CVD layers of graphitic hexagonal basal planes parallel to the normal axis of the fiber and an inner filament with graphitic planes in the “stacked cup” morphology, canted at very small to ~ 25° angles to the filament axis (Figure 1.6.a). These fibers are hollow cylinders. The planes, formed at the interface of the catalytic Fe particle that initially grew into the filament, exhibit a degree of graphitization. The degree and morphology of graphitization are temperature dependent. The interior filaments are covered on their outer surfaces with vapor-deposited carbon of somewhat less graphitic nature, deposited after filament growth has concluded. These conical inner filament sections are about 20 nm in diameter (Figure 1.6.b). The fibers are often curved and tend to nest (Figure 1.6.c). Dispersing them into polymers, resins, and solvents has remained
1.6.a. Conical (stacked cup) structure of the inner graphitic carbon planes.

1.6.b. A Carbon nanofiber.

1.6.c. Carbon fibers tend to form aggregates and nests.

Figure 1.6. Carbon nanofibers.

Figure 1.7. Canted graphitic basal planes surrounded by turbostratic carbon layer.
a challenge (Figure 1.7). Heat-treated carbon nanofibers have a nominal diameter in
the range of 50-200 nm and lengths of 1-100 microns. Applied Science, Inc., (ASI) is
the only producer of carbon nanofibers in the United States. The carbon nanofibers
produced by ASI are called Pyrograph III®. Many grades are now available. Major
classes include PR-19 and PR-24, which vary in their average diameters. The
complete designation depends on the treatment performed on the fibers. The outer
surfaces of the carbon nanofibers have been oxidized and functionalized by nitric acid
and oxygen plasma treatments [42-44].

These nanofibers have high electrical, thermal, and mechanical properties,
making them suitable for nanocomposite applications. They are enormously resistance
to oxidation. Their low cost and potential for property enhancement make these fibers
very desirable for nanocomposite applications.
Type of Clay Nanocomposites

Polymer-clay composites can be generally classified into “conventional composites” and “nanocomposites”. Phase mixing in conventional composites typically occurs on a macroscopic (µm) length scale. In contrast, a nanocomposite is formed when phase mixing occurs on a nanometer length scale. The overall properties of composite materials are determined not only by the parent components, but also by the unique composite phase morphology and interfacial properties. Thus, nanostructured materials have attracted considerable fundamental research and applications attention [45].

Conventional Clay/Polymer Composites

Clay is dispersed as a particulate in conventional clay/polymer composites. The registry of the clay nanolayers is retained when it is mixed with polymers. There is no intercalation of the polymer into the clay structure. Consequently, the clay fraction in conventional clay composites plays little or no functional role and acts mainly as a filling agent for economic considerations. An improvement in tensile modulus is normally achieved in conventional composites, but this reinforcement benefit is usually sacrificed in other properties, such as strength or elasticity. Processing of particulate composites is usually difficult due to the high percentage of clay loading required [45].
Intercalated Clay/Polymer Composites

Small molecules can enter between clay galleries because of relatively weak forces between clay layers. Intercalated nanocomposites are formed when one or a few molecular layers of polymer are inserted into the clay galleries to give fixed interlayer spacings. In these types of composites, clay layers keep their original structural registry, but the $d$-spacing increases (Figure 1.8) [45].

![Figure 1.8. Polymer chains enter between clay galleries and form intercalated nanocomposites [46].](image)

Polymers can be directly intercalated, while others can be intercalated by \textit{in-situ} polymerization of monomers, which have been preintercalated between the layers of the host material [46]. Utilizing preintercalated monomers is important because the kinds of polymers that are intercalated directly are limited. However, the control of molecular weight of the \textit{in-situ} formed polymers is normally difficult [46].

Intercalated materials have the following characteristics.
a) Various kinds of compounds are synthesized by the combination of a wide variety of both layered materials and polymers.

b) Polymers can be accommodated in the interlayer region with the retention of the structural registry of the layered material. This yields anisotropic arrangement of polymers in a two-dimensional nanoenvironment (inside the layered material galleries).

c) Interlayer spacings can be changed with the size of guest polymers.

d) Guest molecules in the interlayer spacings are affected by the environment characteristic of the surrounded adjacent layers. Their properties are controlled by the interactions between layered materials and polymer molecules in addition to the their individual properties. Structural, chemical, and thermal stabilities due to rigid surrounding inorganic are expected to work as a barrier for various guest polymers.

Among the large number of layered materials that can be intercalated, layered silicates are typical. In particular, the smectite group of clay minerals, montmorillonite, saponite, and hectorite, has mainly been used because they can be intercalated. Application of different layered silicate materials with different polymers results in a variety of layered silicate-based nanocomposites with new compositional and structural properties that can be used in new applications [47].
Fully Exfoliated Clay Nanocomposites

Exfoliated nanocomposites are formed when one-nanometer alumina silicate nanolayers are individually dispersed in the polymer matrix. In these types of nanocomposites, the minimum distance between clay nanolayers is comparable with the radius of gyration of the polymer (Figure 1.9). The average distance between the segregated layers depends on the clay loading. The separation between the exfoliated nanolayers may be uniform (regular) or variable (disordered). Successfully exfoliated nanocomposites would show greater phase homogeneity compared to intercalated nanocomposites [45]. The majority of reported exfoliated clay/polymer nanocomposites contain a mixture of platelets and tactoids (highly delaminated nanocomposites).

Figure 1.9. 1 nm alumina silicate layer sheets are dispersed with polymer matrix and form exfoliated nanocomposite [46].
Highly Delaminated Nanocomposites

In all well dispersed clay/polymer nanocomposites, tactoids still exist [48]. When there is a mixture of individual 1 nm clay nanolayers and small tactoids dispersed within a polymer matrix, a highly delaminated nanocomposite is formed (Figure 1.10). These tactoids could be as small as 2-20 clay nanolayers per tactoid [49-51]. In some cases, intercalation of a polymer chain [52], or insertion of monomers followed by polymerization within tactoids [53], has occurred. In some composites, clay could be well dispersed locally, but not uniformly throughout the matrix.

Figure 1.10. A mixture of 1 nm clay layers and small tactoids are dispersed within polymer matrix. These are called highly delaminated nanocomposites [46].
REFERENCES


CHAPTER II

LITERATURE REVIEW AND THEORY

The previous research performed on clay nanocomposites is discussed in this chapter. Explanations of the theoretical and experimental approaches to prepare and characterize clay composites, as well as the achievements made in this effort, are included in this chapter.

Clay Nanocomposites

Hybrid organic-inorganic materials have received considerable attention due to their superior physical and mechanical properties [1-7]. Composite materials reinforced by nanoscale phases, such as carbon nanotubes and carbon nanofibers [8-10], polyhedral oligomeric silsesquioxane (POSS) [11-14], and montmorillonite clay are of great interest. The most important approach to prepare these composites is to disperse the reinforcing phase on the nanometer scale. This has remained a challenge for researchers.

Montmorillonite clay consists of 1 nm thick alumina silicate sheets stacks that are continuous in the $a$ and $b$ directions and stacked in the $c$ direction [15]. Toyota
researchers, Kato et al., reported the intercalation of 6-aminocaproic acid in various ionic (Na⁺, Ca²⁺, Mg²⁺, Cu²⁺) montmorillonite clays and preparation of montmorillonite/6-aminocaproic acid complexes in 1979 [16]. Their infra-red studies confirmed that interactions between the exchangeable cations and 6-aminocaproic acid existed. These interactions increased in the following order, Na⁺, Ca²⁺, and Mg²⁺ < Co²⁺ < Cu²⁺ for the montmorillonite/6-aminocaproic acid complexes. After subsequent heating of the 6-aminocaproic acid/intercalated montmorillonite, condensation of the exchanged 6-aminocaproic acid within the interlayer spacing occurred. This resulted in the formation of small amounts of nylon between the clay layers. Thus, nylon-montmorillonite pillared complexes were formed [16].

Montmorillonite can be modified by alkyl ammonium ions via a cation exchange reaction to change from hydrophilic to hydrophobic. This reaction provides long alkyl chains inside the clay galleries, which results in improved interaction of montmorillonite clay with organic monomers and polymers. Pinnavaia et al. reported exfoliation of organically-modified montmorillonite in an epoxy resin matrix and the effect of the alkyl ammonium chain length on this exfoliation [17]. They found that the extent of silicate layer separation was governed by the alkyl ammonium chain length, the clay layer charge density and the acidity of the cations. They also examined epoxy composites prepared using NH₄⁺ and Na⁺ Montmorillonite. These composites did not exhibit any exfoliation or intercalation. Pinnavaia used CH₃(CH₂)₃NH₃⁺, CH₃(CH₂)₇NH₃⁺, CH₃(CH₂)₉NH₃⁺, CH₃(CH₂)₁₁NH₃⁺, CH₃(CH₂)₁₅NH₃⁺, and CH₃(CH₂)₁₇NH₃⁺. The chain length of the alkyl ammonium ion greatly affects the
extent of clay expansion upon epoxide solvation. The epoxide solvation increases in proportion to the chain length of the onium ion. It was assumed that the clay gallery cations, upon solvation with epoxy, reorient from their initial monolayer, bilayer, or paraffin-like orientation to a vertical orientation relative in the clay basal surfaces (Figure 2.1). The calculation of basal spacings based on the vertical orientation was in agreement with measured basal spacings.

Figure 2.1. Proposed model for the swelling of alkyl ammonium-exchanged clay by an epoxy resin. A is a low charge density clay with a lateral bilayer structure. B is a high charge density clay with a paraffin structure. The ellipses represent the intercalated resin molecules [17].
Pinnavaia et al. also examined the effect of different ammonium head groups on C\textsubscript{18}-substituted ammonium ion pillars [17]. C\textsubscript{18}-substituted primary, secondary, tertiary, and quaternary alkyl ammonium ion exchanged montmorillonite showed the same initial basal spacings. The epoxy-solvated clays had essentially the same basal spacings, which were controlled by the C\textsubscript{18} long alkyl chain. Alkyl chain controlled intercalation has also been confirmed by using clays with different charge densities [17, 18]. Interlayer alkyl ammonium cations with chain lengths of 8 carbons or less resulted in intercalated nanocomposite architectures and conventional phase segregated composites, respectively. However, using montmorillonite modified by alkyl ammonium with chain lengths longer than 8 carbons yielded exfoliated (delaminated) epoxy/clay nanocomposites. The mechanical properties of rubbery epoxy/exfoliated clay composites are reported to undergo greater improvements than glassy epoxy/exfoliated clay composites. Both the tensile strength and the modulus of epoxy clay nanocomposites increased with increasing clay loading levels in rubber matrices [17]. Composites containing 15% clay, modified with C\textsubscript{18} alkyl ammonium exchanged montmorillonite, showed a 10-fold increase in tensile properties [17].

Lan et al. studied the effect of the alkyl ammonium modifier length on the exfoliation of montmorillonite clay in the epoxy polymer matrix [19]. They reported the exfoliation of montmorillonite clay in bisphenol A diglycidyl ether (DGEBA) epoxy resin. Exfoliation is said to occur when the DGEBA undergoes ring-opening self-polymerization while heated with the acidic ammonium ion exchanged form of montmorillonite to generate polyether-clay nanocomposites. They characterized the
composites using X-ray diffraction (XRD), transmission electron microscope (TEM), and differential scanning calorimetry (DSC). DSC showed that two exothermic catalytic processes occur during the ring-opening polymerization of the DGEBA epoxy group to form a polyether. The lower temperature exotherm was attributed to the polymerization of the pre-intercalated epoxide on internal gallery surfaces where the proton concentration is maximum. Polymerization of the extragallery epoxide on the external and internal surfaces of the clay particle occurred at higher temperature [19].

Vaia et al. investigated the interlayer structure and the phase state of alkyl ammonium chains in organically modified mica-type silicates using transmission Fourier transform infrared spectroscopy (FTIR) [20]. They reported a wide range of molecular environments from liquid-like to solid-like within the gallery spacings depending on the interlayer packing density of alkyl chains, alkyl ammonium ion chain lengths, and temperature. As the interlayer packing density or chain length decreased or the temperature increased, the chains adopted a more disordered, liquid-like structure. In intermediate cases, the chains were neither solid-like nor liquid-like but exhibited a liquid-crystalline character [20].

Chin et al. extended the epoxy/montmorillonite exfoliation studies [21]. They used C_{18} alkyl ammonium-treated montmorillonite and DGEBA. When the DGBA was cured with equimolar or higher amounts of curing agent, only intercalated nanocomposites were formed. Exfoliated nanocomposites were achieved only when the amounts of curing agent were less than the stoichiometric ratio or when no curing
agent was used. In these latter cases, the epoxy rings underwent self-polymerization to provide polyether structures. Both extragallery and intragallery polymerization occurred during the reaction of DGEBA with the curing agent in the presence of alkyl ammonium modified montmorillonite to give normal cured epoxy resins. An exfoliated nanocomposite can be formed, as long as the intragallery polymerization occurs at a comparable rate with the extragallery polymerization [21].

The exfoliation of organically modified montmorillonite in other thermoset resins has been investigated. Choi et al. examined the morphology of the clay with different organic modifications in a linear novolac phenolic resin [22]. They used clay with different organic pretreatments, such as C\textsubscript{12} and C\textsubscript{18} alkyl ammonium modification as well as benzyldimethyl C\textsubscript{18} ammonium-modified hectorite. Two preparation methods were used to form clay/phenolic composites: 1) sequential intercalation and curing; and 2) simultaneous mixing and curing. They found that the intercalated structure (d-spacing of 36.6 Å) was maintained after curing when benzyldimethyl C\textsubscript{18} ammonium-modified hectorite was used. In contrast, the phenolic resin deintercalated out from between the clay platelets after curing when C\textsubscript{18} alkyl ammonium-modified montmorillonite was employed. Better solvation by the benzyl groups of the benzyldimethyl C\textsubscript{18} ammonium ions by phenolic resin monomers within galleries may account for this behavior. Chio et al. suggested that the favorable interaction between the phenolic resin and organic modifiers, containing a benzene ring, prevented deintercalation of resin from the clay galleries. Choi et al. concluded that the modification of the alumina silicate layers and the resulting interaction
between the organic modifier and the phenolic resin is important in determining the final structure and morphology of the composite [22].

Byun et al. prepared resole phenolic resin/clay composites by melt intercalation [23]. The clays were ω-amino acid-modified montmorillonite systems. Different amino acid chain lengths were used. 6-Aminocaproic acid-modified montmorillonite had the best compatibility with the resole phenolic resin. Intercalation and exfoliation of clay in linear and low molecular weight polymers is possible. However, preparing and preserving intercalated and/or exfoliated clay morphology in a three-dimensional phenolic network has remained a challenge. The lower the molecular weight of the initial uncured resole, the easier the diffusion of the resin becomes into clay galleries. Partially exfoliated clay/phenolic resin nanocomposites were prepared by melt intercalation. A significant increase in the mechanical properties of silicate-layered composites with low weight percentages of clay was reported. The phenolic clay/nanocomposite, prepared with 6-aminocaproic acid-modified montmorillonite, had the greatest mechanical property improvements due to better dispersion of clay layers and good adhesion between the silicate layers and phenolic resin [23].

Ryu et al. prepared polymethyl methacrylate (PMMA)/clay composites in a two-stage sonication/melt blending process [24]. Sonication led to enhanced breakup of clay agglomerates and size reduction of the dispersed phase. Cavitation during sonication causes clay aggregate size reduction. During cavitation, the bubbles, induced by alternating expansion and compression cycles of ultrasound traveling
through the medium, collapse [26]. Clay/PMMA nanocomposites were prepared through \textit{in-situ} polymerization and melt blending under ultrasonic irradiation. A special intensive mixer equipped with an ultrasonic generator was used (Figure 2.2). Hydrogenated-tallow modified montmorillonites, Cloisite 10A and 20A, were dispersed by sonication in methyl methacrylate (MMA) in the presence of the initiator (2, 2'-azoisobutyronitrile (AIBN)) for 10 min. Radical polymerization of MMA proceeded during the sonication in the presence of AIBN. A dispersion of clay in low molecular weight PMMA was obtained, which was later mixed with high molecular weight PMMA. The second stage of mixing and sonication was performed in a melt mixer equipped with a sonicator at a temperature of 230$^\circ$C.

PMMA/clay composites prepared with this method showed enhanced exfoliation, improved mechanical properties (storage shear moduli), and thermal stability compared to PMMA/clay composites prepared by conventional melt blending. A better overall homogeneity was achieved by this method, which resulted in property improvements. Lower viscosities were reported for the exfoliated composite prepared by this method. The lower viscosity was attributed to mechanical chain cleavage caused by the ultrasonic wave action on polymer chains [24].
Figure 2.2. PMMA/clay nanocomposites formed by a two-stage sonication process. a) First-stage, and b) Second stage [24].
Most studies use X-ray diffraction and transmission electron microscopy to characterize clay exfoliation [16-24]. X-ray diffraction is based on Bragg’s law \( n\lambda = 2d\sin\theta \) and is a very useful technique to study crystalline structures (Figure 2.3). TEM is another tool that is necessary and complimentary of the obtained XRD data of the clay/polymer nanocomposites. In most of the reviewed research, these techniques have been used to verify the extent of exfoliation/intercalation of the clay within the nanocomposites [16-26].

![Figure 2.3. Diffraction of X-rays by the atoms of a crystalline structure.](image)

The disappearance of the basal spacing peak, \( d_{001} \), in XRD has been used to indicate exfoliation [17-26]. Morgan et al. reviewed several clay/polymer composites including cyanate ester, polystyrene, nylon 6, and polypropylene-g-maleic anhydride clay composites that were prepared by their group [25, 26]. They suggested that TEM is the best characterization method for clay composites, especially when mixed
morphologies are present. XRD is a useful technique for measuring \( d \)-spacings in intercalated composites, but it cannot always observe low clay loadings (<5 wt\%) or be used as a method to identify an exfoliated nanocomposite where no XRD peak is present. XRD peak disappearance alone cannot be a criteria for exfoliation, but it is complementary with TEM. Many factors, such as concentration and clay order, can influence the XRD patterns of layered silicates. When clay is not well ordered, it will fail to produce Bragg diffraction peaks. Thus, it is incorrect to conclude that the disappearance of the XRD peak confirms the presence of a highly disordered and exfoliated structure. When properly interpreted and combined with TEM results, XRD can give a clearer picture of the actual nanoscale dispersion and overall global dispersion of the clay in the polymer [28].

The above idea has been well investigated by Vaia et al. [28]. Characterization of polymer layered silicate nanocomposites (PLSN) with scattering and diffraction methods is important, especially at small angles, which correspond to large basal spacings. Careful sample preparation and data evaluation, complemented by TEM are necessary, because \( \theta \) exhibits a strong dependence on both theoretical and experimental factors at low values of \( 2\theta \). These factors are more crucial for PLSN’s with low clay volume fractions and where exfoliation occurs. Vaia also emphasized that XRD alone cannot be used as a criteria to describe the PLSN’s morphology [28]. It is necessary to characterize the PLSNs on the microscale. Swelling of the interlayer tactoid spacings to larger than 10nm does not mean that a uniform distribution of platelets exists within the polymer matrix [28].
Figure 2.4 shows the Bragg diffraction geometry. The scattering intensity, $I(\theta)$, at a scattering angle of $\theta$ is defined as:

$$I(\theta) = L_p(\theta) \phi(\theta) F^2(\theta)$$  \hspace{1cm} (2.1)$$

$L_p(\theta)$ is the Lorentz polarization factor and depends on the scattering distribution and geometric factors. $\phi(\theta)$ is the interference function and depends on the distance and the extent of coherency between units. $F(\theta)$ is defined as the structure factor and depends on the type and position of atoms in the unit cell [28].

The structure factor for PLSNs represents the relative distance and orientation between the inorganic layers, and not the crystal structure of the individual layer.
For these layers, the structure factor is defined as:

\[ F(\theta) = \sum_n P_n f_n \cos(4\pi z_n \sin(\theta/\lambda)) \]  

(2.2)

where the summation is over all atoms of type n in the unit cell. \( z_n \) is the Z coordinate of nth atom. \( P_n \) is the number of atoms of type P in the atomic layer \( Z_n \), and \( f_n \) is the temperature-corrected atomic scattering factor of atom P. The structure factor describes scattering from a single independent, randomly oriented layer. In most cases, clay platelets exist as finite stacks. Interference due to layer-layer correlation influences the scattering intensity. The generalized interference function for a one-dimensional structure with a repeat distance \( D \) and a mean strain \( \alpha \) is defined as: [28]

\[ \phi(\theta) = \frac{1}{\langle N \rangle} \left[ \langle N \rangle + 2 \sum_{N=N_1}^{N=N_2} P(N) \sum_{n=1}^{n=N-1} (N-n) e^{-8\alpha^2 \sigma^2 \sin^2 \theta / \lambda^2} \cos(4\pi nD \sin(\theta / \lambda)) \right] \]

(2.3)

where;

\[ \sum_{n=1}^{n=N-1} (N-n) \] is the finite stack size

\[ \sum_{N=N_1}^{N=N_2} P(N) \] is the stack polydispersity

\( e^{-8\alpha^2 \sigma^2 \sin^2 \theta / \lambda^2} \) describes inhomogeneities in structural order

\[ \langle N \rangle = \sum P(N) \cdot N \] is the mean number of layers in a crystallite
P(N) is the distribution of coherently stacked layers, and \( N_1 \) and \( N_2 \) are the number of the layers in the smallest and largest stacks, respectively [28].

Equation (2.3) assumes that the stacking disorder of the layers is described by a distortion of the first kind in which displacement of the scattering units from the ideal lattice with spacing \( D \) is given by a Gaussian probability with a mean square displacement \( \alpha \). Clay tactoids have finite sizes and they are often curved and bent (a degree of structural disorder). Therefore, consideration of these factors (\( D \) and \( \alpha \)) is very important in understanding experimental scattering profile and reproducing the data [28].

The \( L_p \) factor accounts for geometric factors associated with the relative orientation of the scatterers with respect to the incident beam. It is assumed that the scattering vector is normal to the sample surface. Reflection will occur only for beams with vibrations parallel to the reflecting atomic plane for an unpolarized beam. Therefore, the total scattered beam energy will be proportional to the polarization factor, \( (1+\cos^22\theta)/2 \) [28].

\[
L_p(\theta) = \frac{(1+\cos^22\theta)}{\sin\theta} \psi(\theta) \tag{2.4}
\]

where \( \psi(\theta) \) is the powder ring distribution factor.

The experimentally observed diffraction intensity, \( I_{\text{exp}}(\theta) \), for layers in an amorphous medium is related to the layers’ ideal diffraction intensities, \( I(\theta) \), by the equation [28]:

\[
I_{\text{exp}}(\theta) = C \cdot A(\theta) [I(\theta) \cdot S(\theta)] + Bg(\theta) + SN \tag{2.5}
\]
C includes $\theta$-independent factors such as the layer volume fractions. $A(\theta)$ represents $\theta$-dependent factors, such as sample alignment and roughness as well as incident beam penetration and breadth, which influence the effective concentration of layers exposed to the incident beam. $S(\theta)$ is the instrument constant. $B(\theta)$ is the background and SN is the noise associated with counting statistics. Peak broadening due to the instrument [convolution of $S(\theta)$ with $I(\theta)$] is normally not critical in PLSN analysis. The contribution of peak broadening is small compared to contributions from finite crystal size and internal disorder. In contrast, the concentration, $\theta$-dependent factors, and background all reduce the effective magnitude of the basal reflection and complicate the determination of the PLSN structure [28].

$\theta$-dependent factors, such as alignment, roughness, and sampling depth, alter the portion of the sample interrogated at different scattering angles. In ideal scattering, the sample is assumed to be in a focusing geometry, and assumed to have a smooth surface. The size and depth of the sample are assumed infinite relative to the size of the incident beam and the scatterer’s distribution within the sample is uniform. In real experiments, achieving all these requirements is not possible. The volume sampled is $2\theta$-dependent. This alters the effective number of layers exposed to the beam. This causes deviation from the ideal scattering assumptions. Therefore, the recorded intensity is not the ideally calculated scattering intensity. This is especially critical for high aspect ratio scatterers at low $2\theta$. The volume of a sample exposed to the incident beam is constant for Bragg geometry. However, the ratio of the penetration depth to the exposed area is dependent on $2\theta$ [28].
Sample absorption also causes a $\theta$-dependent penetration depth of the incident radiation. The X-ray penetration depth depends on the sample’s absorption cross section. This depth decreases logarithmically with distance within the absorbing material, $t$ [28]:

$$\frac{I_x}{I_0} = \exp(-2\mu t / \sin \theta)$$

(2.6)

where $I_0$ is the incident intensity, $I_x$ is the attenuated intensity, and $\mu$ is the absorption coefficient. The absorption coefficient is determined with respect to the composition’s mass-weighted average of the fundamental scattering entity [28].

The surface roughness and global alignment of the sample will also alter low-angle scattering. Roughness and alignment displace the sample from perfect focusing geometry. If one considers the sample surface as mosaic units, each with a finite angular deviation $\omega$ from the sample’s normal, the intensity $I/I_0$ is expressed [28]:

$$\frac{I}{I_0} = \frac{1}{2} \left[ 1 + \left( \frac{\sin(\theta - \omega)}{\sin(\theta + \omega)} \right) \right]$$

(2.7)

Powder diffraction data contains a large amount of information about interlayer height, crystallite size, and disorder. However, careful sample preparation and data evaluation are necessary and should be complemented by TEM observation because of the strong $\theta$ dependence of theoretical and experimental factors at low $2\theta$. 
This is especially more critical for PLSN with low clay volume fractions where exfoliation of clay layers is investigated [28].

Small-angle scattering techniques using either X-rays or neutrons are versatile tools for obtaining information on the size, morphology, and dispersion of colloidal systems in complex materials such as clay polymers, clay/solvent dispersions, carbon nanofiber polymer/solvent dispersions, and materials of industrial importance. Processes such as self-assembly, aggregation, crystallization, and phase separation can be studied at relevant conditions [29a]. Two important features that make small-angle neutron and X-ray scattering techniques valuable in materials research are their high sensitivity in the length scale from 1 to 1000 nm and the unique contrast available with X-rays and neutrons. Small angle X-ray or neutron scattering (SAXS or SANS) are experimental techniques used to obtain size and shape parameters of large molecules and particles which can not be determined by other methods (such as microscopy or X-ray diffraction). These techniques can also be used for studying the morphology of complex aggregates and polymeric systems as a function of process parameters. The source of scattering in neutron scattering is the difference in the scattering length densities of the atoms and molecules. In contrast, the difference in electron densities causes scattering when atoms and molecules are irradiated by X-rays. Generating neutrons with high intensity for scattering studies is expensive and few sources are available in the world. However, producing high intensity X-rays is not as costly as neutrons and many sources are accessible. The two scattering techniques are parallel and complementary. Contrast variation techniques can be used to analyze multi-
component materials in SANS measurements. In the contrast variation method, the scattering data from a two-phase system are obtained by matching the contrast of two phases at each time. A set of scattering experiments yields a set of equations of known contrasts and unknown partial structure functions. One of the special features of X-ray scattering is time-resolved measurement, which enables millisecond resolution for the measurements. X-rays also have superior wave vector resolution. Magnetic fields can be examined by neutrons and neutrons are conductive in extreme environments such as high pressure and high temperature. Neutron scattering is a non-destructive technique and a small sample volume is required. X-ray scattering experiments also require a small sample volume, but radiation damage to some samples is a possibility. Parasitic scattering may produce more complications in X-ray scattering compared to neutron scattering. However, incoherent scattering and strong scattering from hydrogen is a complication of neutron scattering techniques.
Principles of Small Angle X-ray Scattering

The fundamentals of X-ray scattering theory were developed by Debye [30], Fournet [31] and Guinier [31] in the 1930s.

Scattering patterns are caused by the interference of secondary waves that are emitted from various structures (electrons for x-rays and light, or nuclei for neutrons) when irradiated. X-ray scattering is caused by differences in electron density, scattering of neutrons is caused by differences in the scattering power of different nuclei and scattering of light is caused by differences in refractive index.

SAXS measurements are typically performed at scattering angles smaller than 4°. According to Bragg's Law, the diffraction information about structures with large d-spacings is obtained from this region [32a]. Therefore, the SAXS technique is commonly used for probing large length scale structures such as high molecular weight polymers, biological macromolecules (proteins, nucleic acids, etc.), self-assembled superstructures (e.g. surfactant-templated mesoporous materials) and high aspect ratio particles (clay, carbon nanofibers, etc.).

SAXS measurements are challenging because of the small angular separation of the intense direct beam and the scattered beam. Large sample-to-detector distances (0.5 m - 10 m) and high quality collimating optics are required to achieve a good signal-to-noise ratio in the SAXS measurement.

Small-angle X-ray scattering patterns do not give morphological information directly as an electron micrograph does. The result of a SAXS experiment is essentially the intensity of the Fourier transform of the electron density and must be
interpreted in order to determine the morphology. One fundamental problem with any scattering experiment is that two different morphologies theoretically can give identical scattering patterns. Generally, one cannot reconstruct the exact microstructure uniquely from a SAXS pattern because in a scattering experiment only the scattered radiation intensity can be measured and all phase information is lost. Therefore, one cannot be absolutely sure that a scattering pattern is due to a particular morphology. However, usually something is known about the system, so that it is often reasonable to assume that if a particular model is fit to the scattering pattern, then the model is a correct description of the morphology. Nevertheless, many different approaches exist to extract morphological information from a SAXS pattern.

SAXS calibrants are used to accurately determine the sample-to-detector distance. This allows one to compute a wave vector, q, (reciprocal-space lengths) for the image on a two-dimensional area detector [32a].

The traditional choice for periodic calibrants are: silver stearate \( (d = 48.68 \text{ Å}) \) and silver behenate \( (d = 58.376 \text{ Å}) \). For larger d-spacings, a common biophysical standard is rat collagen. The lattice constant \( d \) is given variously in the literature as 668 Å - 670 Å. The silver stearate and silver behenate calibrants are easy to prepare. Silver stearate and silver behenate are strong scatterers, so there will be a sufficient signal [32a, 33].
General X-ray Key Features

A sample is bombarded with highly energetic X-ray beams with the help of Gobel mirrors (Figure 2.5). The light scattered from the sample gets evenly scattered after passing through glassy carbon and eventually falls on the gas-detector. The scattered intensity is two dimensionally arranged around the beam stop. This is a radiography application to detect the position of the sample in the X-Y plane and to examine the microstructure. SAXS spectra could give information about the morphology and the periodic arrangements of the sample.

SAXS instruments can be used at elevated temperatures. The main characteristics are given below.

* High Brilliance X-rays from Gobel Mirrors (Specially designed curved mirrors)

* High Resolution Pin-hole Camera

* HI-Star 2-Dimensional area detector

* High signal to background ratio for spectrum

* XY scan for sample radiography

* Heating and cooling stage (-50°C ~ 300°C). The range of scattering wave vector q: (0.1nm⁻¹ to 4nm⁻¹) or the range of particle size: 1 ~ 600nm

* Short measuring cycle

* No slit-smearing

* Suitable for both liquids and solid samples
Figure 2.5. Schematic of X-ray scattering instrument.
Principles of Neutron Scattering

Neutron scattering principles are similar to those of light scattering and X-ray scattering. Neutrons are particulate in nature with wavelength properties. If \( m \) and \( v \) are the mass and velocity of the particle, respectively, and \( h \) is Planck’s constant, then the wavelength is defined as \( \lambda = \frac{h}{mv} \) [33,34].

A neutron beam is scattered by the layers of a crystalline lattice according to Bragg law:

\[
n\lambda = 2d \sin \theta \tag{2.8}
\]

If \( n \) is an integer, a relationship between the neutron wave vector (wave length and direction) and a sample property (crystal lattice spacing) is obtained. Figure 2.6 shows the neutron wave vector with a magnitude of \( 2\pi/\lambda \) interacting with an atom or nucleus. The scattering event is elastic and the final wave vector, \( \mathbf{k}_f \), has the same magnitude as the initial wave vector, \( \mathbf{k}_i \). Only the direction of the wave vector changes. The wave vector change, \( \mathbf{q} \), is defined as \( \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \). The magnitude of \( \mathbf{q} \) is defined as [32a,33,34]:

\[
|\mathbf{q}| = q = \frac{4\pi}{\lambda} \sin(\theta) \tag{2.9}
\]

Combining equation 2.8 and 2.9 for \( n=1 \), \( q=2\pi/d \) is obtained.

The wave vector change, \( \mathbf{q} \), is known as the scattering vector and is often called the momentum transfer. All neutron scattering events relate to the spatial properties of the scattering sample in real space and are defined in terms of \( q \). The inverse relationship between the distance and \( q \) is fundamental. Very small values of \( q \)
are required for exploration of large-scale structures within the sample. Conversely, small spatial scales are observed via large q values. The value of q can be varied by changing either neutron wave length or scattering angle [33]. Figure 2.7 depicts the 30m NG-3 SANS instrument at National Institute of Standards and Technology (NIST).

Figure 2.6. Principles of neutron scattering [32b].
Figure 2.7. The 30m small angle neutron scattering instrument in the Neutron Center for Research at National Institute of Standards and Technology (NCNR-NIST) [32b].
A variety of approaches have been employed to examine clay/solvent dispersions using neutron scattering techniques and will be discussed [35-40]. While the principles of neutron scattering and X-ray scattering are the same, different nomenclature and definitions have been used to define the mathematical expressions employed in these two classes of techniques. Here, commonly used definitions have been mentioned for clarity.

Hanley et al. examined the dispersion of laponite clay and cetyltrimethylammonium bromide (CTAB) in both water and D_2O using neutron scattering [33a]. They assumed a disk shaped morphology for the clay particles and observed a scattering intensity pattern for their samples consistent with the scattering response from a thin disk (fitting to thin cylinder model). After addition of CTAB and contrast matching by isotopic substitution of the solvent, the scattering response of the dispersion still indicated the presence of a disk shaped morphology. Laponite clay resembles natural clay, hectorite, consisting of hydrous magnesium silicate platelets with diameters of 25-30 nm and a thickness of about 1 nm [35a]. Each sheet consists of octahedral magnesium oxide, which is sandwiched between two silica tetrahedral sheets. Due to isomorphous substitution of Mg in the octahedral layers by Li, platelet surfaces have negative charges. The small angle neutron scattering (SANS) technique measures the scattering intensity, I(q), as a function of q, the scattered wave vector, where q=(4πsinθ)/λ, where λ is the incident neutron wavelength. The coherent contribution to the scattered intensity, I(q), from a monodisperse suspension of N
particles in volume \( V \) is proportional to the differential cross section per unit volume of the sample \( d\Sigma/d\Omega (\text{cm}^{-1}) \) [36a]:

\[
\frac{d\Sigma}{d\Omega} = (N/V)|F(q)|^2 S(q)
\]

where \( F(q) \) is the scattered wave amplitude and \( S(q) \) is the structural factor. \( F(q) \) is defined as [35a]:

\[
F(q) = \sum_j b_j \exp(iq \cdot X_j)
\]

in which \( X_j \) is the position of atomic nucleus \( j \), with neutron scattering length \( b_j \) and the structural factor is defined as [35a]:

\[
S(q) = \frac{1}{N} \left< \sum_j \sum_{j'} \exp(iq \cdot (R_j - R_{j'})) \right>
\]

\( S(q) \) is averaged in all directions \( \langle \cdot \rangle \), and \( R_i \) is the vector for the center of the mass of the particle \( i \). The experimental scattering from a species is measured with respect to the scattering length density of the medium \( \rho_m \). Therefore, equation 2.10 becomes equation (2.12) [35a].

\[
F(q) = \int d\mathbf{r} [\rho(\mathbf{r}) - \rho_m] \exp(i\mathbf{q} \cdot \mathbf{r})
\]
The molecular scattering length density of a particle is calculated from
\[ \rho(r) = \rho_{\text{mol}} \Sigma b_j N(j), \]
where \( \rho_{\text{mol}} \) is the molecular density, and \( N(j) \) is the number of nuclei of type \( j \) in a particle. \( \rho_m \) is the weighted number fraction of the scattering length densities of the medium’s molecular components. The equation for the scattering from a system of interacting particles is defined as:

\[ I(q) = A \phi V_p (\rho - \rho_m)^2 P(q) S(q) \quad (2.13) \]

\( A \) is an apparatus constant, \( \phi \) is the volume fraction \( \phi = (N/V)V_p \), and \( V_p \) is the volume of the particle. \( P(q) \) is the orientationally averaged \( F(q) \), written in dimensionless form. \( P(q) \) is the form factor that defines the shape of the particle. For a finite cylinder with the thickness of 2H and radius of R, \( P(q) \) is expressed by the equation 2.14 [35a].

\[ P(q) = 4 \int_{0}^{\pi/2} \left( \frac{\sin^2(qH\cos \beta)}{(qH)^2 \cos^2 \beta} \right) \frac{J_1^2(qR \sin \beta)}{(qR)^2 \sin^2 \beta} \sin \beta d\beta \quad (2.14) \]

This equation simplifies to the Karatky-Porod expression (equation 2.15) [40] when \( qH \ll 1 \), since the first term in the integral is equal to zero.

\[ P(q) = \frac{2}{(qR)^2} \left[ 1 - \frac{J_1(2qR)}{qR} \right] \quad (2.15) \]

If one does not want to neglect the effect of a finite value for H, the asymptotic formula, shown in equation 2.16, derived by Guinier and Fournet, [31] is used for large qR:
According to this equation, a logarithmic plot of intensity versus $q$ for a noninteracting disk-shaped system will result in a slope of -2 for $qR>2$, when $qH<<1$ (Figures 2.8 and 2.9).

\[
P(q) = \frac{2}{(qR)^2} \exp[-\frac{(qH)^2}{3}]
\]  

(2.16)
Scattering from Dilute, Homogeneous Particles

\[ I(\mathbf{Q}) \propto \frac{d\Sigma(\mathbf{Q})}{d\Omega} = \frac{1}{V} \left| \int_V \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{r} \right|^2 \]

for identical particles

\[ \frac{d\Sigma(\mathbf{Q})}{d\Omega} = \frac{N}{V} \left( \rho_p - \rho_n \right)^2 V_p^2 \left| \frac{1}{V_p} \int_{V_p} e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{r} \right|^2 \]

\[ \text{Contrast Factor} \quad \text{Particle Shape} \]

\[ |F_p(\mathbf{Q})|^2 \quad \text{Form Factor} \]

Figure 2.8. Scattering from a monodispersed particle system [32b].
Figure 2.9. The theoretical scattering response from a non-interacting monodispersed disk shape particle [32b].

Form Factors for Some Simple Shapes:

3) Thin Disks

\[
\text{Form Factor}^2 \quad \text{for Thin Disks of Diameter, } D = 80 \text{ nm, and Thickness, } t = 4 \text{ nm}
\]

\[
\langle |F(Q, L)|^2 \rangle
\]

\[
\frac{2\pi}{D}
\]

\[
\frac{3\pi}{t}
\]

Grunier region
slope = -2
\[
\frac{1}{Q} \sim (1/Q)^2 \exp(-1/2 Q^2) t^2
\]

slope = -4
Hanley et al. modified this equation slightly for their clay/CTAB study. Scattering from the clay/CTAB suspension originates at either clay platelets, where the sodium ions on the surface have been replaced by CTAB, or at free CTAB micelles. CTAB micelles have a structure with hydrophobic tails at the center and a surface of ammonium ion head groups [35b]. Clay is assumed to be the core, which is coated with surfactant. If the clay core has a scattering length density of $\rho_1$ and the surface has a characteristic scattering length density, $\rho_2$, the scattered intensity from a system of non-interacting particles ($S(q)=1$) is defined as equation 2.17 [35a].

$$I(q) \sim \{(\rho_2 - \rho_m) [V_T P_T(q) - V_T P_1(q)] + (\rho_1 - \rho_m) V_T P_1(q)\}^2 \quad (2.17)$$

This simplifies to:

$$I(q) \sim \{(\rho_1 - \rho_2) V_T P_1(q) + (\rho_2 - \rho_m) V_T P_T(q)\}^2 \quad (2.18)$$

where $V_1$ is the core’s volume and $V_T$ is the total particle’s volume. The SANS data from clay/CTAB dispersions indicated that the clay (or complexed clay) existed as isolated disks [35a].

Ho et al. extended the disk assumption for the clay to the stacked disk model [36]. They investigated the dispersion of hydrogenated tallow-modified montmorillonite (Cloisite 15A) in chloroform, benzene, toluene, p-xylene, octane, and cyclohexane, using wide angle X-ray scattering and SANS.
The scattering intensity from an organically-modified single alumina silicate sheet is defined as [36]:

\[ I_{\text{OrganicModifiedSingle}}(q) = N_{\text{OMMT}} \int_{0}^{\pi/2} \left[ \Delta \rho_1(V_{\text{total}} f_{\text{total}}(q) - V_c f_c(q)) + \Delta \rho_c V_c f_c(q) \right]^2 \sin \beta \, d\beta \]  

(2.19)

The form factor for the alumina silicate core is:

\[ P_c(q) = \int_{0}^{\pi/2} \left[ \frac{\sin(qH \cos \beta)}{qH \cos \beta} \left(\frac{2J_1(qR \sin \beta)}{qR \sin \beta}\right) \right]^2 \sin \beta \, d\beta \]  

(2.20)

\[ P_t(q) = \int_{0}^{\pi/2} \left[ \frac{\sin(q(q + H) \cos \beta)}{q(q + H) \cos \beta} \left(\frac{2J_1(qR \sin \beta)}{qR \sin \beta}\right) \right]^2 \sin \beta \, d\beta \]  

(2.21)

\[ P_{tc}(q) = \int_{0}^{\pi/2} \left[ \frac{\sin(q(q + H) \cos \beta)}{q(q + H) \cos \beta} \left(\frac{\sin(qH \cos \beta)}{qH \cos \beta} \right) \left(\frac{2J_1(qR \sin \beta)}{qR \sin \beta}\right) \right]^2 \sin \beta \, d\beta \]  

(2.22)

where \( P_{tc} \) is the total form factor of organically modified clay. The other terms are as defined by Hanley et al. [36a]. Assuming the nearest neighbor distance in a stack of parallel plate (tactoids) obeys a Gaussian distribution, \( S_q(q) \) was first calculated by Karatky and Porod [40] as:
Where \( N \) corresponds to the total number of stacked platelets, and \( D \) and \( \sigma \) are the next neighbor center-to-center distance and the Gaussian distribution, respectively. The total coherent scattering from a stacked disk is defined as [36]:

\[
S_s(q) = 1 + \frac{2}{N} \sum_{k=1}^{N} (N - k) \cos(kDq \cos \beta) \exp[-k(q \cos \beta)^2 \sigma^2 / 2]
\]

(2.23)

For a non-interacting single platelet, \( N = 1 \), and \( S_s(q) = 1 \).

Ho et al. reported a low-q slope of -2.2 for the dispersion of Cloisite 15A in chloroform [34]. This low value is indicative of substantial clay platelet exfoliation in this solvent. Clay remained as tactoids in benzene, toluene and \( p \)-xylene, but clay aggregated, forming particles, in octane and cyclohexane. They developed a stacked disk model. When parameters were fit, their values indicated that the thickness of the tallow layer increased while the Gaussian standard distribution of the next neighbor center-to-center distance decreased with increasing solvent solubility parameters. The dispersion of Cloisite 15A in chloroform did not exhibit concentration-dependent scattering within the range of concentrations examined. A concentration-independent slope of \( \sim -2.36 \) was obtained from the benzene, toluene, and \( p \)-xylene/clay
dispersions, indicating the presence of platelet stacks (tactoids). The number of platelets per tactoid was predicted by fitting SANS data from benzene, toluene, and p-xylene/clay dispersions using the developed stacked model [36-39].

Ho et al. extended the studies of the clay dispersions in different solvents, by examining Hansen’s solubility parameters, \( \delta_0^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \) [38]. They found that the dispersion force of the solvent, reflected by \( \delta_d \), is the principle factor determining whether the clay platelets remain suspended in the solvent. The polar (\( \delta_p \)) and hydrogen bonding (\( \delta_h \)) forces primarily affect the tactoid formation and the structure of the suspended platelets. They reported the precipitation of Cloisite 15A in any solvent with strong hydrogen bonding groups. Hansen’s solubility correlation was employed to identify the interactions of clay with trichloroethylene [36, 37].

The investigation of clay solvent dispersions using SANS was continued in 2003 by Hanley, Glinka, and Ho at the National Institute of Standards and Technology [37]. They used Cloisite 15A in toluene since the SANS data on Cloisite 15A were available and a preliminary analysis on toluene/Cloisite 15A had been obtained in their previous work [36]. The proposed disk shaped model for clay platelets, described by equations (2.8) – (2.17), and the stacked disk model, described by equations (2.19) – (2.23), were used. The dispersion of Cloisite 15A in toluene consisted of platelets and stacks of disks as found earlier. The clay was well dispersed into a complex with clusters of three to six ditallow coated montmorillonite platelets. Estimates were obtained for the size of these clusters, the amount of ditallow adsorbed on a montmorillonite platelet, and an estimate of the thickness of the adsorbed layer.
They also evaluated an approximate surface coverage using the contrast-matching feature of the neutron scattering technique. The surface coverage was estimated by the method introduced by Hanley et al., which does not require any assumptions regarding the surface morphology. A shift toward scattering for a sample in various solvents is proportional to the number of moles displaced by the scatterers. The scattering power, $\Delta_{ab}$, of 1 mole of scatterers that displaces $x_{ab}$ moles of solvent b is defined by[39]:

$$\Delta_{ab} = \left[ \sum_{i=a} b_i - x_{ab} \sum_{i=b} b_i \right]^2$$

(2.25)

If 1 mole of scatterers has $x_c$ moles of a surface compound c attached to it, and species c displaces $x_{cb}$ moles of solvent b, the scattering power is expressed as:

$$\Delta_{acb} = \left[ (\sum_{i=a} b_i - x_c \sum_{i=c} b_i) - \sum_{i=b} b_i (x_{ab} + x_{cb}) \right]^2$$

(2.26)

In this case, $x_c$, is the number of ditallow moles that form the surface layer of 1 mole of CNa+ (alumina silicate layer). [39]

The consensus in all of these studies, [27, 28, 35-40] agreed that use of a single technique is insufficient for understanding the morphology and structure of clay within the medium (polymer or solvent). Scattering techniques, X-ray diffraction, small angle X-ray scattering, and neutron scattering are useful tools to examine the dispersion of clay, but all of these should be combined with direct observation methods such as
transmission electron microscopy (TEM), atomic force microscopy (AFM), and high-resolution transmission electron microscopy (HR-TEM).

The major goal of clay incorporation into a polymer matrix is improvement of mechanical properties such as elastic moduli, flexural moduli, impact properties, viscoelastic properties, (storage moduli), as well as thermal properties such as glass transition temperature (Tg) and heat distortion temperature (HDT). Dynamic mechanical thermal analysis (DMTA) is a valuable technique used to examine viscoelastic properties, storage elastic moduli, and glass transition temperature. In order to provide a better foundation for the DMTA measurements, the basic theory is discussed.
Viscoelasticity

The strain will not remain constant if a polymeric filament is suspended under uniform tensile stress. Instead, it will increase with time. Molecular rearrangements in the solid induced by stress are responsible for this effect. When the stress is released, the molecules rearrange until they regain their thermodynamically more favorable spatial arrangement. The strain will return to zero if the initial process is purely elastic. It is a consequence of viscoelasticity. A viscoelastic material is elastic because it recovers, but it is viscous because it creeps [41].

Polymers are viscoelastic at all temperatures. They cannot be considered simple elastic solids. Therefore, in designing a material for the specific strain, both the stress and the time for which the stress is applied should be considered. Since the viscoelastic properties are also highly temperature dependent, the maximum working temperature should be specified [41].

The major difference between elastic solids, metals and metal alloys, and polymers is that polymer molecules have long chain lengths and cohere as solids even when discrete sections of the chains (or branches) are undergoing Brownian motion and moving by diffusional jump processes from place to place. In the liquid phase, the whole polymer chain undergoes strong Brownian motion. The molecules move as a whole by “snake-like” motions as explained in the theory of rubber elasticity [41, 42]. In the glassy state, a polymer chain is immobile, but very limited segmental motion is possible before the activation of the quasi-liquid-like segmental motion at the glass transition temperature. When a mechanical stress applied, the polymer will experience
a time dependence in the strain. This effect occurs because the mobile sections of the macromolecules undergo not only torsional (rotational) motion but also some translational motion begins to occur under applied stress. Some recovery can occur (elastic recovery) when the stress is removed. If the applied stress is left on for a long period of time, deformation will have an elastic component and a viscous component. The viscous component (non-recoverable strain) is due to translational motion of the polymer chains. Polymers used in creep resistant materials resist creep indefinitely at the applied loads they are designed for. They can recover completely when the stress is removed, provided the stress is below a critical amount and the temperature is low (e.g. typically below Tg) [41].

Maxwell, Boltzmann, and Kelvin established the fundamental of theoretical and experimental studies of viscoelasticity in the nineteenth century. Viscoelasticity became a significant subject for engineers largely because of the increased use of polymers as engineering materials in the latter part of the twentieth century. Viscoelastic effects must be considered during a quantitative design [41].

**Creep**

Figure 2.10 shows the results of a typical creep experiment. If a constant shear stress, $\sigma_1$, is applied to a viscoelastic material, the strain is time dependent. When the material is allowed to recover, a larger constant stress of $\sigma_2$ is applied. The time dependent strain will be observed (b). If the strain at a time, $t_a$, after application of the stress, is plotted against the stress, it is observed that the strain, $\gamma(t_a)$, is linear in the
stress (c). At a later time, \( t_b \), after the application of the stress, the strains, \( \gamma(t_b) \), are again linear in the stress. Thus, for an arbitrary time,

\[
\frac{\gamma_1(t)}{\sigma_1} = \frac{\gamma_2(t)}{\sigma_2}
\]  

(2.27)

The strains in the two experiments taken are proportional to the applied stresses at the same time \( t \). Therefore, the creep compliance at time \( t \) is defined as:

\[
J(t) = \frac{\gamma_1(t)}{\sigma_1} = \frac{\gamma_2(t)}{\sigma_2}
\]  

(2.28)

In general, for stress \( \sigma \)

\[
J(t) = \frac{\gamma(t)}{\sigma}
\]  

(2.29)

Polymer creep behavior in the low stress region (below \( \sim 0.5 \times 10^{-2} \)) is linear. The plot of strain versus stress at a specific time is known as an isochronal in a creep experiment [41].

Figure 2.10.(d) demonstrates the change of \( J(t) \) measured over a number of decades of time and plotted against \( \log t \). \( J(t) \) is almost constant at very short and at very long times. Between these extremes, the curve of \( J(t) \) versus \( \log t \) has a sigmoidal shape [41].
Figure 2.10. Linear viscoelastic creep

(a) constant stress $\sigma_1$ applied at $t=0$ leads to time-dependent strain $\gamma_1(t)$; 
(b) A higher stress $\sigma_2$ applied at $t=0$ leads to time dependent strain $\gamma_2(t)$;  
(c) from (a) and (b) the strains at $t_a$, $\gamma(t_a)$, and at time $t_b$, $\gamma(t_b)$, are linear in stress;  
(d) the observed dependence of $J(t)$ on log $t$ through one complete relaxation. $J_U$ and $J_R$ are the unrelaxed and relaxed compliances [41].

Several isochronal plots of stress-strain are made to distinguish the strain range where the material is linearly or nonlinearly viscoelastic. The non-linearity results in faster creep compared to the linear region (Figure 2.11).
Figure 2.11. Isochronals at $t_a$ and $t_b$. Low stress region is linear viscoelastic and higher stress regions in non-linear viscoelastic [41].

In the linear elastic region, $J(t)$ is stress independent. When $J(t)$ is known over a range of time, then the strain for any stress and time is known [41].

**Stress Relaxation**

If a constant shear strain, $\gamma_1$, is applied at zero time, $\sigma(t)$ is required to maintain the shear strain. Shear stress decreases with time (Figure 2.12). If this material is allowed to recover and a larger strain of $\gamma_2$ is applied, the time dependence is shown in Figure 2.12. At low strains (same as creep), the isochronals are linear.
Figure 2.12. Linear viscoelastic stress relaxation

(a) Constant stress of $\gamma_1$ applied at $t=0$ leads to a time dependent stress of $\sigma_1(t)$,

(b) A higher strain $\gamma_2$ is applied at time $t=0$ which leads to a time dependent stress of $\sigma_2(t)$;

(c) from (a) and (b) the stresses at times, $t_a$, $\sigma(t_a)$ and at time $t_b$, $\sigma(t_b)$, are linear stresses.; (d) the observed dependence of $G(t)$ on log $t$, through one complete relaxation.$G_U$ and $G_R$ are unrelaxed and relaxed moduli [41].
At an arbitrary time, one can write:

\[
\frac{\sigma_1(t)}{\gamma_1} = \frac{\sigma_2(t)}{\gamma_2}
\]  \hspace{1cm} (2.30)

The stress relaxation modulus is defined as:

\[
G(t) = \frac{\sigma(t)}{\gamma}
\]  \hspace{1cm} (2.31)

This is another way of expressing linear viscoelasticity. All polymers show linear viscoelasticity in the low strain range \(\sim 0.5\times10^{-2}\) [41].

If \(G(t)\) is plotted against log \(t\), it exhibits the form as shown in Figure 2.12.d. At very short times and very long times, \(G(t)\) tends toward the limiting values, \(G_U\) and \(G_R\). In these extended regions, the polymer becomes more elastic and \(G(t)\) becomes time independent.

Figure 2.13 shows the linear and non-linear viscoelastic limit range. Viscoelastic behavior of polymers is linear in the low strain regions and it becomes non-linear at high strain regions. The structural parts are always designed that the maximum strain-strain stays in the linear viscoelastic region.
The simplest way to determine $G(t)$ is in a thin walled tube. At $t=0$, the tube is rotated through an angle $\theta$, and the time dependent torque, $\Gamma(t)$, which keeps $\theta$ constant, is measured. The shear stress exerted on the polymer is calculated [41]:

$$\sigma(t) = \frac{\Gamma(t)}{2\pi r^2 s}$$  \hspace{1cm} (2.32)

and the constant strain is $\gamma = r\theta/L$.

Thus, the time dependent shear modulus is obtained:
G(t) is measured, determining \( \Gamma(t) \) for a fixed \( \theta \).

If the mode of stress is tension instead of shear, then the time dependent tensile modulus is expressed as:

\[
E(t) = \frac{\sigma(t)}{\varepsilon} \tag{2.34}
\]

where \( \varepsilon \) is the constant tensile strain applied to the specimen and \( \sigma(t) \) is the tensile stress [41].

**Dynamic Properties**

Another manifestation of viscoelasticity is the mechanical damping property of viscoelastic materials. Damping has valuable applications in shock absorbers and in plastics structures subject to forced oscillations and mechanical vibrations at the natural frequencies of the structure, which do not easily build up due to the high damping capacity of the plastics. A high damping characteristic means that generated vibrations are not sustained and transmitted to become a nuisance. Understanding damping changes with frequency is important. To quantify dynamic viscoelastic properties, it is assumed an oscillatory shear strain of angular frequency of \( \omega \) is applied to the polymeric material [41].
For a linear viscoelastic material, the stress response is also sinusoidal, but out of phase with the strain.

\[ \gamma = \gamma_0 \sin \omega t \]  (2.35)

\[ \sigma = \sigma_0 \sin(\omega t + \delta) \]  (2.36)

The strain lags behind the stress by a phase angle, \( \delta \). Figure 2.14 illustrates a vector method showing the dependence of \( \gamma \) and \( \sigma \) on \( \omega t \). The following expression is obtained when equation (2.36) is expanded [41]:

\[ \sigma = (\sigma_0 \cos \delta) \sin \omega t + (\sigma_0 \sin \delta) \cos \omega t \]  (2.37)

Figure 2.14. Vector representation of an alternating stress leading an alternating strain by phase angle \( \delta \) [41].
The stress consists of two components: one in phase with the strain ($\sigma_0\cos\delta$), the other, out of phase ($\sigma_0\sin\delta$) in equation (2.37). The dynamic relationship is defined by:

$$\sigma = \gamma_0 [G'\sin\omega t + G''\cos\omega t]$$

(2.38)

where $G' = (\sigma_0/\gamma_0)\cos\delta$ and $G'' = (\sigma_0/\gamma_0)\sin\delta$. Thus, the component of $G'\gamma_0$ is in phase with the oscillatory strain, while the component $G''\gamma_0$ is 90° out of phase.

This formulation is analogous to the relationship between current and voltage in an electric circuit, where a complex representation is used. If we define, $\gamma^* = \gamma_0 \exp(i\omega t)$ and $\sigma^* = \sigma_0 \exp(i(\omega t + \delta))$, then the complex shear modulus is $G^* = \sigma^*/\gamma^* = (\sigma_0 \exp(i\omega t + \delta))/(\gamma_0 \exp(i\omega t))$, which simplifies to $G^* = \sigma_0/\gamma_0 \exp(i\delta) [41]$. The exponential term can be written in terms of sine and cosine, $G^* = \sigma_0/\gamma_0 (\cos\delta + i\sin\delta)$, which is $G^* = G' + i\cdot G''$. $G'$ is termed the real part of the modulus, and $G''$, the imaginary part. Conversely, the complex shear compliance is used as a parameter,

$$J^* = \gamma^*/\sigma^* = [\gamma_0 \exp(i\omega t)]/[\sigma_0 \exp(i(\omega t + \delta))].$$

This equation is simplified in terms of sine and cosine, $J = (\gamma_0/\sigma_0) \exp(-i\delta)$, or $J^* = (\gamma_0/\sigma_0) (\cos\delta - i\sin\delta)$ and $J^* = J^* - iJ^*$, in which $J = (\gamma_0 \cos\delta)/\sigma_0$ and $J = (\gamma_0 \sin\delta)/\sigma_0$. The tangent of the phase angle is:

$$\tan\delta = \frac{J''}{J'} = \frac{G''}{G'}$$

(2.39)
Damping and \( \tan \delta \), is zero for a pure elastic solid. Examples of low-damping solids are metals and quartz. Polymers have several degrees of \( \delta \). Damping, \( \delta \), may approach 30° in certain temperature ranges (for instance the glass to rubber transition). This very high damping is useful in technical applications [41].

\( G^* \) can be determined at a certain frequency and temperature, so \( J^* \) also can be obtained (\( G^* = 1/J^* \)). But \( G(t) \neq J(t)^{-1} \), although it can be used as an approximation in practical design.

The phase angle is related to the logarithmic decrement. The logarithmic decrement determines the rate at which a stimulated oscillation dies away when the stimulus is removed. An example is the torsion pendulum shown in Figure 2.15. The lower end of the specimen is clamped rigidly and the upper clamp is attached to the inertia arm. By moving the masses of the inertia arm, the rotational moment of inertia can be adjusted to obtain the required resonant frequency of rotational oscillation. An electromagnetic transducer detects rotation. The specimen is not under axial stress since it is counterbalanced [41].
Figure 2.15. Torsional pendulum for the determination of shear modulus and damping as function of temperature at frequencies around 1Hz [41].
The system is rotated slightly from its null position by a deflecting torque to obtain measurement. The specimen and support wire are consequently twisted. The support wire is long and has a small diameter, so that induced torque in it is negligible. The only significant torque is induced by the twist in the sample, which tends to restore the pendulum to its null position [41].

The deflecting torque is then removed and the system begins to oscillate. The frequency of oscillation, $\omega$, is defined by the pendulum’s moment of inertia around the central axis, $M$, and the produced torque by the sample for unit rotation ($\theta=1$) $\Gamma_1$

$$\omega = \sqrt{\frac{\Gamma_1}{M}} \quad (2.40)$$

If the specimen is a circular rod of length $l$ and radius $a$, then

$$\Gamma_1 = \frac{NG'}{l} \quad (2.41)$$

in which $N$ is the polar second moment of area, $N=\pi a^4/2$.

The resonant oscillation at frequency $\omega$ decays. The ratio of successive amplitudes, $A_n$ and $A_{n+1}$, yields the logarithmic decrement:

$$\Lambda = \ln \frac{A_n}{A_{n+1}} \quad (2.42)$$

The relationship between $\Lambda$ and $\tan \delta$ (for $\Lambda<<1$) is
This experiment gives both $\tan \delta$ and $G'$.

\[
G' = \frac{1}{2} \frac{M \omega^2}{N} \tag{2.44}
\]

$G''$ is obtained from $G'' = G' \tan \delta$. This method is precise even for low values of $\tan \delta$ since the amplitude can be observed over many oscillations [41].

Applying oscillatory torque $\Gamma$ results in a direct determination of the phase angle, using a tubular sample [41].

\[
\Gamma^* = \Gamma_0 \exp(i(\omega t + \delta)) \tag{2.45}
\]

This is achieved with an electrical torque transducer in which an oscillatory current of $I^* = I_0 \exp(i(\omega t + \delta))$ generates the oscillatory torque of $\Gamma^* = k_i I^*$, where $k_i$ is a constant. The torque and current, and torque and stress, are in phase. For a thin-walled tube, the relationship between torque and stress is expressed as:

\[
\sigma^* = \left(\frac{1}{2 \pi r^2} \right) \Gamma^* \tag{2.46}
\]

Thus, the current and the stress are exactly in phase. The strain can be obtained from the following equation:
\[ \gamma^* = \left( \frac{\Gamma}{\Gamma_0} \right) \theta^* \] 

(2.47)

This means that the strain and the rotational angle \( \theta \) are in phase. Thus the phase angle between two observables, \( \theta^* \) and \( I^* \), is the same as the phase angle between \( \gamma^* \) and \( \sigma^* \). Since \( \theta^* = \theta_0 \exp i \omega t \) [41], then

\[ G' + iG'' = \frac{\sigma^*}{\gamma^*} \] 

(2.48)

or

\[ G' + iG'' = \left( \frac{1}{2 \pi^3 s} \right) \frac{\Gamma^*}{\theta^*} \] 

(2.49)

\[ G' = \left( \frac{lk_1}{2 \pi^3 s} \right) \frac{l_0 \cos \delta}{\theta_0} \] 

(2.50)

\[ G'' = \left( \frac{lk_1}{2 \pi^3 s} \right) \frac{l_0 \sin \delta}{\theta_0} \] 

(2.51)

Thus, \( G' \) and \( G'' \) are derived by measuring \( l_0, \theta_0, \) and \( \delta_0 \). It is difficult to determine \( \delta \). The best method is to convert \( \theta \) into voltage with a rotational transducer. The phase difference between this voltage and the torque current can be measured by precise electrical methods. This forced-oscillation technique is used most efficiently at frequencies different from the system’s resonant frequency [41].

Forced oscillation has two advantages over the torsional pendulum. First, it has higher reliability for high damping values compared to the torsional pendulum.
instrument. Second, changing frequency is simply performed by rotation of the frequency control knob on the sine wave generator. By appropriate design, the obtainable frequency spectrum lies between $10^{-3}$ and $10^4$ Hz [41].

The determination of $G'$ and $\tan\delta$ (or any equivalent pair of dynamic mechanical parameters) is valuable both in research and in quality control. The measurements are performed at constant frequency over an extremely wide temperature range. Figure 2.16 shows a graph of the $G'$ versus temperature at a constant frequency of about 1 Hz. $G'$ decreases with increasing temperature. The decrease in $G'$ is rapid in two temperature regions, one centered at $50^\circ$C and the other at $110^\circ$C. $\tan\delta$ exhibits a peak in these same temperature regions. Figure 2.16 shows that $\tan\delta$ is a measure of the slope of $G'$. It is also a measure of the slope in the log $G'$ versus temperature curve. The peak at the highest temperature is the $\alpha$-process ($\alpha$-relaxation), and the peak at the next lowest temperature is the $\beta$-process ($\beta$-relaxation) [41]. All the above equations are also applied to the bending modulus as well.
The temperature where $\alpha$-relaxation occurs is also called the glass transition temperature. Segmental motion of the polymer chains begins at the glass transition temperature. The polymer is in the glassy state below $T_g$ where it has a high stiffness, hardness and modulus. In this state, polymer chains only have vibrational and some rotational motion. The polymer molecules are translationally frozen. Polymer chains have more energy with increasing temperature, and eventually at the glass transition temperature, molecular and segmental motion of the polymer chain begin, especially
at the entanglements. These accelerate all types of viscoelastic processes. The polymer reaches its rubbery region with increasing temperature. The motions of the molecules are long range at this stage, involving motions of the units on the order of the length of the molecule itself. Viscous effects are more important when the polymer is under stress at the rubbery stage and the recoverable component of the deformation is relatively small [44].

**Three Point Bending**

The standard tests for stiffness of a plastic are performed using either tensile or flexural measurements. The tensile test has the advantage that the stress in uniform in the gauge length, and that the corresponding strains can be measured directly. On the other hand, the three-point bending test, as shown in Figure 2.17, can be carried out with a very simple apparatus. Flexural modulus is calculated by applying the standard equations for a beam undergoing small elastic deflections. When the force is applied, the stiffness of the system should not allow the total elastic deformation to exceed 1% of the total deflection of the test specimen during the test, otherwise appropriate corrections should be made. The three-point bending test should be performed according to standard ASTM D 790M.
The Flexural modulus, $E_f$, is expressed as:

$$E_f = \frac{L^3P}{4bd^3\Delta} \quad (2.52)$$

The maximum stress occurs at the midspan in the outer fibers, and is given by:

$$\sigma_{\text{max}} = \frac{3PL}{2bd^2} \quad (2.53)$$

The maximum shear stress occurs in the neutral plane at the center of the bar and is defined as $\tau_{\text{max}}=3P/4bd$. These equations are valid only for small deflections where the polymer is linearly viscoelastic.

Values of modulus determined in tension or flexural at one or more temperatures are not adequate for the engineering design of materials. Additional time dependent information provided in tensile creep measurements is necessary [41, 44].
Clay has been used extensively to enhance the mechanical properties, chemical resistance, thermal properties, barrier properties, and flame resistance of polymers. Montmorillonite clay is the most common type of clay that has been used in clay composites. Its advantages include the possibility of overcoming the attractive forces between platelet sheets and its dispersion as nanophases as well as its availability and low cost. However, other types of clay, laponite, hectorite and saponite, have been examined as well. Montmorillonite has been organically modified to be compatible with organic matrices and achieve a better dispersion. Achieving a good dispersion of the 1 nm thick alumina silicate platelets within a polymer matrix has remained a challenge. Many papers have reported exfoliation of clay within a polymer matrix, but in almost all cases, composites containing a mixture of platelets and tactoids have been made. Many attempts have been performed and some degree of clay dispersion in a variety of both thermoplastic and thermoset polymer matrices has been reported. Clay composites have been prepared by in-situ polymerization, melt blending, and solution mixing techniques. Sonication has been reported to be one technique that promotes exfoliation. The characterization methods used by the majority of researchers are XRD and TEM. In many cases, it has been concluded that an exfoliated composite has been prepared without sufficient characterization of the composite. No reports of the characterization of clay/polymer composites using neutron scattering were found in the literature. Both X-ray scattering and neutron
scattering are powerful techniques to examine the structure and morphology of the nanophases in the range of 1-1000 nm. Assuming that clay has a disk shape, a stacked disk model has been developed to obtain quantitative information about the clay platelets and tactoids in the solution. No reports of neutron scattering on a clay nanocomposite have been found in the literature.

The objective of dispersing the clay in the polymer matrix is to obtain a nanocomposite with enhanced properties containing relatively low amounts of clay. The thermal-mechanical properties of clay composites are of considerable interest. Many researchers have reported enhancement of the tensile strength and elastic moduli for clay/polymer composites. Measuring the viscoelastic properties of the composites via DMTA can give valuable information about the elastic bending moduli and glass transition temperature of the composites.
REFERENCES


CHAPTER III

RESEARCH OBJECTIVES AND APPROACH

Research Objectives and Approach

Montmorillonite clay has been used as a reinforcement agent that can be dispersed at the nanometer scale within polymer matrices. Clay has many advantages including low cost, capability to be dispersed as nanosized platelets and tactoids, and the ability to improve matrix properties upon adding a small amount to the polymers. Therefore, clay is a good candidate to use as a nanoreinforcement agent. Pinnavaia et al. (1994) reported the exfoliation of montmorillonite clay in an epoxy resin matrix. Vaia et al. (1996) reported preparation of nanocomposites from polymer layered silicates and polystyrene by the melt intercalation technique.

The objectives of this study are to prepare a clay/polyDCPD nanocomposite, to examine the exfoliation/delamination of organically modified montmorillonite clay in dicyclopentadiene resin, and to develop a predictive model for stress-strain behavior. Dicyclopentadiene resin is a thermoset polymeric material. The first goal is to prepare and characterize highly delaminated/exfoliated clay polydicyclopentadiene resin composites. Experimental studies combined with modeling will provide information about the nanocomposites’ mechanical properties, morphology, the relationship
between morphology and mechanical properties, and stress strain behavior. Experimental studies are necessary to prepare the highly delaminated composites. A detailed characterization is required to verify the structure and morphology of clay within the polymer matrix. A micromechanical model will be developed to predict the deformation and stress distribution within the polymer matrix.

Approaches:

- Evaluation of the methods to disperse clay in dicyclopentadiene resin;
- Identification of the most effective way to delaminate clay in the monomer, and consequently, in the resin;
- Modification of clay and studying the effect of different clay modification on the delamination process;
- Preparation of the clay/polydicyclopentadiene polymer composites;
- Investigation of the rheological behavior of clay/monomer dispersions;
- Examination of the microstructure changes of the clay in the dispersion and its correlation to the overall viscosity of the media;
- Characterization of the prepared composites;
- Mathematical modeling of the experimental data to predict quantifying information about clay delamination;
- Development of a finite element model, which describe the stress-strain behavior of the clay nanocomposites
CHAPTER IV

DELAMINATED ORGANICALLY MODIFIED CLAY/DICYCLOPENTADIENE RESIN NANOCOMPOSITES

Preparation, Characterization and Properties

This dissertation section describes a new approach for preparation of well-dispersed highly delaminated organically modified montmorillonite clay/polydicyclopentadiene nanocomposites. Highly delaminated polydicyclopentadiene/clay nanocomposites were synthesized by \textit{in situ} polymerization of dicyclopentadiene/organically-modified montmorillonite clay dispersions. Dicyclopentadiene/clay suspensions were sonicated for various times to enhance the degree of delamination prior to curing. The d-spacings of the clay in nanocomposites were monitored using X-ray diffraction and the extent of delamination was examined by TEM and preliminary neutron scattering studies. A new approach, use of confocal laser microscopy, was employed to follow the dispersion of clay layers, tagged by a fluorescent dye, within the liquid monomer. It is evident that XRD cannot be used alone as a criteria for exfoliation. TEM showed that increasing the clay concentration
at constant sonication gave an increase in average tactoid size. The largest improvement in composite mechanical properties occurred at clay loading levels (0.5-1wt%). Significant increases in Tg, elastic bending moduli, flexural moduli and flexural strengths were found at 0.5-1wt% clay loadings, where the highest degree of delamination/exfoliation also occurred.

**Introduction**

Hybrid organic-inorganic materials have shown superior physical mechanical properties compared to conventional materials [1-8]. In order to optimize the performance of these materials, it is usually desirable to disperse the inorganic component within the organic component at the nanoscale level [9-11]. Polymer layered silicate nanocomposites, containing small amounts of the inorganic phase, have exhibited superior properties to those of the pure polymers. For example, modulus, strength, thermal expansion coefficient, toughness, gas permeability barrier and flammability resistance all may be improved [12-17]. Montmorillonite (MMT) is a crystalline, 2:1 layered clay mineral. A single layer of this clay has a central alumina octahedral sheet, which is sandwiched between two silica tetrahedral sheets [18]. By overcoming the forces between layers, small molecules may enter into clay galleries and be polymerized [19-20].

In general, the polymer/clay composites can be divided into three categories: (1) conventional composites in which clay tactoids and particles exist in their original aggregated states; (2) intercalated nanocomposites where individual platelets are interlayered by a few polymer molecules; and (3) exfoliated nanocomposites, where
individual 1nm thick clay layers are separated in the continuous polymer/matrix [12,14,16]. Another category can be defined that makes a distinction between fully exfoliated nanocomposites and intercalated nanodispersions. This category can be called the highly delaminated nanocomposites. In fully exfoliated nanocomposites, clay layers are well dispersed as 1nm thick non-interacting clay layers. However, in highly delaminated nanocomposites, stacks of between 2 to 20 layers of clay (small tactoids) are well dispersed in the polymer matrix. In this type, the XRD peak of the ordered structure disappears despite the fact that stacked layers still exist [21, 22]. We are not aware of any reports demonstrating completely exfoliated clay nanocomposites.

Three main approaches have been used to form clay nanocomposites: melt blending, solution blending and in situ polymerization [11,12,14,16]. In this paper, we report the partial exfoliation of organically-modified montmorillonite clay to a highly delaminated state in the low viscosity, nonpolar monomer, dicyclopentadiene (DCPD), followed by an in situ ring-opening polymerization/curing which captures this highly delaminated clay in a crosslinked polymer network. The delamination process was aided by sonication in some cases.
Experimental Section

Materials

The organically-treated montmorillonite clays, Nanomer® I-28 modified with trimethyl-octadecyl ammonium ion and Nanomer® I-44pa modified with dimethyldidecyl ammonium ion, were used as received in this work. The clays were purchased from Nanocor, Inc. Greater than 95% of all ions had been exchanged for the quaternary ammonium ions. Both I-28 and I-44pa exhibited d-spacings of 2.56 nm. DCPD (purity of 99.2%) was obtained from Cymetech, LLC., under the name brand of Ultrene™99. Cyclopentadiene (CPD) (4 wt%) was added to the pure DCPD. This monomer combination was used in all of the composites. Pure DCPD melts at 39°C. The presence of small amounts of cyclopentadiene lowers the melting point of DCPD below room temperature, which allowed mixing and sonication of the clay with the monomer to be carried out at room temperature (Table 4.1).

Dichloro(3-methyl-2-butenylidene)-bis-tricyclopentyl-phosphine ruthenium (a Grubbs’-type catalyst, Figure 4.1) [26-27], obtained from Cymtech LLC., was employed as the ring-opening metathesis polymerization (ROMP) catalyst [23-27]. Safranine O, a fluorescent dye, was used to tag clay layers in the I-28 clay/DCPD dispersion. Safranine O (4g in 200ml of denatured alcohol and water) was obtained from Becton Dickinson and used as received.
Table 4.1. Experimental materials

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Co-monomer</th>
<th>Reinforcing Agents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dicyclopentadiene</td>
<td>Cyclopentadiene</td>
<td>Organically Modified montmorillonite</td>
</tr>
</tbody>
</table>

- Octadecyl ammonium modified MMT
- Didecyldimethyl ammonium modified MMT

0.5-5 wt%

Figure 4.1. The structure of Dichloro(3-methyl-2-butenylidene)-bis-tricyclopentyl-phosphine ruthenium (a Grubbs’-type catalyst)
**Preparation of Nanocomposites**

Highly delaminated DCPD/nanoclay composites were prepared by dispersing the clay (0.5-5wt%) into the liquid DCPD and then polymerizing/curing the DCPD to form the solid composite. Clay I-28 was dispersed in liquid DCPD by stirring for 1h followed by sonication for 3h under nitrogen at 20 kHz and a wave amplitude of 30 using a 500W sonication Model GE501 ultrasonic processor (Ace Glass Incorporated). Each sonication batch contained 10-15g of the clay I-28/DCPD dispersion. Samples (8-10g of dispersion) were cured by adding the Ru-based catalyst (0.01875g catalyst/10g of monomer; DCPD/catalyst mole ratio of 2860) to the nanodispersion and subsequent heating. Mole fractions of catalyst less than 0.0002 are sufficient [23-27]. A few droplets of methylene chloride were added to the catalyst to wet the surface. Then the DCPD/clay nanodispersion was added to the wetted catalyst, followed by mixing for 3-5 minutes. The exothermic polymerization reaction started at room temperature and then the viscous polymerizing dispersion was poured into a preheated steel mold (76°C) where gelation occurred as the cure continued within about 2-3 min (Figure 4.2). The mold was placed into a hot press at 1 atm for 15 min at 76°C, 25 min at 138°C, 40min at 160°C and finally 1h and 15min at 260°C. The pressure was increased to 5 atm when the temperature increased to 260°C during molding (Figure 4.3). All samples used in mechanical property testing were also postcured for 2h at 280°C under high purity helium. The chemical reactions of the ROMP are shown in Figures 4.2-4.3.
I-44pa clay/polyDCPD nanocomposites were prepared by stirring I-44pa into DCPD for 1h without sonication. These dispersions were then cured by the same protocol used for the I-28 composites.

**The Structure of Materials and Mechanisms**

The structure of Dichloro(3-methyl-2-butenylidene)-bis-tricyclopentyl-phosphine ruthenium is shown in Figure 4.1. Figure 4.2 shows the ROMP mechanism, which proceeds at lower temperatures. Figure 4.3 shows the mechanism for high temperature curing.

**X-ray Diffraction Measurements**

XRD analysis was used to follow the clay’s d-spacing in the cured nanocomposites versus the extent of mixing and sonication used during dispersion. XRD data on clay powder and nanocomposites samples were collected on a Phillips diffractometer, Model X’Pert, using Cu Kα radiation (λ=0.154056nm). Scans were taken over the 2θ range of 1 to 10°, with a step size of 0.03° at 1s per step.

**Small Angle X-ray Scattering**

SAXS experiments were performed on the Oak Ridge National Laboratory’s (ORNL) 10-m SAXS instrument[28,29], with a sample-detector distance of 1.119m using Cu Kα radiation (λ = 1.54Å) and a 20x20 cm² two-dimensional position-sensitive area detector with each virtual cell (element) of about 3mm apart. Corrections were made
Figure 4.2. The ring-opening metathesis polymerization mechanism.

Figure 4.3. High temperature thermal crosslinking reaction.
for instrument background, dark current due to cosmic radiation and electronic
noise in the detector circuitry, and the detector non-uniformity and efficiency (using a
Fe\textsuperscript{55} radioactive isotope standard, which emits x-rays isotropically by electron
capture) on a cell-by-cell basis. The data were radially (azimuthally) averaged in the q-
range, 0.01 < q < 0.4 Å\textsuperscript{-1}, \( q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \), where \( \lambda \) is the X-ray wavelength, and \( \theta \) is
the scattering angle. Then these data were converted to an absolute differential
scattering cross section by means of pre-calibrated secondary standards [30]. The
absolute scattering intensity is in cm\(^{-1}\) units.

A Molecular Metrology Small Angle X-ray Scattering System was used to study
small angle X-ray scattering at a sample to detector distance of 5 m. The X-ray source
was a copper, K\( \alpha \), micro-focused X-ray beam with a wavelength of 1.542 Å operating
at 45 kV and 0.66 mA. A multi-wire detector consisting of a 2-dimensional array of
wires was used. The data were radially averaged and converted to an absolute
differential scanning scale. The same composite samples were used in measurements
with the two SAXS instruments.

**Mechanical Properties**

**Three-Point Bending**

A Zwick material testing machine (Model 1435) was used for 3-point bending
tests to obtain flexural moduli and flexural strengths at ambient temperature. Sample
thicknesses ranged from 2 to 3 mm, widths of ~10-11 mm and lengths from 38 to 40 mm. A span of 20 mm was used in a 50kN load cell.

**DMTA**

Dynamic mechanical thermal analysis was performed using a Rheometrics Scientific Model MK III instrument between 50-320°C at both 1 Hz and 10 Hz using sample thicknesses from 1.5 to 2.5mm and widths of 4-5mm.

**Transmission Electron Microscopy**

A JEM-100CX II transmission electron microscope (60kV) was used to examine clay morphology and orientation. Nanocomposite samples were ultramicrotomed to thicknesses of 70-85nm at room temperature using a Reichert-Jung Ultracut E ultramicrotome equipped with a diamond knife. The samples were placed on a Formvar-coated 200 mesh copper grid. The clay versus polymer matrix contrast was sufficient to permit electron micrograph imaging without staining.

**Confocal Laser Microscopy**

A Leica TCSNT Confocal laser scanning microscope with laser wavelengths of 476nm, 488nm and 568nm was used. Clay was tagged with Safranine O, a fluorescent probe with an excitation at λ=495 nm and emission at λ=586 nm [31]. A solution of Safranine O (4g in 200ml denatured alcohol and water) was used. Then I-28 clay (0.5g) was dispersed in the 15ml of this solution, stirred overnight, filtered and
dried. Then a 1wt% Safranine O-tagged I-28/DCPD dispersion was made by stirring. An aliquot was sonicated for 3h. The liquid dispersions were then analyzed.

Results and Discussion

Polymerization of DCPD

DCPD polymerizes in the presence of the Ru catalyst via a highly exothermic living ROMP mechanism [23-27]. Linear polymerization was initiated at temperatures of 40-60°C as the strained norbornene double bond undergoes ring-opening metathesis (ROMP). This was followed by crosslinking, via metathesis of cyclopentadiene double bond, when the temperature exceeds 80°C. The exothermic reaction and programmed heating caused the temperature to rise and crosslinking occurred far more rapidly at 150°C.

Delamination in PolyDCPD/clay Nanocomposites

DCPD is a non-polar organic monomer, requiring a montmorillonite clay that has been modified by a nonpolar organic layer in order to be exfoliated. Preliminary attempts to disperse I-28 into DCPD by stirring this clay in liquid DCPD resulted in monomer migration into the clay galleries. Gallery expansion was indicated by an increase in d-spacing from 2.56nm to 4.15nm (XRD, Figure 4.4). Untreated sodium montmorillonite clay does not undergo gallery expansion, illustrating the ability of octadecyl hydrophilic chains to permit DCPD intercalation.
Sonication in DCPD further delaminated the I-28 clay. A series of DCPD/clay samples were cured after sonicating the clay/liquid DCPD suspensions for various times. The d-spacing increased with increasing sonication time as seen from the shift of the XRD peak to smaller 2θ angles.

The intensity of the XRD basal diffraction peak also decreased, indicating delamination was proceeding. After three hours of sonication, nanocomposites exhibited XRD plots, which resembled those of polydicyclopentadiene containing no clay (Figure 4.4). Gilman pointed out that XRD analysis alone can lead to false interpretations of the extent of exfoliation [21, 22]. Thus, TEM studies are necessary to verify the extent of delamination and exfoliation achieved [21, 22].

X-ray scattering methods give averaged correlation information in a far larger volume of the sample than TEM. This disadvantage of TEM was partially overcome by studying several slices from a sample and examining a large area in each slice. TEM micrographs were obtained on 0.5wt% I-28/polyDCPD nanocomposites versus a series of sonication times employed before curing. After sonicating 1h (Figure 4.5), clay nanolayers and tactoids have started to separate from the original clay particles. Some large tactoids were observed together with a small fraction of exfoliated individual platelets and some very small tactoids. Clay particles, however, were still clearly evident. The TEM of a 0.5wt% I-28 sample which had been sonicated for 3h is shown in Figure 4.6. This is a highly exfoliated nanocomposite and no clay particles or large tactoids were evident after studying many TEM micrographs.
XRD of 0.5wt% I-28 Clay/ PolyDCPD Nanocomposites; Effect of Sonication Time

Figure 4.4. XRD plots of I-28 clay, polyDCPD and 0.5wt% I-28/polyDCPD composites delaminated by stirring or sonication.
A small tactoid was observed in the upper center of Figure 4.6 where intercalation of polyDCPD into clay nanolayers was clearly evident. Most of the clay has been exfoliated into individual platelets or small tactoids of a few to 15 platelets thick. In this nanocomposite, clay nanolayers are relatively well dispersed. In this case, both XRD and TEM confirmed that a highly delaminated clay/polyDCPD nanocomposite was achieved.

Further characterization of the extent exfoliation of single 1nm thick clay platelets was undertaken by detailed high resolution TEM and neutron scattering techniques [32]. A preliminary analysis of small angle neutron scattering (SANS) data was employed to fit the scattering data to a stacked disk model [32-34]. Nanocomposites with 0.5-2 wt% clay I-28 were studied. The slopes of the scattering intensity, I(q), versus wave vector, q, curves increased with increasing clay I-28 loading levels, indicating the average number of platelets per tactoid increased as the clay concentration increased when compared at equal sonication exposures. High resolution TEM and SANS studies have been reported in detail elsewhere [32].
Figure 4.5. PolyDCPD contains 0.5wt % clay I-28 after one hour sonication.

Figure 4.6. Highly delaminated 0.5wt % I-28/PolyDCPD nanocomposite. The clay I-28/DCPD suspension was sonicated for 3h, followed by curing (magnification 50,000X).
The effect of increasing I-28 clay concentrations (from 0.5 to 5wt%) on the extent of exfoliation at constant sonication (3h) was also studied using TEM and by following changes in the d-spacing by XRD. These samples were prepared by stirring clay into DCPD for 1h and then sonicating for 3h before curing. The XRD peak disappeared in each of the nanocomposites (0.5wt% I-28 sample in Figure 4.4 and 1, 2 and 5 wt% I-28 samples in Figure 4.7). Increasing the clay concentration to 1, 2, 3 and 5wt% at constant sonication time (3h) generated more tactoids in the respective nanocomposites. A constant amount of sonication energy per unit time was delivered over the same length of time. As the wt% of I-28 was increased, this constant amount of input energy operated on more clay. Thus, the extent of nanodispersion and degree of exfoliation dropped as clay wt% increased. Furthermore, as nanodispersion progressed the viscosity increased, slowing the exfoliation process. Thus, at an equal degree of nanodispersion, the viscosity will be higher if the wt% of clay is higher.

Upon increasing the clay concentration to 2wt% at 3h of sonication (Figure 4.8.a), significant exfoliation and a high degree of delamination was still observed.

However, the maximum thickness of the small tactoids produced has increased to about 30nm based on analyzing many TEM micrographs. Upon further increasing the concentration of clay I-28 to 3wt% and 5wt%, highly delaminated nanocomposites continue to be obtained. These dispersions have a distribution containing single clay platelets and multilayer tactoids in the range of 30-100 nm (Figure 4.8.b) and 50-150 nm (Figure 4.8.c) thick for 3wt% and 5wt% clay concentrations, respectively.
XRD of I-28 clay/PolyDCPD Nanocomposites. Clay Concentration 0.5-5wt%

Figure 4.7. XRD plots of cured I-28 clay/polyDCPD composites containing different clay loadings but delaminated at a constant sonication time (3h). Pure I-28 is shown for comparison.
4.8.a.  2wt% clay I-28/polyDCPD.

4.8.b.  3wt% clay I-28/polyDCPD.
4.8.c. 5wt% clay I-28/polyDCPD.

Figure 4.8. Representative TEMs of I-28/polyDCPD composites versus clay loading prepared using the same sonication time (3h) in liquid DCPD prior to curing (at 50,000 magnification). a) 2wt% I-28 clay/DCPD, b) 3wt% clay I-28/polyDCPD and c) 5wt% clay I-28/polyDCPD. All samples clay I-28/DCPD dispersions were sonicated for 3 hrs and then cured.

Average tactoid thickness increased with higher clay loadings at constant sonication. Detailed high resolution TEM and neutron scattering studies of these tactoid distributions have been discussed elsewhere [32].

Small angle X-ray scattering (SAXS) was also employed to study clay I-28 and clay I-28/polyDCPD composites with clay loading levels of 0.5-2 wt%. The scattering from as-received clay I-28 powder exhibited a peak at q=0.277 Å⁻¹, corresponding to a clay platelet d-spacing of d=2.24nm (Figure 4.9).
The I-28/polyDCPD composite scattering data were plotted as $I(q^2)$ vs. $q$ to better observe possible peaks related to ordered structures (Figure 4.10). Clay loadings from 0.5-2 wt% in polyDCPD were examined. No peaks indicating the existence of ordered structures in the $q$ region between 0.017 to 0.4 Å$^{-1}$ were observed. This range corresponds to d-spacings from 15.7 to 369Å.

![Small Angle X-ray Scattering of Clay I-28](image)

Figure 4.9. Small angle X-ray scattering of I-28 clay powder.
Clay I-44pa was dispersed into DCPD only by stirring for 1h (without sonication). Then these dispersions were polymerized. No significant XRD peak was observed corresponding to ordered clay structures in the cured samples, even when the I-44pa loading was increased to 5wt% (Figure 4.11). Therefore, the extent of nanodispersion achieved upon simple stirring of I-44pa appears substantially greater than that of I-28, according to XRD observations. In contrast, the I-28 swelled to a $d$-spacing of 4.15nm but exhibited an intense well-formed peak after stirring into DCPD (Figure 4.4). The high intensity of this peak indicates a large amount of the clay exists in particles and larger tactoids with reasonably well ordered stacking of platelets. I-44pa was pillared with dimethyldidecyl ammonium ions (155 meq/100g of clay vs. uptake of 132 meq/100g of clay trimethyl/octadecyl ammonium ions in Clay I-28). These values were calculated from a carbon analysis assuming all carbon in the sample came from the ion exchange, so they represent maximum values. The ion exchange capacities are not supplied by Nanocor Inc. but are considered proprietary. They are in the range of 120-160 meq/100g of clay based on the sodium Bentonite clay from which they are prepared. The disappearance of the I-44pa XRD peak suggests some greater degree of nanodispersion. Nevertheless, TEM and other
Figure 4.10. Small angle X-ray scattering of clay I-28/polyDCPD composites.

Figure 4.11. XRD of Nanomer I-44pa clay and its 0.5 to 5wt% clay/polyDCPD nanocomposites.
techniques are required to definitely determine if more highly delaminated I-44pa structures were actually formed [21, 22].

Representative TEM micrographs of a polyDCPD/0.5wt% I-44pa sample are shown in Figures 4.12.a. and 4.12.b. These TEMs clearly demonstrate that highly delaminated or exfoliated nanocomposites were not achieved, even at the lowest (0.5wt%) clay loadings. Although the XRD scan does not show a clear peak corresponding to basal diffraction, the TEM micrographs show that clay exists in partially ruptured and partially intercalated particles with overall dimensions up to a few microns together with some large tactoids. However, very little exfoliation was found. The XRD instrument used could detect the $d$-spacing at 20 angles as small as 1.5 degrees. This corresponds to 5.87 nm ordered layer structures. Expansions between the clay layers beyond the small angle detecting range of XRD could result in the XRD peak loss. Alternatively, the sample’s form, as either a powder or solid smooth surface may change the orientation of ordered structure. Disordered or poorly ordered clay stacking can cause the disappearance of the basal reflection peak [21, 22]. Also, mixtures of various layer spacings within tactoids reduces and broadens any XRD peaks. In general, nanodispersed clay tactoids appear too disordered to give coherent scattering, even when platelet layers remain stacked within tactoids. Thus, careful examination of the I-44pa clay/polyDCPD composites demonstrated that the extent of exfoliation/delamination of clay nanolayers must be determined by the use of TEM and other methods, which supplement the use of XRD [21, 22].
4.12.a. Magnification: 10,000X.

4.12.b. Magnification: 40,000X.

Figure 4.12. TEM of a 0.5wt% I-44pa/PolyDCPD composite. The clay was mechanically stirred in DCPD for 1h prior to curing. Clay particles still exist with some tactoids.
Viscoelastic Properties

The viscoelastic properties of polyDCPD and its highly delaminated clay nanocomposites were determined on samples which had been cured as described in the experimental section and then postcured at 280°C for 2h. These samples have a high crosslink density. The glass transition temperature (Tg defined at the tanδ peak) of the neat polyDCPD was 259°C at 10Hz and 257°C at 1Hz (Figure 4.13). The Tg of the 0.5 wt% I-28 clay nanocomposite was higher: 274°C at 10Hz and 270°C at 1Hz. This significant increase (13-15°C) for such a small amount of clay reflects the highly delaminated nature of this sample. The tanδ plots at 10Hz for the composites with 0.5, 2, 3 wt% I-28 are shown in Figure 4.13. The Tg values for both 2 and 3 wt% clay samples were close (258 and 254°C at 10Hz and 254 and 252°C at 1Hz, respectively) to those for the neat polyDCPD.

As the clay loading increased, the intensity of the bending tanδ peaks increased (Figure 4.13), indicating an increase in chain motion freedom. The degree of clay delamination within the polyDCPD matrix decreased as clay loading increased. More large tactoids were present. Individual exfoliated clay platelets or very small tactoids have higher aspect ratio and higher surface areas per unit weight than large tactoids and particles. They appear more effective than large tactoids at restricting segmental motion. This may contribute to the higher Tg for the more highly delaminated 0.5 wt% clay sample. However, the degree of cure is dependent on both ruthenium-catalyzed ring-opening metathesis and complex thermal reactions. The ruthenium carbene catalyst is destroyed between 180-215°C. The effect of clay platelet surfaces on the operation of the catalyzed ROMP and thermal crosslinking is unknown.
Figure 4.13. Bending tanδ vs. temperature response of polyDCPD and I-28/polyDCPD nanocomposites.
The bending storage moduli, $E'$, of all the I-28 clay/polyDCPD nanocomposites were greater than those of polyDCPD from 40$^\circ$ C to above 220 $^\circ$C, at both 1Hz and 10Hz (Figure 4.14). The $E'$ values at 50$^\circ$ C for pure polyDCPD and the 0.5 and 3wt% I-28 composites were 0.813, 1.622 and 1.863GPa, respectively. At temperatures up to ~180$^\circ$ C, samples with higher clay loadings (to 3wt %) had somewhat higher bending moduli at both 1 and 10Hz (Figure 4.14). This modulus remained higher than that of polyDCPD for the 0.5wt% I-28 composite to above 285$^\circ$C while the modulus of the 5 wt% I-28 composite dropped below that of polyDCPD around 240$^\circ$C.

The flexural moduli, $E_f$, and flexural strengths, $F_s$, of polyDCPD and its I-28 clay nanocomposites were examined using the 3-point bending test. Equation 4.1 was employed and linear viscoelastic behavior was assumed for the flexural moduli [35]. Flexural strength was calculated using equation 4.2.
Figure 4.14. Viscoelastic bending response, the storage modulus of the polyDCPD and clay I-28/polyDCPD at 10 Hz.
In equations 4.1 and 4.2: \( L \): length; \( b \): width; \( d \): thickness; \( P \): maximum force and \( \Delta \): maximum deflection.

The flexural moduli of all I-28 nanocomposites were higher than the 3731 MPa value of the pure polyDCPD (Table 4.2). The flexural moduli of the nanocomposites increased from 3937.1 MPa (0.5\% I-28) to 4361.8 MPa (1\% I-28). However, further increases in clay loading to 2 and 3\% decreased moduli to 3992 MPa and 3879 MPa, respectively. The 1\% clay nanocomposite had both highest flexural modulus and flexural strength. The flexural strength increased from 22.5 MPa to 52.9 MPa by the addition of only 0.5\% I-28. This further increased to 62.1 MPa in the 1\% I-28 sample. As clay loading continued to increase, the flexural strengths dropped to 53.2 MPa for 2\% clay and then drastically to 21.6 MPa for 3\% clay.

The drops observed in flexural moduli and strengths correspond to a drop in the extent of clay delamination found with higher clay loading (especially in the 3\% clay sample). If all of the composites were as highly delaminated as the 0.5\% sample and the spatial dispersion was excellent, the flexural moduli and strengths might continue to increase as the wt\% of clay went up. However, as the clay loading increased, the extent of exfoliation/delamination dropped. The loading trends versus the extent of exfoliation/delamination operate in opposite directions, causing the
mechanical properties to peak at about 1wt% I-28. Superb enhancements in the strength and moduli might result if 3 to 5wt% I-28 samples could be exfoliated and nanodelaminated to the same extent as the 0.5wt% sample. Since the presence of clay influences the cure process (Figure 4.13), a single variable cannot be isolated to account for the observed property changes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Flexural Modulus (MPa)</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PolyDCPD</td>
<td>3731</td>
<td>22.5</td>
</tr>
<tr>
<td>0.5wt% I-28 composite</td>
<td>3937</td>
<td>52.9</td>
</tr>
<tr>
<td>1wt% I-28 composite</td>
<td>4362</td>
<td>62.13</td>
</tr>
<tr>
<td>2wt% I-28 composite</td>
<td>3992</td>
<td>53.17</td>
</tr>
<tr>
<td>3 wt% I-28 composite</td>
<td>3879</td>
<td>21.64</td>
</tr>
</tbody>
</table>
Fluorescence Study of Clay Dispersion

Safranine O-tagged I-28 clay particles in DCPD liquid dispersions were studied by confocal laser microscopy. Figure 4.15 shows Safranine O exchanged clay I-28 particles after stirring for 1h in DCPD monomer. Safranine O has an ammonium ion function, which enables some of this dye to intercalate into the clay via a cation exchange reaction. The 1wt% I-28 clay/DCPD suspensions were studied after DCPD had been imbibed into the tagged clay’s galleries during mechanical mixing. The same dispersions were also studied after sonicating the tagged clay/DCPD dispersion for 3h to give the largest degree of clay delamination.

Safranine O is widely used as a fluoroprobe in confocal laser microscopy studies, acting as a counterstain [31, 36, 37]. At laser wavelengths of 476nm, 488nm and 568nm, the Safranine O-tagged clay, which had been mechanically stirred in DCPD for 1h, is observed by its emitted green light. Excess Safranine O particles are observed as red spots (Figure 4.15). The clay in this sample still largely exists in particulate form with some large tactoids. However, after dispersion was promoted by 3h of sonication, green emissions were seen as spots with diameters decreasing into the nanometer size range using the highest instrumental magnification (2000X) (Figure 4.16). Excess Safranine O, precipitated as particles in DCPD, were observed as larger red spots.
Figure 4.15. Confocal laser microscopy of the 1wt% Safranine O-exchanged clay I-28 particles in DCPD after clay was stirred in the monomer 1h.
Figure 4.16. Highly delaminated 1wt% Safranine O-exchanged I-28 clay particles in the clay I-28/DCPD dispersion after 3h of sonication.
Fluorescence labeling is one convenient method to follow the delamination process in the monomer as a function of mixing conditions prior to curing. TEM can only be used after curing the monomer. At a numerical aperture of 1.4, the smallest image field possible on this instrument was 12 by 12 μm. Using a sampling frequency of 49 nm and a resolution/sampling frequency ratio of 2.8, a resolution limit of about 130 nm is achieved. The intensity of the green emission was sufficient to detect much smaller clay tactoids (estimate of 20 nm) but, when detected, they could not be displayed as having the smaller size due to the ~ 130 nm resolution limit. The largest clay particle size detected after sonicating for 3h was 135 nm (Figure 4.17).

![Figure 4.17. The intensity of green and red emission vs. the particle lengths of a 1wt% I-28 clay/DCPD monomer dispersion.](image-url)
Summary

Highly delaminated clay nanodispersions and nanocomposites can be synthesized in the highly nonpolar hydrophobic monomer DCPD, and polyDCPD. The degree of delamination was examined by XRD, SAXS, and TEM. Confocal laser microscopy with a fluorescent probe was used for the first time to study clay I-28/liquid DCPD dispersions. XRD cannot be used alone as a criteria to determine if highly delaminated composites have been obtained or that exfoliation has been achieved. In mechanically mixed I-44pa clay/polyDCPD samples, no XRD peaks relevant to an ordered structure were present, but TEM studies demonstrated that clay particles still existed and highly delaminated nanocomposites were not achieved.

It is clear that highly delaminated nanocomposites, where tactoids exist having 2-15 platelets, represent a different class of composites than fully exfoliated or intercalated systems. We emphasize this distinction between a fully exfoliated system, in which all platelets are non-interacting (at large distances from each other) and highly delaminated nanocomposites where small tactoid stacks containing 2 to ~15 individual platelets are well dispersed along with some exfoliated platelets.

The 2 to ~15 clay platelet layers of small tactoids could be observed by TEM in the highly nanodispersed, low wt% clay samples. However, the XRD and SAXS peak, clearly observed in the original clay particles, disappeared as nanodispersion advanced. This occurs because the nanodispersed systems are too disordered to give coherent scattering [21, 22]. It is well known that minerals may produce somewhat irrational reflections if the crystallites are exceedingly thin (less than ten unit cells per crystallite) [38]. This situation is common with clay minerals and must be true as large
tactoids get smaller. Size effects have been noted by Mering [39], MacEwan et al. [40], Reynolds [41], Ross [42], and Trunz [43]. Thin tactoids are frequently curved. This buckling can contribute to irregularities in the interlayer spacing. In addition, layer spacings may vary slightly based on whether or not those layers underwent ion exchange with the quaternary ammonium pillars. In addition, the ends of these small tactoids frequently are partially splayed apart as some platelet separation is beginning to occur due to monomer infusion. Such partial disordering and the relative abundances of these components will cause reflection spacings to be more irrational. The low (<3%) weight percent of clay present is another major contributor. This magnifies the loss of a distinct peak, caused by all the other factors, reducing coherent scattering.

The glass transition temperature of the highly delaminated polyDCPD/0.5 wt% I-28 clay sample increased about 13°C compared to the Tg of pure polyDCPD. The extent of delamination/exfoliation dropped as the wt% of clay increased at constant sonication energy input. The presence of larger tactoids and particles did not significantly contribute to raising Tg, E’, E’’ or the flexural strength. Thus, the enhancement of properties was maximized at ~1wt% clay (~0.5wt% clay for Tg). Some properties of the composites actually decreased relative to pure polyDCPD at high clay loadings where the degree of nanodelamination was poor. For example, the largest increase in flexural modulus and flexural strength was observed at 1wt % clay loading level, but at 3wt% clay, the flexural strength was slightly less than polyDCPD.

Clay dispersions were tagged with the fluorescent dye Safranine O by ion exchange into clay galleries at the particulate stage. Confocal microscopy was then
used after 3h of sonication to follow delamination/dispersion of clay within the liquid monomer during mixing or sonication, prior to curing. Thus, the extent of nanodispersion could be followed down to a size of ~130nm prior to curing. While the resolution is not as good as TEM, this method can be employed to follow the mixing process for quality control.
REFERENCES


CHAPTER V

CORRELATION BETWEEN VISCOSITY AND THE STATE OF DELAMINATION OF DICYCLOPENTADIENE/ORGANICALLY MODIFIED CLAY DISPERSIONS

Review

This chapter discusses the nanodispersion of clay in DCPD monomer and the correlation between viscosity and the extent of clay delamination. As stated in previous chapter, a highly delaminated dispersions of clay I-28 in liquid dicyclopentadiene (DCPD) were prepared. In-situ ring opening metathesis polymerization of I-28/DCPD nanodispersions generated nanocomposites. When cured under shear, tactoid alignment was captured. The state of clay delamination was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Viscosities of the nanodispersions exhibited thixotropic flow behavior. Flow behavior changed from Newtonian for DCPD to shear thinning for clay/DCPD nanodispersions with increasing clay concentration and clay delamination. The time dependent viscosity effects became more pronounced with an increase in clay delamination. Initial viscosities increased with progressive generation of clay platelets during clay delamination and nanodispersion within the liquid monomer. Viscosity can be used as
a criteria to follow clay exfoliation/delamination. Small angle neutron scattering $(\lambda=6\text{Å})$ studies in a 0.5mm gap co-rotating cylinder viscometer were unable to detect anisotropic scattering. The surface of a 2wt% I-28 clay/poly(DCPD) nanocomposite was treated with oxygen plasma, which eroded the matrix, exposing clay tactoids which protruded from the surface. These surfaces were examined by SEM and energy dispersive X-ray spectroscopy (EDS).

**Introduction**

Rheological studies of nanodispersions are becoming more significant with an increase in the applications of nanophases in engineering materials. The thixotropic behavior of the clay particles in water suspensions, including yield stress measurements and shear thinning behavior, has been well studied [1-7]. In montmorillonite/water dispersions, clay particle aggregation can occur with temperature changes. Electrolytes strongly affect the flow behavior of such suspensions [3, 8]. Clay suspensions also produce gel like structures and their deformations under applied stresses have an elastic component [2, 5]. The time scales of these measurements are important since clay suspensions are viscoelastic fluids [2, 4, 5, 9].

Montmorillonite clay consists of stacks of platelets. Each 1nm thick platelet is an alumina octahedral sheet sandwiched between two silica tetrahedral sheets. Montmorillonite clays are the most widely employed dispersed clay phases for nanodispersions and nanocomposites [1-17]. Their nanocomposites have shown superior mechanical properties, gas permeability resistance and flame resistance [10-
The viscosity behavior of organically-modified montmorillonite clay/monomer nanodispersions is particularly important during processing, before monomer polymerization or resin curing. Rheological properties are critical during the compounding/processing of layered silicates in polymer melts (melt intercalation or exfoliation). Rheology is also a major variable when infusing nanoparticle/resin formulations into fiber preforms and between the fibrils of fiber tows in VARTM and related processes [18].

In this chapter, we report the viscosity of alkyl ammonium ion-modified montmorillonite clay/dicyclopentadiene dispersions and how the degree of exfoliation/delamination of the clay affects viscosity behavior.

Low clay weight percent suspensions were used because layered silicate nanocomposites often exhibit significant property improvements with small quantities of nanodispersed alumina silicates relative to the pure polymer. Thus, viscosity responses of low weight fractions nanodispersed clays in organic monomers are of practical interest. Dicyclopentadiene (DCPD) is a low viscosity monomer that can be polymerized to a highly crosslinked polymer network [19-23] In-situ polymerization has already been used as an efficient method to incorporate nanodispersed clay into poly(dicyclopentadiene) (PDCPD) [23]. Highly delaminated, organically-modified montmorillonite/polyDCPD composites have been examined by a variety of methods (XRD, SAXS, TEM, SANS, HR-TEM) and have been reported in detail [23, 24].

The state of clay dispersion in a solvent or monomer is critically important during the delamination process, before in-situ polymerization of the monomer or mixing into an existing polymer. A correlation between the increase in viscosity and
the degree of clay delamination is reported herein. Viscosity can be used as an online measurement criteria to estimate the degree of clay delamination. Alignment of clay tactoids and exfoliated platelets in the DCPD under shear was captured by in-situ polymerization of this monomer by ring-opening metathesis polymerization (ROMP).

**Experimental**

**General Procedure**

Nanomer® I-28 was provided by Nancor, Inc., and used as received. I-28 has been ion exchanged with trimethyldodecadecyl alkylammonium ion and has a d-spacing of 2.25nm [11]. Dicyclopentadiene (DCPD) was provided by Cymetech, LLC, under the trade name of Ultrene™99 (99.2% pure). A first generation Grubbs’ metathesis catalyst, dichloro(3-methyl-2-butenylidene)-*bis*-tricyclopentylphosphine ruthenium, was used to cure the I-28 clay/DCPD dispersions. Ethylene glycol monoethyl ether (2-Ethoxyethanol, 99%) was provided from Aldrich.

Clay I-28 was dispersed in liquid DCPD by stirring for 1hr followed by sonication for 3h under nitrogen at 20 kHz with a wave amplitude of 30 using a 500W sonication Model GE501 ultrasonic processor (Ace Glass, Incorporated). The concentration range of clay employed in this study was 0.005-5wt%. Cyclopentadiene (4wt%) was used as a co-monomer to reduce the melting point of DCPD from 39°C to below room temperature. The d-spacing of clay layers within liquid DCPD was followed by X-ray diffraction after curing each sample and these values were reported elsewhere [23, 24]. The viscosities of low clay concentration dispersions were
measured in Cannon-Ubbelhode viscometers. A Couette flow corotating cylinder viscometer was used to examine the viscosity of the suspensions as a function of clay nanodispersion in DCPD and clay loading levels.

Sufficient catalyst was added to the 2 and 5wt% I-28 clay/DCPD dispersions, while shearing, in order to effect rapid in-situ ring-opening metathesis polymerization and capture the alignment of clay layers under the shear within the poly(DCPD) matrix. The temperature was increased to facilitate fast curing and capture the clay alignment.

The specific surface area of clay I-28 was determined experimentally using the ethylene glycol monoethyl ether (EGME) method described by Carter et al. (1986). In this method, it is assumed that a monolayer of EGME is adsorbed to the clay surface [25]. EGME (3ml) is added to the clay (1g) and stirred. The suspension placed in a vacuum oven for 24h until EGME is removed. Then, the specific surface area of clay is calculated from SSA= W_a/0.000286W_s, where SSA is the specific surface area, W_a is the adsorbed EGME and W_s is the original weight of clay.

**Viscometry Measurements**

A Brookfield concentric cylinder viscometer, model DV-I, with LV spindles was used. Viscometry measurements were performed at 29°C in a Couette flow concentric cylinder geometry. The outer cylinder was stationary and the inner cylinder (spindle) was rotating. The torque signal was transformed to shear stress and the data were collected using Camile 2200® control software to monitor the process. Then, the
Signal was processed and transformed to a viscosity value using the CamileTG® software.

Shear rate and shear stress in a co-rotating cylinder are calculated from the following equations:

\[
S = \frac{2\omega R_c^2 R_b^2}{x^2 (R_c^2 - R_b^2)} \tag{5.1}
\]

\[
F' = \frac{T}{2\pi R_b^2 L} \tag{5.2}
\]

where \(S\) is the shear rate, \(\omega\) is the angular velocity, \(R_b\) and \(R_c\) are the inner and outer cylinder radii, \(x\) is the radius at which shear rate is being calculated, \(F'\) is the shear stress, \(T\) is the torque, and \(L\) is the cylinder length. Viscosity is the ratio of the shear stress to shear rate.

**X-ray Diffraction Measurements**

XRD analysis was used to follow the clay’s d-spacing in the cured nanocomposites versus the extent of mixing and sonication used during dispersion. XRD data for the starting clay powder and for the clay/P(DCPD) nanocomposites were collected on a Phillips diffractometer, Model X’Pert, using Cu K\(\alpha\) radiation (\(\lambda=0.154056\)nm). Scans were taken over the \(2\theta\) range of 1 to 10°, with a step size of 0.03° at 1s per step.
Transmission Electron Microscopy

A JEM-100CX II transmission electron microscope (60kV) was used to examine clay morphology and orientation. Nanocomposite samples were ultramicrotomed to thicknesses of 70-85nm at room temperature using a Reichert-Jung Ultracut E ultramicrotome equipped with a diamond knife. The samples were placed on a Formvar-coated 200 mesh copper grid. The clay versus polymer matrix contrast was sufficient to permit electron micrograph imaging without staining.

Scanning Electron Microscopy

A Leo Stereoscan 360 scanning electron microscope, 15 kV, with a resolution of 25Å with a tungsten filament was used to examine the surface of the clay/polyDCPD composites. This instrument was equipped with X-EDS spectrometer and Princeton Gamma-Tech eXcalibur software for electron beam-induced energy dispersive X-ray analysis.

The surfaces of the composites were coated with Ag/Pd by sputter coating using a Polaron E5100 sputter coater to produce a nominal thickness of 40-50nm Au/Pd on the surface of the composites. Target to specimen distance was 50mm. Sputter coating was performed in an ionized Argon gas at low pressure using a 2.5kV voltage.

Oxygen Plasma Treatment

Oxygen plasma treatments were performed using Technics PEII-A plasma generator using RF (radio frequency) under 30-35 mtorr vacuum and 100W power. Samples were treated for 30s and 60s.
Small Angle Neutron Scattering (SANS)

SANS experiments were performed using an NG-3 small angle neutron scattering instrument at the National Institute of Standards and Technology (NIST). A highly delaminated 5wt% I-28 clay/DCPD dispersion was sheared in a quartz 0.5mm gap co-rotating cylinder viscometer, while being subjected to a 6Å wavelength neutron beam to obtain the anisotropic scattering from clay platelets, which have become oriented in the shear field.

Results and Discussion

Stirring clay I-28 into DCPD caused expansion of clay layers to a $d$-spacing of 4.15nm [23]. This expansion is the result of nonpolar DCPD intercalating into the clay galleries which have been pillared by the long dodecyl hydrocarbon chain of the exchanged ammonium ions. The separation of clay particles in the suspension to a highly delaminated mixture of clay platelets and tactoids was achieved after 3h of sonication (Figure 5.1.a) [23, 24]. The progressive loss of the 4.15nm $d$-spacing XRD peak as sonication proceeded (Figure 5.1.a) illustrates this advance in nanodispersion. The polyDCPD 1-5 wt% I-28 clay nanocomposites were then prepared by polymerizing these DCPD/I-28 liquid nanodispersions. The XRD peak in these nanocomposites had disappeared (Figure 5.1.b). Extensive X-ray and neutron scattering studies verified the existence of a highly delaminated clay nanocomposite after 3h sonication treatment of clay I-28 in DCPD monomer prior to curing [24]. Figure 5.2.a shows a clay particle, some tactoids and a few exfoliated platelets after a
5.1.a. XRD plots of 0.5wt% I-28 clay composite.

5.1.b. XRD plots of 1-5wt% I-28 clay/composites

Figure 5.1. PolyDCPD composites delaminated by stirring and sonication.
5.2.a. Partial delamination of clay (1h sonication)

5.2.b. Highly delaminated clay I-28/polyDCPD composite (3h sonication).

Figure 5.2. Delamination of clay I-28 in polyDCPD (0.5wt%) versus sonication time.
1h sonication of 0.5wt% clay I-28 in polyDCPD followed by curing. Clay platelets and tactoids are being splayed apart from the original particle. Another aliquot of this same dispersion was subjected to longer sonication (3h) and then polymerized. TEM micrographs (Figure 5.2.b) confirmed the existence of a highly delaminated nanocomposite containing dispersed platelets and tactoids.

The viscosities of the I-28 clay/DCPD dispersions were studied both as a function of clay loading level and the degree of delamination. A Cannon-Ubbelhode viscometer was used to examine low clay concentrations (0.005-0.5 wt%). Only suspensions at the highest degree of delamination (after 3h of sonication) were studied. The relative viscosities $\eta_{rel}$ were determined from the viscosity of the dispersion, $\eta'$, and the viscosity of liquid DCPD, $\eta$, ($\eta_{rel}=\eta'/\eta$). The relative viscosities were 1.15, 1.16, and 1.28 for the 0.05, 0.08, and 0.14wt% I-28/DCPD dispersions, respectively. These viscosities did not exhibit time dependent behavior. Changes of viscosity with measurement time were observed at a clay concentration of 0.5wt%. The clay particles remained as well-dispersed tactoids and platelets in the very low concentration suspensions (0.005-0.5wt.%). The increased clay surface area due to delamination is not yet significant because the concentration is very low. This results in negligible time dependent behavior of the dispersion.

The viscosity measurements of clay suspension concentrations above 0.5wt% were followed using the corotating cylinder viscometer. Increased clay concentration resulted in a time dependent viscosity behavior. The 5wt% I-28/DCPD suspension exhibited viscosities that were dependent on both the time of shearing and clay loadings (Figure 5.3). The viscosity decreased with shearing time, indicating a
thixotropic behavior of this suspension. The initial viscosities (at the start of shearing) increased as more clay nanolayers, small tactoids and platelets were formed (extended sonication time). The differences between initial and steady state viscosities become larger as clay delamination proceeded at constant clay concentration. Increased thixotropic flow behavior was observed with increased delamination of clay nanolayers when holding the clay loading level constant at 5wt%, (Figure 5.3). More resistance to flow occurs with more platelets present, resulting in a stronger thixotropic behavior. At constant clay concentration, viscosity increases are caused by the generation of more surface area as delamination occurs. The difference between the initial and steady state viscosities becomes larger as a larger number of randomly oriented clay nanophases are generated, which resist flow. Viscosity decreases rapidly from its initial value because the nanolayers tend to align themselves in the direction of flow.

After 3h sonication, the viscosity of the dispersion did not further increase with continued sonication. This indicates that no further significant nanodispersion/exfoliation was occurring. This was observed even for the 5wt% clay I-28/DCPD dispersion after 3h of sonication.

The shear stress versus shear rate plot of the highly delaminated 5% I-28 in DCPD exhibited hysteresis (Figure 5.4). In general, hysteresis indicates the presence of destructive and constructive interchanges within the dispersion, which depend on the time scale of measurement [26]. Changes in nanoparticle orientation and randomness and a breakdown of loose aggregation occurred under external shear forces. The clay platelets and tactoids underwent translational and rotational motion to
orient themselves in the direction of flow. When the shearing was stopped, these nanophases progressively regained their aggregated and disordered orientation, returning to a thermodynamically more stable state. However, this new equilibrium is different from the original state. After shearing stopped for 10 min and was then started again, the viscosity did not fully recover its original state. The shear stress versus shear rate curve showed a change of flow behavior from Newtonian for DCPD to non-Newtonian for clay/DCPD dispersion. A yield stress occurred at the start of shearing, followed by shear thinning (Figure 5.4).

The shear stress versus shear rate of the 0.5wt% I-28/DCPD dispersion was studied as a function of sonication time during delamination (Figure 5.5). As delamination increased (with increasing sonication time), the behavior changed from Newtonian to Non-Newtonian. A yield stress was present as shearing started. Then, the high viscosity (initial resistance of the platelets to flow) decreased rapidly with shear rate. The same type of flow behavior was observed for 0.5 and 5wt% clay I-28/DCPD nanodispersions. A yield stress followed by a shear thinning behavior was observed for all dispersions.

Viscosity measurements provide a means to follow the progress of nanodispersion in the lab or as a process control method. Accurate viscosity measurements versus the state of clay delamination can serve as a criteria for evaluating the degree of clay dispersion/delamination. Furthermore, viscosity measurements are a tool to determine whether or not highly delaminated dispersions are achieved.
The average as-received I-28 clay particle size was 6-8 microns (range from ~1-16 microns). Assuming these particles are spheres with an average diameter of 7 microns, half of the spherical surface area of one clay particle is $1.54 \times 10^8$ nm$^2$. Subtracting the lateral surfaces of the empty interplatelet space disk shapes, with a thickness of 1.6 nm, the lateral surface area of the platelet disks in a half spherical particle will be $1.06578 \times 10^8$ nm$^2$. Each clay nanolayer has a 2.6 nm $d$-spacing and consists

![Graph](image)

Figure 5.3. Viscosity of 5 wt% clay I-28/DCPD dispersions. The viscosity were measure both as a function of time and the degree of delamination at constant shear rate ($21.09 \text{s}^{-1}$).
Figure 5.4. Hysteresis in the highly delaminated 5wt% clay I-28/DCPD dispersion (after 3h sonication).
of a 1nm thick alumina silicate layer and 1.6 nm thick surfactant (interplatelet) layer (Figure 5.6). Therefore, the number of clay nanolayers within a single 7-micron diameter spherical particle is ~2,700. Each platelet is a thin disk 1nm thick with a radius that depends on its location in the sphere. The total surface area of all platelets (top and bottom surfaces of these disks + lateral dimensions) for half of the sphere is

Figure 5.5. Shear stress vs. shear rate plots for the 0.5wt% clay I-28/DCPD dispersion as a function of sonication time.
6.915x10^{10} \text{ nm}^2, \sim 650 \text{ times larger surface area for one half of the original 7 micron diameter clay particle. This factor is for spherical clay particles and it will increase for any fractal shape. A single gram of clay (7 micron diameter) contains 2.65 \times 10^9 particles using a particle density of 2.1\text{g/cm}^3. This calculation results in a 355 \text{ m}^2/\text{g} of clay when full exfoliation occurs compared to 0.565 \text{ m}^2/\text{g} for lateral surfaces of the disks in a spherical particle. If monodisperse lateral dimensions are assumed, then the specific surface area will be 600\text{m}^2/\text{g} (Figure 5.7). The specific surface area determined experimentally using EGME adsorption method was 503 \text{ m}^2/\text{g} for clay I-28. This value is larger than calculated value for disks inside a spherical particle, due to several reasons. First, clay platelets have irregular shapes and fractal surfaces. Second, the distributions of the disk’s lateral dimensions are not as polydisperse as that of a sphere.

The clay surface area increased enormously when it was highly delaminated, causing a large viscosity increase in the highly delaminated clay dispersions compared to particulate dispersions. Figures 5.8 and 5.9 show platelet and tactoid alignments in the direction of shear which were captured by starting the curing reaction while shearing. Figure 5.8 shows alignment of 5wt% clay I-28 in DCPD dispersion sonicated for 1h and cured while shearing. A mix of large tactoids, small tactoids, and
5.6.a. Schematic of a particle consisting of many disk shaped layers.

5.6.b. Area Calculation.

Figure 5.6. Spherical clay particle consists of many disk shape particles.
platelets are aligned in the direction of shear field. Figure 5.9 demonstrates the alignment of 2wt% clay I-28 in DCPD after 3h sonication, cured while shearing. A high degree of delamination/nanodispersion was present in the sample. Platelets and tactoids were oriented in the shear field. Figure 5.10 shows the lateral surface of a clay platelet (tactoid) with the lateral dimensions of about 200 by 350 nm².
5.8.a. 1h sonication, magnification 8,000X.

5.8.b. 3h sonication, magnification 40,000X.

Figure 5.8. The 5wt% clay I-28/DCPD dispersion after polymerization were conducted in the shear field.
Figure 5.9. Orientation of 2wt% I-28 clay/DPCD dispersion under shear.

Figure 5.10. Lateral dimension of a stack of clay nanolayers.
Attempts were made to obtain anisotropic neutron scattering (SANS) from clay tactoids and platelets while clay dispersions were being sheared in DCPD. A highly delaminated 5 wt% I-28 clay/DCPD dispersion was sheared in a quartz 0.5mm gap co-rotating cylinder viscometer in a 6Å wavelength neutron beam. The dispersion was sheared in a range of rotational frequencies of 50Hz-1500Hz while in the neutron beam. This corresponds to a shear rate range from 3770 to $5.65 \times 10^5$ s$^{-1}$. This range extends far above the shear rates used in Figures 5.4 and 5.5. The 2-dimensional scattering data did not show any discernable anisotropic scattering from high aspect ratio particles, after data reduction and averaging. However, it is clear from viscosity measurements (Figures 5.3 through 5.5) and TEMs of subsequently cured composites that net alignment does occur [27]. It is unclear why the clay orientation in the neutron scattering experiment was not detected. When a montmorillonite dispersion was sheared in the neutron beam in similar experiments by other researchers, the same results have been found [28].

The surface of the 2wt% clay I-28 composite was subjected to an oxygen plasma erosion treatment. A low pressure, cold, radio frequency oxygen plasma was employed. Such oxygen plasmas contain O$^+$, O, O$_2^+$, O, O$_3$, ionized ozone, metastably excited O$_2$ and free electrons [29-32]. The electrons, ions and free radicals in the plasma act on the exposed resin surfaces, generating free radicals at (-CH$_2$-), (-CH-), and (-CH$_3$) groups of the hydrocarbon matrix followed by oxidative erosion. The rate of hydrocarbon resin oxidation in the plasma is much faster than the rate of reaction with the alumina silicate platelet sheets. This progressively exposes clay tactoids and platelets at the surface. After 30 s of
oxygen plasma exposure, alumina silicate started to protrude from the surface (Figure 5.11a). After 60 s exposures to the plasma, nanowalls [32] appear that are rising out of surface (Figure 5.11b). In Figures 5.11a and 5.11b, the spacings between the platelets and tactoids were determined to be in the range of 100-937 nm. Figure 5.11b shows a random tactoid orientation of platelets and tactoids. Lateral dimensions of platelets and tactoids were determined to be in the range of ~200 to 300 nm. The resolution was not high enough to obtain numerical values for the nanowall thicknesses.

Energy dispersive X-ray spectroscopy (EDS) was performed to specify the elements present on the surface of the composite (Figure 5.12). EDS verified the presence of aluminum, silicon, oxygen, carbon and ruthenium and chlorine. Chlorine was present in the ruthenium polymerization catalyst. Spectra were taken at different surface locations. Since imaging and EDS were taken at a 45° tilt angle to sample surface, the detector will receive emission of X-rays both from the surface and below the surface. Each spectra revealed some aluminum, silicon and oxygen, indicating the presence of clay platelets both on the surface and also under the surface. Monte Carlo calculations predict that X-rays are scattered from the surface and beneath the surface up to a depth of about 4-5 microns for a 40kV voltage [33]. Thus, EDS can not show specific clay platelet locations.
5.11.a. Surface exposed to cold oxygen plasma for 30s.

5.11.b. Surface exposed to cold oxygen plasma for 60s.

Figure 5.11. Oxygen plasma treated surface of the 2wt% clay I-28/polyDCPD composite.
Figure 5.12. EDS spectra of the oxygen plasma-treated surface of the 2wt% I-28clay/polyDCPD composite.
**Summary**

XRD and TEM showed that highly delaminated I-28clay/polyDCPD composites were formed by sonating 1-16 micron clay particles in liquid DCPD followed by *in-situ* ring-opening metathesis polymerization. Clay loadings ranged from 1-5wt%. Viscosity was related to the degree of delamination. Very low clay concentrations (0.005-0.5wt%) did not show any time dependent viscosity behavior. At a 0.5wt% clay concentration, thixotropic behavior was observed for the nondispersed clay in DCPD. A Newtonian to non-Newtonian transition occurred at constant clay loading as the degree of nanodispersion increased during sonication. Thixotropic behavior was observed at concentrations above 0.5wt% to 5wt% I-28 in DCPD, which became more pronounced with increasing clay delamination and higher clay loadings. Viscosity versus shear time, shear stress vs. shear rate and hysteresis are consistent with the alignment of tactoids during shear from an original randomly oriented state. This produces a yield stress and a highly thixotropic behavior. Rapid shear thinning suggests that orientation of clay layers occurs in the direction of flow. The viscosity increase is related to the increase in clay tactoid surface area occurring during delamination. TEM studies showed that alignment of the clay layers in the direction of flow could be captured by *in-situ* polymerization. The lateral dimensions of some clay platelets (tactoids) lying parallel to the surface were observed. Viscosity measurements could be used as a simple criteria for process control and verification of the degree of delamination. Oxygen plasma treatment of the 2wt% clay I-28/polyDCPD composite surface led to 3D observations of protruding clay tactoids.
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CHAPTER VI

INVESTIGATION OF CLAY I-28/DCPD DISPERSION STRUCTURES IN THE SHEAR CELL OF THE NEUTRON BEAM

Clay DCPD Dispersions

This chapter discusses the results of neutron scattering experiments on clay/DCPD dispersions. Previous studies have shown that highly delaminated clay/DCPD dispersions with clay concentrations larger than 0.5 wt% exhibit thixotropic behavior [1]. These dispersions have been subjected to mixing and sonication for 3 hours. Ring-opening metathesis polymerizations were performed on the clay/DCPD dispersions under shear using dichloro(3-methyl-2-butenylidene)-bis-tricyclopentylphosphineruthenium (a Ru-based Grubbs’ catalyst). TEM studies of the resulting solid composites showed alignment of clay platelets and tactoids when the liquid DCPD/clay dispersion had been subjected to shear [1]. A highly delaminated 5 wt% I-28 clay dispersion was sheared in a co-rotating, dual-cylinder, fused silica viscometer in the neutron beam. The neutron scattering from these dispersions showed negligible non-symmetrical scattering. This result was unexpected for aligned non-isotropic particles in the suspension. However, other researchers performed similar
experiments on dispersions of montmorillonite clay under shear, and obtained similar results. The reasons are not yet clear why neutron scattering was not able to detect the orientation of montmorillonite clay under shear. This question is under investigation.

**Introduction**

Anisotropic clay platelets have been shown to undergo structural transitions under shear [1-5]. Montmorillonite clay consists of stacks of 1nm platelet sheets with large lateral surface areas. When particles are separated into individual platelets or smaller tactoids, this results in high aspect ratios (200-1000). The dispersion of clay in solvents or in polymers under shear has been investigated [1-5]. Characteristic length scales of the structure and fractal shape of thixotropic colloidal suspensions of synthetic clay have been studied by Pignon et al. using light scattering, X-ray scattering and neutron scattering techniques [2]. Laponite clay suspensions in water containing different percentages of sodium chloride were investigated. Two characteristic length scales for the reinforcing phase particles were detected in these yield stress suspensions. The first, measuring tens of nanometers, was linked to a fractal dimension of three. The second, on the order of 1 micron, was linked to fractal behavior of dimension D, that increases with the particle volume fraction. Consequently, the structure of the dispersion at rest is probably composed of subunits measuring a few tens of nanometers that combine to form dense aggregates measuring about 1 micron. They examined these dispersions at larger length scales by obtaining data in the very low q-range corresponding to 1-5 microns. At this length scale, these micron-sized aggregates are rearranged to form continuous three-dimensional
isotropic structures that have fractal dimensions. The particle volume fraction, the ionic strength, and the gelation time are correlated to a hardening of the mechanical properties at rest.

Rennie et al. examined the structural changes of colloidal clay dispersions and aqueous Ni(OH)$_2$ dispersions under shear using neutron diffraction and scattering [3]. The microscopic dynamics of clay particles were studied using an oscillatory shear rheometer. Isolated platelets can display unusual features illustrated by scattering from a kaolinite clay dispersion in pipe flow. Scattering experiments showed that kaolinite platelets were aligned parallel to the pipe wall, near the center of pipe. Wall effects were larger than the flow alignment in this geometry at a flow rate of 1.5 ml/s. The maximum clay alignment in the dispersion was found similar to that in nematic liquid crystalline fluids. Therefore, different structures may co-exist or even be formed under shear. A “phase transition” under shear was reported for the dispersion of platelets [3].

Schmidt et al. studied the influence of shear on viscoelastic polyethylene oxide (PEO)-laponite clay suspensions using neutron scattering under shear (30-150 s$^{-1}$) [5, 6]. SANS was used to examine the shear-induced orientation of both PEO and clay platelets. Enhanced nonisotropic scattering was reported at higher shear rates. This was attributed to increased orientation of the clay platelets in the shear field. The contrast matching method was used to identify the orientation of PEO and clay platelets. Clay platelets oriented first with increasing shear, followed by stretching and alignment of the polymer. Cessation of shear led to fast recovery of random platelet orientations and random coil PEO geometries, indicating the highly elastic nature of the dispersion.
Montmorillonite clay/DCPD dispersions were subjected to shear in the present work, to examine the changes in the clay structure due to the shear field. Scattering data were obtained while the dispersion was sheared in the neutron beam. The scattering from a 5 wt% clay/DCPD dispersion was examined at several shear rates corresponding to frequencies from 10 Hz to 1500 Hz. Negligible platelet alignment in the shear field was detected. This result was unexpected.

**Materials**

A dispersion of 5 wt% I-28 clay in DCPD was prepared. Furan (4 wt%) was added to lower the melting point of DCPD, facilitating mixing. This dispersion was used in the viscosity experiments.

**Characterization Method**

SANS experiments were performed using the NG-3 30m SANS instrument at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) [7, 8]. A monochromatic beam of neutrons with a wavelength of \( \lambda = 6 \) Å and a wavelength resolution of \( \Delta \lambda/\lambda = 0.11 \) was used. A Couette flow co-rotating cylinder viscometer with outer diameter of 60mm was used. The inner cylinder was stationary while the outer cylinder rotated. The cylinders were made of fused silica (Suprasil), which has excellent optical properties and is transparent to cold neutrons. The shear cell was equipped with a vapor barrier to prevent solvent evaporation. Evaporation would result in a concentration change in the dispersion. Design details and specifications of the shear cell are given elsewhere [9]. The 0.5
(0.489) mm gap shear cell was used. Measurements were performed at a 12 m
detector-to-sample distance with a neutron wavelength of 6 Å. The dispersion was
sheared at rotational speeds (frequencies) of 10 Hz, 50 Hz, 100 Hz, 500 Hz, 1000 Hz,
and 1500 Hz. The frequency and shear rate are related by equation (6.1):

\[ \gamma \sim \frac{2\pi R f}{g} \tag{6.1} \]

where \( R \) is the radius of the fluid annulus, \( g \) is the gap width, and \( f \) is the rotational
frequency of the cylinder. The shear rate, \( \gamma \), was evaluated using this expression.

Data were collected over four 15 minute time intervals. The Couette viscometer was
stopped for an interval of five minutes between each shear rate examined.

The raw scattering intensity, \( I(q) \), versus \( q \) wave vector \( q = \frac{4\pi}{\lambda} \sin(\theta/2) \) and \( \theta \)
(scattering angle for each sample) data were reduced and averaged (annular
averaging). The data were then converted to the absolute scale.

**Results and Discussion**

Figures 6.1-6.6 show the scattering intensity, \( I(q) \), versus \( q \) on the absolute
scale. Figures 6.7-6.12 depict reduced 2-dimensional data for the samples. The
averaged scattering intensity versus \( q \) data exhibit an oscillation of intensity for all of
the shear rates in the measured range of the wave vector, \( q \). This indicates the presence
of anisotropic particles and some degree of alignment. At all shear rates, scattering
intensity vs. \( q \) curves exhibit the lowest oscillation in the last 15 minutes of shearing.
This could be explained by the appearance of large domains within the experimental
time frame. Lengthy shearing in the narrow gap of the Couette viscometer at a high shear rate could cause large high centrifugal forces, which are exerted on the clay platelets. However, once the shearing stopped, the clay platelets return to a disordered state. This relaxation occurs because the interaction between layers of the existing domains is not strong. The two dimensional neutron scattering (Figures 6.7-6.12) is slightly nonsymmetric when the frequency of rotation was 10 and 50 Hz, but is almost completely symmetrical for higher rotation frequencies.

The alignment detected by these experiments was much less than expected from alignment of anisotropic particles with aspect ratios of 300-1000 (montmorillonite nanolayers). This could be due to the medium’s low viscosity, which might allow clay layers to reaggregate into stacks during the experiment as they are exposed to the shear field in the 0.5 mm thin gap and are subjected to high centrifugal forces.
Figure 6.1.  \( I(q) \) versus \( q \) SANS plots for 5wt\% I-28/DCPD dispersion when sheared at a rotational frequency of 10 Hz in 15 min intervals (4 x 15 min).
Figure 6.2. I(q) versus q SANS plots for 5wt% I-28/DCPD dispersion when sheared at a rotational frequency of 50 Hz in 15 min intervals (4 x 15 min).
Figure 6.3. I(q) versus q SANS plots for 5wt% I-28/DCPD dispersion when sheared at a rotational frequency of 100 Hz in 15 min intervals (4 x 15 min).
Figure 6.4. I(q) versus q SANS plots for 5wt% I-28/DCPD dispersion when sheared at a rotational frequency of 500 Hz in 15 min intervals (4 x 15 min).
Figure 6.5. $I(q)$ versus $q$ SANS plots for 5wt% I-28/DCPD dispersion when sheared at a rotational frequency of 1000 Hz in 15 min intervals (4 x 15 min).
Figure 6.6. I(q) versus q SANS plots for 5wt% I-28/DCPD dispersion when sheared at a rotational frequency of 1500 Hz in 15 min intervals (4 x 15 min).
Figure 6.7. Two dimensional neutron scattering data obtained during the first 15 min for a 5wt% I-28/DCPD dispersion sheared at a rotational frequency of 10Hz (reduced data).
Figure 6.8. Two dimensional neutron scattering data obtained during the first 15 min for a 5wt% I-28/DCPD dispersion sheared at a rotational frequency of 50Hz (reduced data).
Figure 6.9.  Two dimensional neutron scattering data obtained during the first 15 min for a 5wt% I-28/DCPD dispersion sheared at a rotational frequency of 100Hz (reduced data).
Figure 6.10. Two dimensional neutron scattering data obtained during the first 15 min for a 5wt% I-28/DCPD dispersion sheared at a rotational frequency of 500Hz (reduced data).
Figure 6.11. Two dimensional neutron scattering data obtained during the first 15 min for a 5wt% I-28/DCPD dispersion sheared at a rotational frequency of 1000Hz (reduced data).
Figure 6.12. Two dimensional neutron scattering data obtained during the first 15 min for a 5wt% I-28/DCPD dispersion sheared at a rotational frequency of 1500Hz (reduced data).
Montmorillonite clay platelets are 1nm thick and they have large lateral surface area. This makes them anisotropic. Previous studies in our laboratory demonstrated shear alignment of clay platelets in liquid DCPD occurs [10]. These alignments have been captured by adding a ring-opening metathesis polymerization catalyst to the dispersion of I-28 clay/DCPD to cure the system while under shear. These cured systems capture clay alignment, which has been observed by TEM [10].

It is possible to detect the alignment of anisotropic particles under shear using neutron scattering techniques [6]. In order to examine the scattering from montmorillonite clay platelets under shear, a nanodispersion of 5wt% I-28 in DCPD was prepared using mixing followed by 3 hours sonication. This dispersion was placed in a co-rotating Couette flow viscometer and sheared at a rate of 10 to 1500Hz while it was in the neutron beam. The scattering from this dispersion showed negligible unsymmetrical scattering at low rotational frequencies and symmetrical scattering at higher rotational frequencies.

It was not possible to observe alignment of montmorillonite clay platelets and tactoids under shear using the neutron scattering technique. The reason for these unexpected results is not yet clear.
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CHAPTER VII

CLAY DELAMINATION IN CLAY/POLY(DICYCLOPENTADIENE) NANOCOMPOSITES QUANTIFIED BY SMALL ANGLE NEUTRON SCATTERING AND HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

Review

In this chapter, the focus is mainly on the characterization of the organically modified clay/polyDCPD composite. Highly-delaminated clay/poly(dicyclopentadiene) nanocomposites were prepared by in-situ ring-opening metathesis polymerization of pre-sonicated mixtures of the liquid dicyclopentadiene (DCPD) and organically-modified montmorillonite clay. Three nanocomposite series (using montmorillonites: I-28, I-44pa) of increasing clay loadings (0.5, 1.0, and 2.0 wt%) and modified montmorillonite PGW (0.5wt%) were synthesized. The dispersed microstructure of the clays in the nanocomposites was characterized by small angle neutron scattering (SANS), ultra small angle neutron scattering (USANS), small angle X-ray scattering (SAXS), and high-resolution transmission electron microscopy (HR-TEM). All clays were highly delaminated and well dispersed within their host
matrices. The mean number of individual clay platelets per tactoid was predicted by fitting SANS data to the stacked-disk model and measured directly from HR-TEM images of a large number of tactoids in each sample. SANS results were in good agreement with HR-TEM for composites with low clay concentrations (0.5 wt%). However, deviations were observed at higher clay loadings (2.0wt%). These deviations are likely a consequence of several factors not taken into account by the stacked-disk model: (a) long-range interactions, which become more important at high loadings; (b) departure of tactoid geometries from parallel stacks of rigid disks; and (c) the polydispersity of tactoid thicknesses. SAXS peaks were not present for most of the synthesized nanocomposites suggesting a high degree of clay delamination was achieved. However, a broad peak was observed for the 2.0wt% I-44pa clay nanocomposite, indicating the presence of some larger tactoids than in the other nanocomposites having a range of d-spacings. The HR-TEM measured distributions of clay platelet d-spacings in tactoids dispersed within the nanocomposites, which were in the range from 8-20Å (12-15 Å average), indicating that the quaternary ammonium ion pillaring agents were no longer present. These quaternary salts either decomposed during the high-temperature (260°C) stage of curing or were not fully exchanged with the interlayer cations present between all platelet interlayers during the original clay modification. Clay/polyDCPD composites were also prepared using PGW clay modified by polyethyleneglycol. This clay dispersed more rapidly, needing less sonication than the other clays. The resistance to delamination of all nanocomposites studied increased with greater clay loading under equivalent synthesis conditions.
**Introduction**

Montmorillonite clay has long been used as a filler and reinforcing agent [1] in polymer systems, because of its availability and low cost. The improvements in physical/mechanical properties of polymers upon forming composites with clays is highly dependent on the degree of clay dispersion [1]. In contrast to micron-sized particles used in conventional composites [2], clays can be delaminated into tens-of-nanometer thick grain (tactoid) sizes and a portion even into individual 1nm thick platelets. Toyota researchers demonstrated that small amounts of well exfoliated organically-modified clay improved mechanical, barrier, and thermal properties as well as flame resistance of Nylon 6 [3-6]. Dispersion of clay into other polymer matrices, including epoxy resins [7-9], silicon elastomers [2], and polyethers [10] has been investigated. In particular, dicyclopentadiene (DCPD), a low viscosity monomer that can be polymerized to a highly crosslinked polymer network, has been used to form clay nanocomposites [11]. Organically-modified montmorillonite in polyDCPD composites, prepared by sonicating the clay in DCPD, were shown to be highly delaminated by X-ray diffraction, confocal laser microscopy, and transmission electron microscopy (TEM) [11].

Unmodified and organically-modified clays in clay/solvent and clay/water-soluble polymer/aqueous systems have been well examined by other researchers [12-22]. However, few attempts have been made to investigate polymer/clay nanocomposites by scattering techniques, and no scattering studies coupled with high-resolution (HR)-TEM have been attempted. Small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS) are powerful techniques for studying the
micro- and nano-domain structures of polymer systems, fillers and particles [17, 18]. Both techniques exhibit high sensitivity to features on length scales of 10-100 nm. Consequently, SANS and SAXS can be used to study phase dispersion in matrices, polymerization, emulsification, colloid stabilization, shear-induced structures, and phase domain behavior in polymers [18]. Furthermore, differences in the manner by which X-rays and neutrons scatter in solids enables complementary contrast variation especially in multi-component materials with ordered structures [18]. Compared to neutron and X-ray scattering techniques, HR-TEM provides detailed microstructural information of localized areas on the 0.2 nm spatial scale. Heterogeneous microstructures (as present in nanocomposites) can be characterized by HR-TEM by examining a large number of representative regions, allowing the comparison of results from HR-TEM and scattering techniques.

In this chapter, polyDCPD/clay nanocomposites [11], using three different montmorillonites, were synthesized by stirring clay into the low viscosity monomer, DCPD, followed by sonication to delaminate the clays and then in-situ DCPD ring-opening metathesis polymerization. The nature of the clay delamination in the clay/polyDCPD nanocomposites was characterized using a combination of SANS [19], ultra small angle neutron scattering (USANS), SAXS, and HR-TEM. We show all clays were highly delaminated in the nanocomposites. Further, SANS data on these composites were fitted to the stacked-disk model [17-22] developed by Glinka [19a], Hanley et al. [20, 21] and Ho et al. [17, 22] Model predictions based on SANS data for the mean number of individual clay platelets per tactoid were compared to a large
number of direct HR-TEM measurements, providing the first experimental test of the stacked-disk model as applied to clay nanocomposites.

**Experimental**

**Clay Material**

Modified montmorillonite clays (Nanomer®: I-28 and I-44pa and PGW), were provided by Nanocor, Inc. The approximate chemical formula \((M^+_{0.374}(Al_{1.626}(MgFe)_{0.374})Si_4O_{10}(OH)_2\cdot nH_2O)\) evaluated from elemental analysis for the precursor clay prior to organic modification. Both I-28 and I-44pa are organically-modified and were used in this work as-received. The organic modifier in I-28 is the trimethyldecadecylammonium ion and the modifier in I-44pa is the dimethyldecylammonium ion. These ammonium ions were exchanged into the clay from their chloride salts by Nanocor, Inc. Both I-28 and I-44pa clays were characterized with XRD to have \(d\)-spacings of 2.56 nm, however we measured \(d\)-spacings of 2.25 nm (I-28) and 3.2 nm (I-44pa) by SAXS. The \(d\)-spacings measured by XRD and SAXS can differ by ~10-20% due to higher sensitivity of the SAXS detector at the small angles. The as-received PGW clay exhibited a \(d\)-spacing of 2.31nm by SAXS. As-received PGW was treated with dimethyldecylammonium bromide (a further ion exchange) and then with polyethylene glycol (PEG), \(M_w=900\). The \(d\)-spacing of PEG-modified PGW increased from its initial as-received value of 2.31 to 3.2nm (SAXS) after treatment.

PGW clay modification was conducted as follows: PGW clay (10g) was dispersed in deionized water (333g) overnight and the following day 2.71g of PEG,
was added to the dispersion. After stirring for 10 min, dimethyldecylammonium bromide (5.34 g) was added and the temperature increased to 55 °C. This dispersion was stirred for another 20 min and then filtered. The modified clay was washed several times with deionized water to remove residual PEG/surfactant, filtered, and allowed to dry [15, 16].

**Preparation of Nanocomposites**

A series of dispersions for each clay (I-28, I-44pa, and PEG-modified PGW) with 0.5, 1.0, and 2.0 wt% was prepared by adding each clay, into the liquid monomer (96:4 mixture of DCPD and cyclopentadiene (CPD)) at room temperature with thorough mixing. DCPD (99.2% purity), under the trade name Ulturene™99, was obtained from Cymetech, LLC. CPD was produced by thermal cracking of DCPD followed by rapid quenching. It was added to DCPD to lower the melting point (39 °C for pure DCPD) of the monomer to well below room temperature. These clay/DCPD mixtures (10 g) were then sonicated using a 20 kHz 500 W ultrasonic processor ModelGE501 (Ace Glass) for 3 h (I-28 clay/DCPD and I-44pa/DCPD), but only 10 min for PEG-modified PGW/DCPD. Highly delaminated clay nanocomposites were formed, following sonication, by catalyst addition and *in-situ* polymerization of the highly-delaminated clay/monomer dispersions. The catalyst used to cure DCPD was dichloro(3-methyl-2-butenylidene)-bis-tricyclopentylphosphineruthenium (a Grubbs’-type catalyst), provided by Cymetech, LLC. However, it was not possible to form DCPD nanocomposites using PEG-modified PGW at loads above 0.5 wt% because
residual bromide ions, from the dimethyldidecylammonium bromide exchange step, deactivated the ruthenium complex ring-opening polymerization catalyst. Full details of these preparations have been previously reported [11].

Characterization Methods

X-ray Photoelectron Spectroscopy (XPS)

XPS experiments were performed on a Physical Electronics PHI Model 1600 surface analysis system. This instrument was equipped with a PHI 10-360 spherical capacitor energy analyzer (SCA) fitted with an Omni Focus III small area lens (800 µm diameter analysis area) and a high-performance multi-channel detector. The electron take off angle was 30° [24, 25]. XPS spectra were obtained using an achromatic Mg Kα (1253.6 cm⁻¹) X-ray source operated at 200 W. Survey scans were collected from 0-1100 eV. High-resolution scans were performed with a pass energy adjusted to 23.5 eV. The vacuum system pressure was maintained at approximately 10⁻⁹ Torr during all XPS experiments.

Non-linear least squares curve fitting software (Spectral Data Processor, version 2.3) was used to deconvolute the XPS peaks. The carbon 1s electron binding energy corresponding to graphitic carbon was referenced at 284.6 eV for calibration [25, 26a, b] The energy resolution of the spherical capacitance analyzer, determined from the full-width half maximum (FWHM) of the 4f⁷/₂ core peak of gold foil, was 1.07 eV. Atomic ratios were calculated from the XPS spectra after correcting the relative peak areas by sensitivity factors based on transmission characteristics of the Physical Electronics SCA PHI 10-360 [24, 25, 27].
Small Angle Neutron Scattering

SANS experiments were performed using the NG-3 30m SANS instrument at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) [28a,b]. A monochromatic beam of neutrons with a wavelength of $\lambda=6$ Å and resolution of $\Delta\lambda/\lambda=0.11$ was used. The monochromatic beam was collimated by circular pinhole irises in a 15 m long evacuated pre-sample flight path. The post-sample flight path consists of a long cylindrical section that forms a vacuum enclosure for a large two-dimensional (2D) position-sensitive detector. The area detector (64x64 cm$^2$ with a 0.5 cm FWHM spatial resolution) moves along rails, parallel to the neutron beam, inside the cylindrical vessel to vary the sample-to-detector distances from 1.3 m to 13.2 m. The detector moves transversely to the beam direction (by up to 30 cm) to extend the $q$ (wave vector) range covered at a given detector distance [29, 30]. Two sample-to-detector distances of 2m and 13m were used covering the $q$ range 0.003 to 0.3Å$^{-1}$. The samples (held at room temperature) were mounted by tape on a 10-position sample holder controlled by instrument control software. Scattered intensities were reduced and corrected for the transmission, background and parasitic scattering using Igor pro® version 4.07 software, from Wavematrics, Inc. The 2-D data were then circularly averaged to produce a one-dimensional graph of scattering intensity, $I(q)$, as a function of the wave vector, $q$, where $q=(4\pi/\lambda)\sin(\theta/2)$ and $\theta$ is the scattering angle [31].
Ultra High Resolution Small Angle Neutron Scattering

USANS experiments were performed using the BT5 perfect-crystal diffractometer (PCD) instrument at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). The PCD increases the maximum size of features, which were accessible with the NCNR’s 30-m long, pinhole collimation SANS instruments by nearly two orders of magnitude, from \( \sim 10^2 \text{nm} \) to \( 10^4 \text{nm} \) [32a]. The PCD is a Bonse-Hart-Type instrument with large triple-bounce, channel-cut silicon (220) crystals serving as monochromator and analyzer. The perfect crystals provide high angular resolution while the multiple reflections suppress the “wings” of the beam profile. This improves the signal-to-noise ratio to values comparable to that obtained by pinhole instruments. This technique, widely utilized for X-rays for many years, has only recently been successfully adapted for neutrons [32a, b, c], as dynamical diffraction effects arising from the deep penetration of neutrons in thick perfect crystals have become understood [32b]. The \( q \)-range of this instrument is \( 0.00005 \text{ Å}^{-1} \) to \( \sim 0.01 \text{ Å}^{-1} \) which probes the size regime of 0.1 to \( \sim 10 \) microns [32a, b, c].

Small Angle X-ray Scattering

Two SAXS instruments were used in order to cover a wide \( q \) range. The same composite sample (from each series) was examined with both instruments. The first experiments were performed on Oak Ridge National Laboratory’s 10-m SAXS instrument [33, 34]. This instrument used a sample-to-detector distance of 1.119m, Cu K\( \alpha \) radiation (\( \lambda = 1.54\text{Å} \)) and a 20x20 cm\(^2\) 2D position-sensitive area detector with each virtual cell (element) about 3mm apart. Corrections were made for instrumental
background (dark current due to both cosmic radiation and electronic noises in the detector circuitry) and detector non-uniformity/efficiency on a cell-by-cell basis (using a Fe$^{55}$ radioactive isotope standard, which emits X-rays isotropically by electron capture). The data were radially (azimuthally) averaged in the q-range, 0.01 < q < 0.4 Å$^{-1}$, q=(4π/λ)sin(θ/2), where λ is the X-ray wavelength, and θ is the scattering angle.

The data were then converted to an absolute differential scattering cross section by means of pre-calibrated secondary standards [35]. The absolute scattering intensity is in cm$^{-1}$ units.

The second SAXS instrument was a Molecular Metrology Small Angle X-ray Scattering System at the University of Tennessee, Knoxville, with a sample-to-detector distance of 5m. The X-ray source was a, Cu Kα, micro-focused X-ray beam (λ = 1.542Å) operating at 45 kV and 0.66 mA. A multi-wire detector consisting of a 2D array of wires was used. The data were radially averaged and converted to an absolute scale yielding the intensity of scattering versus wave vector q.

Transmission Electron Microscopy

Nanocomposites were ultramicrotomed with Reichert-Jung Ultracut E ultramicrotomes using a diamond knife at room temperature providing sections with nominal thickness of 70-85 nm. Microtomed slices were mounted on Formvar or amorphous-carbon coated copper TEM grids. The contrast between the dispersed clays and polymer matrix was sufficient for imaging without staining.

A JEOL JEM-100CX II 80kV transmission electron microscope was used to study the dispersion of the clay layers and tactoids. HR-TEM imaging was performed using a JEOL JEM-3010 analytical transmission electron microscope at the Naval
Research Laboratory, Stennis Space Center, operating at 300kV with a LaB$_6$ filament, an EM-30022HT pole piece, and a measured point-to-point resolution of 2.1Å. The HR-TEM instrument is equipped with a side-entry motorized 5-axis goniometer, a Noran energy dispersive X-ray spectroscopy (EDS) system, a Gatan 764 multi-scan camera (MSC), and a Gatan imaging filter (GIF200). All HR-TEM images were recorded on film at 250 kX magnification using a 60 micron objective aperture.

Results and Discussion

XPS Study of PGW Clay Modification

The surfaces of the PGW clay platelets were modified using both PEG and dimethyldidecylammonium bromide. The exchange reaction replaces interlayer cations with dimethyldidecylammonium ions. In the process, molecules containing -OH, -NH$_2$, and -NH$_3^+$, or -NR$_3^+$ functions can be adsorbed to clay platelet surfaces by hydrogen bonding, van der Waals interactions and coulombic attractions (in the case of –NH$_3^+$ and –NR$_3^+$) [36]. Adsorption of PEG to platelet surfaces or into ammonium ion-pillared galleries might be promoted by dipole, van der Waals and hydrogen bonding interactions [15, 16]. XPS analysis of the as-received PGW clay indicated the presence of Al, Si, C, N and O. The presence of N in this alumina silicate layered clay indicates that prior alkyl ammonium ion exchange had been performed (Figure 7.1). A XPS scan of PEG-modified PGW indicates the presence of Al, Si, O, C, N, and Br. The atomic compositions (atom percents) of Al, Si, and O (from alumina-silica sheets), decreased from 5.6, 7.1, and 45.5% to 3.4, 5.5, and 32.1%, respectively, after
Figure 7.1. X-ray Photoelectron spectra of as-received PGW clay versus polyethyleneglycol (Mw 900)-modified PGW clay, which was pretreated with dimethyldidecylammonium bromide.

Figure 7.2. Atomic composition of the Al, Si, O, N and bromine in PGW clay and after PEG modification.
PEG modification (Figure 7.2). There was no change in the alumina silicate sheet compositions. The adsorption of PEG and dimethyldidecylammonium ions to the clay’s alumina silicate platelets increased the carbon, hydrogen, and nitrogen content. XPS photoelectrons have limited penetration depth and are very sensitive to adsorbed surface species. After modification, part of this depth consists of PEG and the quaternary ammonium species adsorbed on the surface and intercalated between the outer platelet layers. The XPS measured C and N atomic percentages increased, (C from 39.3 to 54.6% and N from 2.4 to 3.7%), after PEG modification, confirming that dimethyldidecylammonium bromide exchange had increased the amount of alkyl ammonium ions over those present in the as-received PGW. The presence of Br 3p and 3d_{5/2} peaks at 67.75 and 68.68 eV (0.6 atomic percent) indicated that adsorption of some residual bromide into the surface regions from the quaternary ammonium salt exchange had also occurred.

Al and Si XPS edges in the as-received PGW clay appear, respectively, at 74.84, and 102.96 eV versus 74.3 and 102.43 eV for the PEG-modified PGW. These assignments were based on the peaks at 74.58 and 102.8 eV reported for Al and Si in Al_{2}SiO_{4}, respectively [37, 38]. The as-received PGW exhibited one carbon 1s peak at 284.5 eV due to C present in the long alkyl chains of the ammonium pillars (e.g. –CH_{2}) [39a]. This was used as the reference binding energy for the XPS spectra (Figure 7.3a). In comparison, two C 1s peaks were observed in PEG-modified PGW clay after deconvolution (Figure 7.3b). The first, at 284.5eV, is attributed to C in (-CH_{2}-) groups in the exchanged alkyl ammonium ions and the second, at 286.4 eV, indicates the presence of the ether-type O–C and of polyethyleneglycol [39a, b]. The nitrogen peak
of as-received and PEG-modified PGW appears at a binding energy of 401.8 eV and 401.4 eV, respectively, in high-resolution spectra (Figure 7.4). We attribute this peak to nitrogen in the exchanged primary ammonium ions, which were originally present in the as-received PGW. This assignment is based on the 401.8 eV binding energy reported for N in ammonium ions (ammonium nitrate, ammonia trifluoroborate) [40, 41]. Deconvolution of the PEG-modified spectra reveals the presence of a second peak at 402.4 eV (Figure 7.4). Quaternary nitrogen from dimethyldidecylammonium ions should exhibit a peak near this energy as suggested by the fact that the N 1s peak for tetrabutylammonium hydrogen sulfate has been reported at 402.2 eV [42].
7.3.a. PGW clay, as received.

Figure 7.3. High-resolution C 1s XPS spectra of as-received PGW and PEG-modified PGW clay.

7.3.b. PEG modified PGW clay.
7.4.a. PEG-modified clay.

7.4.b. PGW.

Figure 7.4. High-resolution N 1s XPS spectra of PEG-modified PGW clay.
SAXS

SAXS studies were performed on all clay powders and all clay/polyDCPD composites. SAXS plots for I-28, I-44pa, and PEG-modified-PGW clays are shown in Figure 7.5 and plots for nanocomposites formed from each of these clays are shown in Figures 7.6-7.8, respectively. The powdered clays (Figures 7.5a, b) exhibited $d$-spacings of 2.25nm (I-28) and 3.2nm (I-44pa and PEG-modified PGW). As-received PGW had a $d$-spacing of 2.31 nm (Figure 7.5b). The intensity of the main SAXS peak for PEG-modified PGW was much higher than that for I-44pa (Figure 7.5a), indicating PEG-modified PGW had a more highly-ordered structure with the same average repeating platelet spacing as I-44pa. Further, a secondary peak was observed for both I-44pa and PEG-modified PGW at a $q$ value of 0.395Å⁻¹. This could be a secondary reflection of the first peak or a reflection from a small population of clays with $d$-spacings of 15Å. It should be noted that a ~15Å mean $d$-spacing was observed by HR-TEM for dispersed PEG-modified PGW within the polyDCPD matrix.

The 0.5, 1.0, and 2.0wt % I-28 clay/polyDCPD composites did not show any SAXS peaks within the $q$ range of 0.017 to 0.4 Å⁻¹ corresponding to $d$-spacings of 15.7 to 369Å (Figure 7.6). This suggests that a high degree of nanometer-scale dispersion was achieved in all of these composites after sonicating the clay in liquid DCPD for 3h. This is consistent with previous XRD and TEM studies of these composites, which showed that partial exfoliation had produced dispersions of individual platelets and a variety of small tactoids within the resin [11]. The lack of coherent SAXS scattering suggests a range of basal layer spacings are present within these small tactoids. In fact, the original I-28 ion-exchanged clay particles exhibited a range of $d$-spacings centered
7.5.a. SAXS data of clay I-28, clay I-44pa, PEG-modified PGW.

7.5.b. SAXS data of PGW clay.

Figure 7.5. SAXS experiments on clay I-28, I-44pa, PGW and PEG-modified PGW clay powders exhibiting d-spacings of 2.25 nm, 3.2 nm, 2.35 nm and 3.2 nm, respectively.
around 2.25nm in the SAXS plot and 2.56nm by XRD. Variable layer spacings can result from several mechanisms: (1) incomplete quaternary ammonium ion exchange with cations present in the as-received clay interlayers; (2) DCPD infusion within some interlayers; (3) variable total Fe or Fe\textsuperscript{3+}/Fe\textsuperscript{2+} composition within a tactoid, which affects clay surface charge; and (4) small tactoid effects, in particular, frayed platelets near the edges of tactoids. Variation in persistence lengths (as observed by HR-TEM) could also result from any of the four factors listed above as well as other reasons. Persistence lengths correspond to regions that have a constant value in the \(d\)-spacing over several adjacent layers within an individual tactoid.

SAXS plots of the 0.5 wt% I-44pa clay/polyDCPD composite did not show any peaks within the range \(0.017 \leq q \leq 0.4 \text{ Å}^{-1}\) (Figure 7.6). The 1.0 wt% I-44pa clay/polyDCPD exhibited a very shallow peak while the 2.0wt% composite exhibited a broad peak in the range \(0.142 \leq q \leq 0.34 \text{ Å}^{-1}\), corresponding to \(d\)-spacings from 1.85 nm to 4.42 nm (Figure 7.7a). The maximum channel of this broad peak occurred at \(q=0.253 \text{ Å}^{-1}\), corresponding to an interplatelet \(d\)-spacing of 2.48 nm. Thus, in addition to individual exfoliated clay platelets, tactoids are present with a distribution of \(d\)-spacings. SAXS plots of I-44pa clay/polyDCPD samples (0.5, 1.0, and 2.0wt% clay) over the range \(0.017 \leq q \leq 0.16 \text{ Å}^{-1}\) (corresponding to \(d\)-spacing from 3.93 to 36.9 nm) did not show any peaks (Figure 7.7b). Finally, no reflections were observed from the 0.5wt% PEG-modified-PGW-clay/polyDCPD composite in either of the q ranges examined (Figures 7.8 a, b). Thus, no ordering could be observed after only 10 min of sonication of this clay in DCPD followed by curing.
Figure 7.6. SAXS experiments on 0.5-2.0wt% I-28 clay/polyDCPD composites. No long-range structural orderings were observed in these samples.
7.7.a. q range from 0.04 to 0.4 Å⁻¹, 2.0wt% I-44pa clay/polyDCPD composite showed a peak at q=0.253 Å⁻¹, d=2π/q=24.8 Å (2.48 nm).

7.7.b. q range from 0.017 to 0.16 Å⁻¹

Figure 7.7. Small angle X-ray scattering from I-44pa clay/polyDCPD composites containing 0.5, 1 and 2 wt% I-44pa clay.
7.8.a. q range from 0.04 to 0.4 Å⁻¹; no peak was observed.

7.8.b. q range of 0.017 to 0.16 Å⁻¹; no peak observed.

Figure 7.8. Small angle X-ray scattering from the 0.5wt% PEG-modified PGW clay/polyDCPD composite.
Small angle neutron scattering studies were performed on all the composite samples. There was no coherent scattering observed from the polyDCPD matrix, however a relatively high incoherent background was present because the polyDCPD matrices were not deuterated. The incoherent scattering background from a pure sample of polyDCPD (average of 0.75cm\(^{-1}\)) was subtracted from the scattering obtained from composite samples. The difference represented scattering from dispersed clay particles. No peaks were observed in any of the plots of intensity versus q, or I.q\(^2\) versus q. The SANS data were fit to the stacked-disk model developed by Glinka [19a], Hanley et al. [20, 21] and Ho et al. [17, 22]. Clay platelets are assumed to be thin disks and tactoids as stacks of thin disks [17] in this model for interpreting SANS data [43-45].

The neutron scattering intensity is generally written as:

\[ I(q) = A\phi V_p (\rho - \rho_m)^2 P(q)S(q) \]  
\[ (7.1) \]

where \( V_p \) is the volume of the particles, \( V \) is the total volume, \( \phi = NV_p/V \) is the volume fraction with \( N \) representing the number of particles, \( \rho - \rho_m \) is the difference between the scattering length density of the particle and the polymer medium (contrast factor), \( P(q) \) is the form factor and \( S(q) \) is the structural factor [19]. \( P(q) \) is the part of the scattering function influenced by the shape of the particle (in this case clay tactoid) and \( S(q) \) is a measure of the interaction between the layers in a tactoid (short range effects), and interaction between particles (tactoids; long range effects). The shape of
clay platelets has been assumed to be thin disks to facilitate calculations [43-45]. For instance, the Glinka [19a], Hanley et al. [20, 21] and Ho et al. [17, 22] stacked-disk model treats clay platelets as thin disks and tactoids as parallel stacks of thin disks. The stacked disk model is applied for the analysis of the experimental SANS data as described below. The form factor for a cylinder of radius $R$ and height of $2H$ is:

$$P(q) = 4 \int_{0}^{\pi/2} \left( \sin^2(qH \cos \beta) \right) J_1^2(qR \sin \beta) \frac{(qH)^2 \cos^2 \beta}{(qR)^2 \sin^2 \beta} \sin \beta \, d\beta$$  \hspace{1cm} (7.2)$$

where $J_1$ is the first order Bessel function, $\beta$ is the angle between the wave vector, $q$, and the major axis of the cylinder. The cylinder height, $2H$, represents a platelet thickness and can be defined as described below. In the limit of a very thin cylinder (i.e., a thin disk), $qH<<1$, the above equation simplifies to the Karatky-Porod expression [46]:

$$P(q) = \frac{2}{(qR)^2} \left[ 1 - \frac{J_1(2qR)}{qR} \right]$$  \hspace{1cm} (7.3)$$

At the limit of very small $q$ values ($q \rightarrow 0$), $P(q)=\exp(-q^2R^2/6)$ [20]. This is an example of Guinier’s law that states the slope should obey a power law with a slope of -2 for a very thin disk.

The form factor for an organically modified clay with core thickness of $2H$ and surfactant layer thickness of $d$ is denoted as $P_{s,c}(q)$ (Figure 7.9). The form
factors of the core platelet, $(P_c(q))$, the core plus exchanged alkylammonium layer, $(P_s(q))$, and total $(P_{s,c}(q))$ are defined, respectively, as [17, 21, 22]:

$$ P_c(q) = \int_{0}^{\pi/2} \left[ \frac{\sin(qH\cos\beta)}{qH\cos\beta} \right] \left[ \frac{2J_1(qR\sin\beta)}{qR\sin\beta} \right]^2 \sin \beta d\beta $$  \hspace{1cm} (7.4) 

$$ P_s(q) = \int_{0}^{\pi/2} \left[ \frac{\sin(q(d+H)\cos\beta)}{q(d+H)\cos\beta} \right] \left[ \frac{2J_1(qR\sin\beta)}{qR\sin\beta} \right]^2 \sin \beta d\beta $$  \hspace{1cm} (7.5) 

$$ P_{s,c}(q) = \int_{0}^{\pi/2} \left[ \frac{\sin(q(d+H)\cos\beta)}{q(d+H)\cos\beta} \right] \left[ \frac{\sin(qH\cos\beta)}{qH\cos\beta} \right] \left[ \frac{2J_1(qR\sin\beta)}{qR\sin\beta} \right]^2 \sin \beta d\beta $$  \hspace{1cm} (7.6) 

Clays occur as ordered stacked layer structures (tactoids) with individual platelets bonded together by ionic attractions between negatively charged clay platelets and cations. For low clay loadings, interactions between well-separated tactoids (i.e., individual stacked disks) are negligible and the scattering response is influenced predominantly by the short-range structural factor, $S_s(q)$, that describes scattering within an individual tactoid. In this case, long-range contributions to the scattering response can be neglected, i.e. $S(q) \approx S_s(q)$. According to equation 7.1, the scattering intensity, $I(q)$, depends on the product of $P(q)S(q)$. $P(q)$ is the square of the scattered wave amplitude averaged over all directions $<f^2>$ (the platelet core, $f^2_c(q)$,
Figure 7.9. Schematic of organically modified clay and neutron scattering length density profiles [17].
the ammonium coated platelet $f_r^2(q)$, and the interaction term $f_c(q)f_s(q)$). Therefore, $S_s(q)$ should be multiplied by $f_c^2(q)$, $f_s^2(q)$, $f_c(q)f_s(q)$ given in equations 7.4-7.6 [17, 21, 22]. If the nearest neighbor-to-neighbor distances in a stack of clay platelets obey a Gaussian distribution, the short range structural factor is written [17, 46]:

$$S_s(q) = 1 + \frac{2}{N} \sum_{k=1}^{N} (N - k) \cos(kDq \cos \beta) \exp[-k(q \cos \beta)^2/2]$$  \hspace{1cm} (7.7)

where $N$ is the number of platelets in a stack, $D$ is the nearest neighbor-center-to-center distances and $\sigma$ is its Gaussian standard distribution (GSD), respectively. Therefore, the total coherent scattering intensity of randomly oriented stacks of clay platelets (from equation 7.1) assuming a dilute dispersion of tactoids, i.e., $S(q) = S_s(q)$, is written as [17]:

$$I_{OMMT}^{\text{total}}(q) = N \int_0^{\pi/2} \left[ \Delta \rho_1 (V_t f_t(q) - V_c f_c(q)) + \Delta \rho_c V_c f_c(q) \right] ^2 S_s(q) \sin \beta d \beta$$  \hspace{1cm} (7.8)

where $N$ is the number of clay platelets in a stack, $\Delta \rho_1$ is the scattering length difference between core (e.g. the clay platelet’s alumina silicate layer) and medium (polyDCPD), $\Delta \rho_c$ is the scattering length difference between the alkylammonium ion layer and the medium (polyDCPD), $V_t$ is the total volume of the alumina silicate core and alkylammonium ion layer, and $V_c$ is the volume of the core [17, 21]. The wave amplitudes, $f_c$ and $f_{c,s}$ are derived from equations (7.4-7.6) via the relations $P_c(q) = <f_c^2(q)>$ and $P_{c,s}(q) = <f_c(q)f_s(q)>$, which are averages over all directions of the
wave amplitudes. The structural factor for a dilute dispersion of tactoids is given by equation (7.7). When all platelets have been completely separated from the stacks and dispersed as individual platelets (e.g. fully exfoliated, N=1), $S_s(q)=1$, so equation (7.8) simplifies to equation (7.9). Only short-range structural factors are important for very low concentrations. However, interactions between stacks become increasingly important with increased clay loading, and in this case, long-range structural factors should then be calculated.

$$I_{\text{Single}}^{\text{OrganicModified}}(q) = N_{\text{OMMT}} \int_0^{\pi/2} \left[ \Delta \rho_i \left(Vf_i(q) - Vf_c(q)\right) + \Delta \rho_c Vf_c(q) \right]^2 \sin \beta d\beta$$  

(7.9)

The incoherent background was subtracted from the scattering intensity for each sample. The slopes of $I(q)$ versus $q$ for the 0.5, 1.0, and 2.0wt% I-28 clay/composites varied between -2.53 to -2.79 over the range $0.003 \leq q \leq 0.05\,\text{Å}^{-1}$ (Figure 7.10). The $I(q)$ vs. $q$ slopes for 0.5, 1.0 and 2.0wt% I-44pa clay/polyDCPD nanocomposites varied from -2.5 to -2.76 over the range $0.003 \leq q \leq 0.06\,\text{Å}^{-1}$ (Figure 7.11). A slope of -2.57 was found for the 0.5wt% PEG modified clay/polyDCPD composite within the range $0.003 \leq q \leq 0.05\,\text{Å}^{-1}$ (Figure 7.12). A slope of ~-2 indicates the presence of non-interacting thin disks while a slope of -3 is given by fractal shapes [31b]. The experimental slopes larger than -2 indicate the presence of platelets and tactoids of various thicknesses, which are bent and curved (fractal contribution to shape). The plots of scattering intensity vs. wave vector within the range $0.003 \leq q \leq 0.05\,\text{Å}^{-1}$ were fitted to the stacked-disk model for each of the composites. The scattering length
7.10.a. SANS and USANS of 0.5 and 2.0wt% I-28 clay/polyDCPD composites.

7.10.b. Small angle neutron scattering from 0.5,1.0 and 2.0wt% I-28/polyDCPD composites. The slopes of I(q) vs. q are between -2.53 to -2.79, for q<0.05.

Figure 7.10. Small angle neutron scattering of 0.5-2wt% clay I-28/polyDCPD composites.
7.11.a. SANS and USANS of 0.5 and 2.0wt% I44pa/polyDCPD composites.

7.11.b. Small angle neutron scattering from 0.5, 1.0 and 2.0wt% I-44pa/polyDCPD composites. The slopes of I(q) vs. q are between -2.54 to -2.76, for q< 0.06.

Figure 7.11. Small angle neutron scattering of I-44pa clay/polyDCPD composites.
Figure 7.12. Small angle neutron scattering from the 0.5wt% PEG-modified PGW clay/polyDCPD composite. The slope is -2.57, for q< 0.05.
densities of the alumina silicate core, alkylammonium ion layer and polyDCPD, were known (Table 7.1), as were the clay volume fraction and the clay layer d-spacings (from SAXS and HR-TEM analysis). These values were used as input to the stacked-disk model from which the mean number of clay platelets per tactoid was predicted for each composite. The results are summarized in Table 7.2.

USANS data showed linear plots with the same slopes that were present in the SANS region for all of 0.5, 1.0 and 2.0 wt% I-28 clay/polyDCPD and 0.5, 1.0 and 2.0 wt% I-44pa clay polyDCPD composites (Figures 7.10a and 7.11a). No Guinier regions were observed in any of these composites. The absence of Guinier regions indicates that interactions between particles exist [23, 32d]. The USANS data for 0.5 wt% PEG modified PGW clay composite were not available due to multiple scattering effects.
<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular mass, (g)</th>
<th>Density, (g/cm³)</th>
<th>Neutron Scattering Length Density, (Å⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(dicyclopentadiene) (C₁₀H₁₂)ₙ</td>
<td>(132.2)ₙ</td>
<td>1.1</td>
<td>1.08x10⁻⁶</td>
</tr>
<tr>
<td>Dimethyldecyl ammonium ion</td>
<td>326.62</td>
<td>2.2</td>
<td>-1.36x10⁻⁶</td>
</tr>
<tr>
<td>Trimethyloctadecyl ammonium ion</td>
<td>312.6</td>
<td>0.9</td>
<td>-3.75x10⁻⁶</td>
</tr>
<tr>
<td>Polyethyleneglycol (HO-(CH₂)₂OH)ₙ</td>
<td>(62)ₙ</td>
<td>1.1</td>
<td>2.15x10⁻⁶</td>
</tr>
</tbody>
</table>
Table 7.2. Comparison of the mean tactoid sizes predicted from SANS data using the stacked-disk model with those measured directly by HR-TEM.

<table>
<thead>
<tr>
<th>Composite Sample</th>
<th>I-28Clay/ Poly(DCPD)</th>
<th>I-44paClay/ Poly(DCPD)</th>
<th>PEG-Modified Clay/PolyDCPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% Clay</td>
<td>0.5 1 2</td>
<td>0.5 1 2</td>
<td>0.5</td>
</tr>
</tbody>
</table>

- **Predicted by stacked-disk model (SANS data)**
  - Mean (GSD)<sup>a</sup> 4 5 14 4 7 11 5
  - Observed by HR-TEM
    - Median 2.8 - 3.2 1.9 - 2.3 4.9
    - Mean 4.2 - 6.2 3.2 - 3.3 6.2

- **Tactoid Size Range (no. of platelets)**
  - 1-26 - 1-102 1-12 - 1-65 1-23

- **Number of tactoids examined**
  - 447 - 454 250 - 309 198

---

*a.* Gaussian Standard Distribution
HR-TEM

A limitation of TEM and HR-TEM studies, in comparison to scattering techniques, is that the region analyzed is relatively small (square micron area multiplied by thickness of thin section) as opposed to neutron and X-ray scattering measurements which sample cubic-centimeter volumes. To provide a more representative characterization of the specimen as a whole, many regions of the nanocomposites were examined by TEM and HR-TEM. Examination by TEM demonstrated that high degrees of clay delamination were achieved within the polyDCPD matrix for all three types of clay at 0.5wt% (Figure 7.13.a-e). To quantify the degree of delamination, two parameters were measured: the mean number of individual clay platelets per tactoid (tactoid size) and the distribution of (001) basal layer spacings ($d$-spacing) for all tactoids. Tactoid size distributions were also measured providing the range of tactoid sizes (platelets per tactoid) present. The results of these measurements are discussed below. They are used to test, for the first time, the application of the stacked-disk model to interpret SANS experiments on nanodispersed clays.
7.13.a.  0.5wt% I-28 clay.

7.13.b.  2.0wt% I-28 clay
7.13.c. 0.5wt% I-44 pa.

7.13.d. 2.0wt% I-44pa clay
7.13.e.  0.5wt% PEG-modified PGW clay

Figure 7.13. TEM micrographs of nanodispersed clay in polyDCPD composites. Samples a-d sonicated for 3h and sample e sonicated for 10min.

A range of microstructures was exhibited in the three nanocomposite series of clay dispersion. The sizes of the dispersed tactoids varied. The smallest mean tactoid sizes were seen in the 0.5wt% I-28 clay/polyDCPD composite while the largest mean tactoid sizes were observed in the 0.5wt% PEG-modified clay/polyDCPD composite (see table 7.2, Page 240). Representative examples of tactoids in these I-28, I-44pa, and PEG-modified-PGW clay/polyDCPD composites are shown in Figures 7.14, 7.15, and 7.16, respectively. On the sides of these figures, magnified micrographs are shown (5nm scale bars) with arrows pointing to the locations in the central portion (20nm scale bars) from which these expanded views were taken. In Figure 7.14a, a tactoid is
shown containing 8 platelets. It has been splayed into two sections at the end, each section consisting of four platelets. Tactoids with thicknesses of 3-5 nm, along with several single-platelets, and two-platelet tactoids are displayed in Figure 7.14b. Some diffusion of polyDCPD (intercalation) appears to occur within the center of the tactoid displayed in the upper left corner. In comparison, the mean size of the tactoids in 0.5 and 2.0wt% I-44pa and 0.5 wt% PEG-modified PGW composites was somewhat larger (e.g., Figure 7.15 and Figure 7.16). In Figure 7.15a, two tactoids with 9 and 5 platelets are shown. Several individual platelets and two-platelet tactoids are present in close proximity with the larger tactoids. In Figure 7.16, one 20-25 nm tactoid splits at a branch point into two smaller tactoids. It appears that the polyDCPD texture extended directly between these tactoid branches and interfaces directly with the tactoid surface. Good surface wetting of the clay platelet tactoids was observed for all composites and no voids were observed.
7.14.a. 0.5wt%I-28.
Figure 7.14. HR-TEM micrographs from I-28 clay/polyDCPD composite.
Figure 7.15. HR-TEM micrographs from I-44pa clay/polyDCPD composites.

7.15.a. 0.5wt% I-44pa

7.15.b. 2.0wt% I-44pa
The distributions of tactoid sizes (platelets per tactoid) for polyDCPD composites with 0.5 and 2.0wt% I-28 clay, 0.5 and 2.0 wt% I-44pa clay and 0.5wt% PEG-modified-PGW clay were measured from a large number of HR-TEM micrographs. The results are shown in Figure 7.17 and summarized in Table 7.2. The mean number of platelets per tactoid for 0.5wt% I-28 was 3.2 (median=1.9) based on the examination of 250 different tactoids (Figure 17a). The largest tactoid observed in this sample had only 12 platelets. There was a significant population of single clay platelets dispersed in this sample. The mean tactoid size for the 0.5wt% I-44pa composites was 4.2 platelets (median=2.8) based on 447 tactoids (Figure 7.17c). However, the largest tactoid observed had 26 platelets, approximately twice as large as that in the 0.5wt% I-28 clay/polyDCPD composite. Upon increasing the I-28 clay concentration to 2.0wt%, the mean tactoid size increased to 3.3 platelets (median=2.3)
based on 309 tactoids (Figure 17.b). The largest tactoid observed for the 2.0wt% I-28 sample, however, had 65 platelets, much larger than the 12 platelets observed in the 0.5wt% I-28 sample. The 2.0wt% I-44pa composite (Figure 7.17d) exhibited a mean tactoid size of 6.2 platelets (median=5.2) based on examinations of 454 tactoids. The largest tactoid found had 102 platelets. The 0.5wt% PEG-modified-PGW clay/polyDCPD composite was prepared by sonicking the clay in DCPD for only 10 minutes prior to curing in comparison to 3h for the I-28 and I-44pa samples. The mean tactoid size in this composite was 6.2 platelets (median= 4.9) and the largest observed tactoid had 23 platelets based on 198 tactoids studied(Figure 17.e). Although the distribution of tactoid sizes for the 0.5wt% PEG-modified-PGW was shifted to somewhat larger sizes than either the 0.5wt% I-28 and I-44pa compositions, the 18-fold smaller sonication time used with this clay indicated that PEG-modified PGW clay delaminated more rapidly than the I-28 and I-44pa clays.

The most common tactoid size in all composites was two platelets. At least 30% of the tactoids had two platelets in the 0.5 and 2.0 wt% I-28 clay/polyDCPD and 0.5 and 2.0 wt% I-44pa/polyDCPD composites. In the 0.5 wt% PEG-modified PGW composite, 19% of the tactoids contained two platelets.
7.17.a. Distribution of tactoid sizes within the 0.5wt% I-28 clay/polyDCPD composite. The mean was 3.2 and the median was 1.9 platelets per tactoid.

7.17.b. Distribution of tactoid sizes within the 2.0wt% I-28 clay/polyDCPD composite. The mean was 3.3 and the median was 2.3 platelets per tactoid.
7.17.c. Distribution of tactoid sizes within the 0.5wt% I44clay/polyDCPD composite. The mean was 4.2 and the median was 3.1 platelets per tactoid.
7.17.d. Distribution of tactoid sizes within the 2.0wt% I-44pa clay/polyDCPD composite. The mean was 6.2 and the median was 5.2 platelets tactoid.
7.17.e. Distribution of tactoid sizes within the 0.5wt% PEG-modified clay/polyDCPD composite. The mean was 6.2 and the median was 4.9 clay layers per tactoid.

Figure 7.17. The distribution of tactoid sizes within the matrices of clay/polyDCPD nanocomposites. Tactoid sizes are expressed as clay platelets per tactoid.

The layer spacing ($d$-spacing) between platelets in tactoids was also measured from HR-TEM micrographs for the clay/polyDCPD composites containing 0.5 and 2.0wt% I-28, 0.5 and 2.0wt% I-44pa, and 0.5wt% PEG-modified PGW (Figure 7.18). The relative populations of basal layer spacings for each specimen (filled squares) are plotted as accumulative percentages on the ordinate in logarithmic scale, and each was linear-least-square fit to a Log-Normal distribution, $df/d\ln(x)$. The error for an
Figure 7.18. Distribution of (001) layer spacings (d-spacing) of the clay tactoids dispersed in poly(DCPD) nanocomposites.
(A) PEG-modified PGW clay (0.5wt%),
(B) I-28 clay (0.5wt%),
(C) I-28 clay (2.0wt%),
(D) I-44pa clay (0.5wt%),
(E) I-44pa (2.0wt%).

Several error bars representing the precision of the individual measurements are placed at the right along the ordinate for visual comparison. The median ($x_m$) and width ($\sigma$) of the distribution were used as the fitting parameters from which the corresponding mode ($x_o$), and mean, of the distribution can be derived.
individual (001) layer spacing measurement was ±0.15 Å (placed at the right along the ordinate for visual comparison).

Of the three series of clay dispersions, the 0.5wt% PEG-modified-PGW clay/composite exhibited the largest mean $d$-spacing of 15.5 Å (and a Log-normal fitted median of 15.4 Å). The mean [and Log-normal fitted median] $d$-spacings for the other examined nanocomposites were 13.4 Å [13.3 Å] (0.5wt% I-28), 12.2 Å [12.1 Å] (2.0wt% I-28), 13.6 Å [13.4 Å] (0.5wt% I-44pa) and 13.7Å [13.6 Å] (2.0wt% I-44pa), respectively. The distributions of $d$-spacings are almost the same within the tactoids in the composites containing I-28 and I-44pa clays. Each of these composites was prepared from clay containing alkyl ammonium ion pillaring agents as the only organic modifier. The $d$-spacings are the largest for the PEG-modified-PGW clay, presumably due to partial PEG intercalation between some platelets within the dispersed tactoids.

The mean clay $d$-spacings within the composites are much smaller than the $d$-spacings of the precursor modified clays used to prepare these composites. The starting clays had $d$-spacings of 22.5 Å (I-28) and 32Å (I-44pa and PEG-modified PGW), as measured by SAXS. However, SAXS plots of these clays exhibited a secondary peak corresponding to 15 Å $d$-spacings possibly arising from a small subpopulation of collapsed clays. Nevertheless, following nanodispersion and DCPD curing, the dominant $d$-spacing dropped sharply. It is unclear what mechanisms are responsible for the reduction in $d$-spacing. Sonication and mixing may have preferentially cleaved tactoids along those platelets which were the most loosely bound, i.e. those separated by the largest spacing due to effective pillaring of alkyl
ammonium ion exchange. If the original distribution of layer spacings in the clays possessed a small population of tactoids with platelet spacings in the 8 to ~15 Å range (as possibly suggested by the secondary SAXS peak), this population may have preferentially survived delamination as larger tactoids were progressively split into smaller tactoids and individual exfoliated platelets. Furthermore, chemical treatment of the clays may not have resulted in complete ion exchange in all the interlayers. Those non-modified interlayers would be more difficult to cleave because they would contain cations that more strongly bound platelets together than those in the modified interlayers. Thus, the fraction of originally unpillared platelet stacks would increase as cleavage occurs between pillared platelets, leaving small tactoids having mostly small d-spacings between platelets. In addition, alkylammonium ion pillars undergo Hoffman elimination reactions at ~200°C. Since a high temperature (above 200°C) curing step was applied to the composites after thorough crosslinking had occurred at 160°C [11], a decrease in the mean d spacings could result as pillars decompose and platelets close together.
Experimental Test of SANS Stacked-Disk Model

The model predictions for the mean number of platelets per tactoid based on the fitting of SANS experimental data (for the three series of nanocomposites) to the stacked-disk model are shown in Table 7.2, along with the mean and median values from HR-TEM analysis. Since HR-TEM sampled a large number of tactoids in each nanocomposite examined, the HR-TEM results are reasonably representative of the tactoid distribution within the whole sample. The SANS stacked-disk model predictions are in good agreement with direct HR-TEM measurements for all three of the 0.5wt% clay nanocomposites (I-28, I-44pa and PEG-modified-PGW clay). However, as the clay loading in the composites increased, differences between the stacked-disk model predictions and HR-TEM results become larger. The stacked-disk model treats clay tactoids as rigid, parallel-stacked thin disks. Although this may approximate the shape of very small clay tactoids, montmorillonite clay tactoids have complex shapes that branch (e.g., see Figure 7.16) and are often curved (e.g., see Figure 7.13). The geometric complexity of the clay tactoids naturally increases with tactoid size, greatly departing from the model treatment. Larger tactoids are far thicker than an individual platelet but the length and width dimensions don’t change as sharply. Thus, the distribution of tactoid surface to thickness (e.g. l x w/thickness) ratios broadens.

It stands to reason that stacked-disk model predictions of large tactoid sizes would be questionable and, in fact, they deviate significantly from direct HR-TEM measurement. Furthermore, the stacked-disk model does not take into consideration
long-range structural factors, which could be increasingly important with greater clay loadings (higher clay volume fractions) where the interactions between different clay tactoids become more significant. In fact, the absence of a Guinier region in USANS data suggests the particles interacted. The number of tactoids per unit area observed by TEM did not increase with clay loading, but the mean tactoid thickness did. Thus, a strong agreement for the increasing contribution of long range structural factors cannot be made. Only short-range structural factors originating from interactions between the stacked platelets in a tactoid are considered in the model. Furthermore, neither the exfoliated platelets nor the tactoids present are uniformly dispersed throughout the polyDCPD matrix. Some regions have more dispersed clay and other regions contain less. The stacked-disk model assumes a uniform distribution and this may account for the small discrepancies with the direct TEM results at low clay loadings. These factors cause the stacked disk model predictions to deviate from the actual mean number of platelets per tactoid. The large number of tactoids sampled in each case by HR-TEM provides confidence that these results are reasonably representative of the tactoid distribution within the whole sample. This compensates for TEM’s limitation as a local analytical technique.
Exfoliation in the Nanocomposites

As clay tactoids exfoliate and become smaller, the resistance to further exfoliation should increase. Exfoliation should become impeded by geometric constraints as delaminated platelets impinge on one another, blocking pathways for further separation. Furthermore, the viscosity of the liquid monomer/clay mixture increases during this process, slowing transport of exfoliated platelets away from their parent tactoids. Evidence supporting this picture is provided by HR-TEM characterizations of the nanocomposite microstructures. The mean number of tactoids (including individual clay platelets) per unit area was measured from many regions of each nanocomposite. If each nanodispersion process encountered no resistance, homogeneous dispersions would result and the density of tactoids (and platelets) would scale with clay loading. In the presence of dispersion resistance, the density of tactoids (and platelets) would be heterogeneous within any one nanocomposite while the process proceeded. Further, the density of tactoids (and platelets) for the same clay loading would vary with dispersion resistance. This all assumes equivalent processing during delamination (i.e., the same sonication times and energies as were applied in this study).

Table 7.3 summarizes the mean number of tactoids (including individual clay platelets) per unit area for each composite and the total surface area examined (HR-TEM). The 0.5wt% I-28 composite had the largest number of tactoids (and platelets) per unit area, $2.21 \times 10^8$ per mm$^2$. The 2.0wt% I-28 composite had $1.91 \times 10^8$ tactoids (and platelets) per mm$^2$. Thus, as clay loading increased, the degree of exfoliation and nanodispersion decreased when sonication time was held constant. The same trend
Table 7.3. Mean number of tactoids per unit area measured by HR-TEM, area examined and total tactoid examined (specimen thicknesses $\approx 75\text{-}80$ nm).

<table>
<thead>
<tr>
<th></th>
<th>I-44paClay/PolyDCPD Composites</th>
<th>0.5wt%</th>
<th>2.0wt%</th>
<th>0.5wt%</th>
<th>2.0wt%</th>
<th>0.5wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Area Examined</strong></td>
<td></td>
<td>2.186x10^{-6}</td>
<td>2.28x10^{-6}</td>
<td>1.13x10^{-6}</td>
<td>1.614x10^{-6}</td>
<td>3.136x10^{-6}</td>
</tr>
<tr>
<td><strong>Total number of tactoids counted</strong></td>
<td>447</td>
<td>454</td>
<td>250</td>
<td>309</td>
<td>198</td>
<td></td>
</tr>
<tr>
<td><strong>Mean number of tactoids per unit area (mm$^{-2}$)</strong></td>
<td>2.05x10^{8}</td>
<td>1.99x10^{8}</td>
<td>2.21x10^{8}</td>
<td>1.91x10^{8}</td>
<td>6.31x10^{7}</td>
<td></td>
</tr>
</tbody>
</table>
was observed for I-44pa clay composites. The 0.5wt% I-44pa composite exhibited $2.05 \times 10^8$ tactoids (and platelets) per mm$^2$ while the 2.0wt% analog had $1.99 \times 10^8$ per mm$^2$. Increasing the clay loadings did not increase the number of clay fragments formed. Therefore, the samples with 2.0wt% loading experienced a higher dispersion resistance than the 0.5wt% loading, so the mean tactoid size did not decrease as much. During sonication, the same amount of energy was applied to each sample. Consequently, less energy was received per clay particle for the higher loadings, and therefore, less cavitation at those clay surfaces. Among the 0.5wt% loadings, the PEG-modified-PGW nanocomposite exhibited the smallest density of tactoids (and platelets), by about one order of magnitude, because this composite was sonicated for only 10 min prior to curing (e.g. $1/18^{th}$ the energy input to the other samples). Measurements of the tactoid size (mean number of platelets per tactoid, see Table 7.2) are consistent with the inferred dispersion resistances based on the measured density of tactoids (and platelets), Table 7.3. In particular, tactoid sizes increased with higher clay loadings indicating less delamination occurred. The clay that exhibited the smallest density of tactoids (and platelets), PEG-Modified-PGW, also exhibited nearly the largest tactoid sizes.
Summary

PolyDCPD/clay nanocomposites were synthesized by delaminating chemically modified montmorillonite clays (Nanomer: I-28, I-44pa and PEG-modified PGW) in the monomer DCPD, followed by curing. The clays were nanodispersed in low viscosity liquid DCPD by stirring and sonication, prior to curing. After dispersion, solid samples were prepared by ring-opening metathesis polymerization. A combination of SAXS, SANS/USANS, and TEM/HR-TEM were used to characterize these composites. The 0.5wt% I-28/poly DCPD composite did not exhibit any neutron scattering (SANS/USANS) or X-ray scattering (SAXS) peaks to indicate the presence of ordered structures. The 0.5wt% I-44pa/polyDCPD composite did not have an observable SAXS peak, but a very shallow peak was observed for the 1.0wt% I-44pa samples and a slightly larger peak was observed for the 2.0wt% composite. No SANS peaks were observed for any of these composites. Lack of a Guinier region in USANS data indicates the presence of interacting particles.

The resulting slopes of intensity vs. q in the low q- region for all clay/polyDCPD composites were in the range of -2.5 to -2.79, after subtracting the incoherent scattering background in SANS data. This indicates that clay tactoids exist as curved disks of various thicknesses (number of platelets varies), providing some fractal nature to disk shapes. SANS data were fitted to the stacked-disk model. Model predictions of the mean number of clay platelets per tactoid were tested, for the first time, by comparison to direct HR-TEM measurements of 200-450 different tactoids per sample. In the regime of low clay loadings (~ 0.5wt%), the model predictions are in good agreement with direct HR-TEM measurements. However, predictions from
the stacked-disk model deviate from HR-TEM results for high clay loadings (≥ 2 wt%). Deviation of the model at high clay loadings is a possible consequence of long-range interactions (important at high loadings), variation in tactoid thickness, irregular tactoid geometric shapes, and other related factors that are not taken into account by the model. Nevertheless, the stacked-disk model is a viable method to interpret SANS data from nanodispersed clay composites at low clay concentrations (~ 0.5wt%). The number of tactoids (plus individual platelets) present in the composites decreased slightly as the clay loading increased from 0.5 to 2.0wt% (when dispersed at equal sonication times). Further, the mean number of platelets per tactoid increased with clay loading. Both observations suggest, with increased clay loading, the resistance to exfoliation increases and/or less energy per clay particle is delivered during sonication at higher clay loadings. The $d$- spacings between platelets in the tactoids, present after nanodispersion, are much smaller, on average (1-1.5nm), than those in the clay particles at the start of the nanodispersion process.
REFERENCE


[16] Chaiko, D. J., 47th International SAMPE Symposium, May 12-16, **2002**.


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CHAPTER VIII

THREE DIMENSIONAL FINITE ELEMENT MICROMECHANICAL MODEL FOR STRESS ANALYSIS OF INTERCALATED AND FULLY EXFOLIATED CLAY/POLYDCPD NANOCOMPOSITES

The interactions between clay nanolayers and polymer molecules are of special interest due to their dramatic effects on the mechanical properties of the final composites [1-7]. Intercalated [8] and exfoliated [9, 10] clay/epoxy nanocomposites have been shown to possess superior physical mechanical properties. Clay composites have been reported to show improved properties including elastic modulus, tensile strength, barrier properties, and flame resistance [8-18].

Highly delaminated organically modified clay/polyDCPD composites were prepared in our laboratory [7]. The dispersed phase was organically modified montmorillonite in these composites.

A 3-D micromechanical model was developed to characterize intercalated and delaminated clay/ polyDCPD nanocomposites. Intercalated and highly delaminated clay/polyDCPD nanocomposites were modeled. Each cell in the model had its own
dimensions of length, width, and height. The properties of the polymer and the clay layers were assigned according to available data and to their geometrical position within the model. The effective composite properties and stress distributions in micro and nanoscale regions corresponding to each composite configuration were predicted according to the fundamental theory and governing equations relevant to the finite element model. A parametric study was performed to examine the mechanical responses of the clay composites as a function of the dispersion and distribution of the clay layers. The model was utilized to establish the dependence of the average stresses within the clay platelets, platelet surfaces, boundary regions, and polymer matrix with changing clay dispersion and distribution. This simulation predicts that improved dispersion of the clay platelets would significantly influence the stress state and deformation within composite constituents.

An improvement in composite elastic bending modulus was achieved when the clay platelets reached the highest degree of delamination [7]. Improvements in the impact resistance and high modulus of intercalated epoxy/clay have also been reported [8]. The interactions between clay platelets and the polymer matrix and the dependence of the average stress distribution and final mechanical properties are complex and are not yet well understood. This work represents the first attempt to use finite element models to predict properties of delaminated and intercalated clay nanocomposites. Studies of this type have not previously been reported in the literature. Micromechanical studies of stress transfer in a multiphase composite have the potential to lead to improved analytical models, failure theories, and understanding of the mechanical constitutive behavior of composites. Micromechanical modeling
may also help to define the best experimental approach to obtain improved composite properties.

**Literature Review**

Wu et al. performed finite element modeling to predict the elastic properties of particulate-reinforced (glass bead-reinforced) composites with a range of filler content [19]. Wu employed an axisymmetric spherical cell finite-element model, originally developed by Guild et al., for modeling elastic properties of rubber particles/epoxy composites with volume fractions of less than 0.5 [20, 21]. The incorporation of a spatial statistical technique, developed by Davy and Guild, is important feature of the axisymmetric FE cell model. This spatial method may provide a real description of a random distribution of filler particles in the matrix. This method was used to calculate and predict elastic properties of particulate-filled composites with a range of filler volume fractions above 0.5, which are of primary interest of dental clinical applications [19-21].

Kati et al. developed a 3-D finite element model of the mechanical response of nacre-based hybrid nanocomposites [22]. Nacre (mother-of-pearl), the inner layer of seashells, is a ceramic laminated bionanocomposite with exceptional fracture toughness and strength. Aragonite, a carbonate mineral with a more compact structure, is composed of triangular carbonate ion groups \((\text{CO}_3)^2\), with a carbon at the center of the triangle and the three oxygens at each corner. The organic layers in the composite play a significant role in the mechanical response of nacres to stresses. The authors used a three dimensional brick and mortar micro-architecture finite element model to
study how nonlinear mechanical responses of the organic component influence the final composite’s mechanical response. To build the model, the individual 3D hexagonal aragonite platelets were constructed based on available microstructural parameters, such as volume percent, composition, microstructure, and elastic modulus. The aragonite brick was constructed from four 8-noded isoparametric elements. The organic layer was attached to all faces of the aragonite bricks. Non-linear elasto-plastic models for organic component were applied to model the mechanical response of nacre [22].

Li et al. developed a finite element model using the Abaqus code (Abaqus, Inc.) to simulate an epoxy/continuous fiber reinforced composite [23]. Carbon fibers were coated with an elastomeric material. A second population of spherical elastomeric phases (two different diameters) were dispersed within the epoxy matrix in the model. The model was complicated due to the presence of multiple composite phases in the composite. The method of cells was utilized and a hexagonal element was used. The model predicted that the interphase elastomer properties would significantly influence the stress state within each of the three composite constituents [23].

Starr et al. used molecular dynamics simulations to study the effects of nano-sized and micron-sized fillers on the structure, dynamics, and mechanical properties of polymer melts and blends [24]. They examined the effects of a single nano-filler on the structure and properties of the surrounding melt. This model predicted that the polymer chain was elongated and flattened near the filler surface. They also developed a finite element model using object oriented finite element (OOF) software, developed
at National Institute of Standards and Technology (NIST) [24]. OOF is a new software tool that facilitates the prediction of mechanical properties using real or simulated structures as input. OOF allows users to assign specific constitutive properties, such as modulus, etc., to the various parts of the microstructure, and perform mechanical simulations using the finite element method.

Ghassemieh et al. developed a finite element model for micro-mechanical analysis of particulate filled composites under an external load [25]. The model was applied to predict the stress distribution in composites containing particulate fillers. The magnitudes and the location of the stress concentrations were found and used to predict the dominant mode of failure and the crack growth mechanism. The authors compared the model predictions with experimental data and demonstrated the range of the model’s validity [25, 26].

The only finite element modeling of clay composites that could be found was reported by Gusev et al. [27]. They developed a finite element model for permeability calculations with multi-inclusion computer models comprised of a random dispersion of non-overlapping platelets for barrier applications. Three-dimensional periodic computer models were comprised of a random dispersion of perfectly aligned and impermeable, round platelets in an isotropic matrix. The presence of nanoplatelets of atomic thickness, possessing a high aspect ratio, can lead to molecular transformations in the matrix [27a]. They concluded that these molecular transformations may give rise to changes in the local gas permeability coefficients, especially in the vicinity of the platelets [26].
In the present work, all simulations were performed using commercially available ANSYS (Version 6.1) software. This program was developed and marketed by Ansys, Inc. The software is comprised of three main sections: 1) Preprocessor; 2) Solution; 3) General post processor.

In the preprocessor, geometry is designed, the element type is chosen, material properties are assigned, and meshing is performed. The Preprocessor component includes: Element type, Real constants, Material properties, Sections, Modeling, Meshing, Checking controls, Numbering controls, Archive model, Coupling, Flotran setup, FSI setup, Loads, and Physics.

Boundary conditions are applied, once the model is built. The computation is then performed, using commands available in the Solution part. The Solution part consists of: Analysis type, Define Loads, Load setup, Solve, and FSI setup. The general postprocessor performs visualization of the calculations once the model has been solved for the particular boundary conditions. This postprocessor part includes: Data and files, Results summary, Read results, Failure criteria, Plot results, List results, Nodal calculations, Element tables, Path operation, Load case, Write results and Submodeling [28].

**Modeling Clay Nanocomposites**

The nanometer-sized clay platelets possess a random size distribution and can bend and twist, because of their flexible nature. They can be stacked in close proximity as tactoids or be well-distributed within the polymer matrix. Well-dispersed clay layers can be oriented by shear in a primary direction or have a random
directional distribution within the polymer matrix. All of these factors are important and present challenges to the FEM micromechanical simulation. First, three-dimensional models are required to simulate the geometrically complicated topology of the different size clay nanolayers dispersed in the polyDCPD matrix. Small, medium, and large sized clay nanolayers were incorporated into the model described here in an attempt to mimic the distribution found for clay platelets within a polymer matrix. The size and distribution of clay platelets was approximated from extensive TEM and HR-TEM studies. Secondly, the required 3-D modeling was computationally intensive. The curvature of the layers complicates the analysis of a representative volume cell.

Several factors make this simulation unique. This model is a three-dimensional model. The clay nanolayers are treated realistically as curved objects possessing a range of high aspect ratios. The model is unique in considering the size distribution and curvature of the clay platelets. It uses a complicated topological geometry. The matrix is discontinuous in the transverse direction and in most portions of the longitudinal direction. Well-defined elastic properties have been assigned to each component. The load can be applied to the model in any direction. The deformation, deformation vectors, stress distribution and its vectors at any location, can be displayed using visualization tools. Unique mechanical properties can be assigned to each different component in this model. This model can also be used to perform structural or thermal analysis.
Some drawbacks of this model are:

1. No interphase layer was employed.
2. Experimental properties for such an interphase layer are not known.
3. Experimental values for the adhesive bonding of the platelets or tactoids to the clay are not known so they couldn’t be used. Thus, perfect bonding was assumed.
4. Each platelet size distribution, volume fraction and platelet geometrical distribution must be independently remeshed. Thus, each calculation represents only that exact geometry employed.
5. Individual montmorillonite platelet mechanical properties are not known and how they vary with curvature is not known. Also, how the properties of a single platelet differ from tactoids of 2, 3, 4, 5, ..n platelets is not known.
6. Only single platelets were employed and tactoids (known to be present in real composites) were never used.
7. Platelets were never randomly distributed within the matrix with the work reported, herein. Instead, the different sized curved planes’ lateral dimensions were aligned.
Finite Element Modeling

The finite element model is a numerical procedure that can be used to obtain solutions to a large class of engineering problems, involving stress analysis, heat transfer, electromagnetism, and fluid flow [27]. In general, engineering problems are mathematical models of physical situations. Some mathematical models are described by differential equations with associated boundary conditions. The differential equations are derived by applying the fundamental laws and principles of nature to a system or to a control volume. These governing equations represent the balance of mass, force, or energy. An exact solution of these equations renders detailed behavior of a system under a given set of conditions [27].

There are many practical engineering problems for which exact, analytical solutions cannot be obtained. This inability to obtain an exact solution may be due either to the complex nature of the governing differential equations or to the difficulties that arise from dealing with the initial and boundary conditions. To handle such issues, numerical approximations are used. Numerical solutions approximate the exact solution only at discrete points called nodes. In contrast, analytical solutions show the exact behavior of a system at any point within the system. The first step of any numerical procedure is discretization. This process divides the medium of interest into a number of small subregions and nodes. There are two common classes of numerical methods: 1) finite difference methods and 2) finite element methods.

With finite difference methods, the differential equation is written for each node, and the derivatives are replaced by difference equations. This approach results in a set of linear equations that must be solved simultaneously. This method becomes
more difficult for complex geometries, for complex boundary conditions, and for materials with nonisotropic properties. In contrast, the finite element method uses an integral formulation rather than a difference equation to create a system of algebraic equations. Moreover, an approximate continuous function is assumed to represent the solution for each element. The complete solution is then generated by connecting or assembling the individual solutions, allowing for continuity at the boundaries of adjacent elements [27].
Geometry of the Model

The geometries presented here are built to mimic an intercalated and well-dispersed clay/polyDCPD composite with net platelet orientation in the x-direction. Figure 8.1.a depicts the intercalated model and Figure 8.1.b shows the exfoliated composite model. The dimension of this model is 0.5 x 0.5 x 1 micron.

8.1.a. A more dispersed, fully exfoliated oriented clay/polyDCPD nanocomposite.

8.1.b. An intercalated clay/polyDCPD nanocomposite.

Figure 8.1. Models of Clay/polyDCPD Composites.
These models have the following features:

1) Clay layers are simulated realistically. The high aspect ratio (200 to 1000) of the clay nanolayers and the bending of the layers have been considered. In order to mimic the real composite, the size distribution of the clay platelets is modeled using platelets of three sizes. The thickness for each of the sizes is constant and set equal to 1 nm, while the lateral dimension is varied and is equal to 200 nm, 500 nm, and 1000 nm, respectively (Figures 8.2 and 8.3).

2) Seven clay platelets were used in the intercalated and in the exfoliated nanocomposites. These seven clay platelets have the same geometry and dimensions in both intercalated and exfoliated composite models. Thus, results regarding the effect of the clay layers’ dispersion and distribution within the polymer matrix on the stress and deformation within the composite block could be more easily compared.

3) A clay tactoid with some polymer infused into it was placed in the composite block to mimic an intercalated nanocomposite. Clay platelets were located in close proximity to the top and the bottom of the tactoid. These platelets maintained their structural registry when the clay layers were expanded. Polymer molecules have diffused into the middle of the tactoid causing them to splay apart. This simulation of the intercalation within tactoids was obtained based on platelet arrangements seen in direct observations from TEM micrographs (Figure 8.4).

4) Clay layers were well dispersed as platelets and they were separated by large distances in the exfoliated nanocomposite.
Figure 8.2. One clay platelet with a thickness of 1 nm and an aspect ratio of 1000.

Figure 8.3. Three clay platelet sizes are present. Thicknesses are 1 nm each, but the lateral dimensions are 200 x 100 nm, 500 x 500 nm and 1000 x 1000 nm.
Figure 8.4. A disrupted tactoid, where three bottom platelets have ordered structures. Some diffusion of the polymer within the middle of the tactoid is observed.

Figures 8.1.a and 8.1.b show a representative volume cell and its cross section in the x-y plane. The dimensions of the bottom plane are 0.5 x 1 microns. The thickness of the model in the y plane is 500 nm. Figures 8.5 and 8.6 show the simulation of clay layers within the intercalated and exfoliated nanocomposites.
Figure 8.5. Ordered structure and orientation of clay platelets within the intercalated nanocomposite model.

Figure 8.6. Orientation of clay platelets and their geometry within the polymer matrix in the exfoliated model.
Clay platelets were generated outside of the composites’ unit cell. Then, each was moved inside the composite using a translational move command. Now, at the space that the platelet is located, there are two volumes, polymer matrix and clay platelet. So a copy of the layer was made and the volume of this copy was subtracted from the volume of the composite block. At this point, the clay platelet is inside the polymer matrix, but it is still not adhered to the matrix. Perfect adhesion between clay platelets and the polymer matrix was specified using the glue command. This process was repeated for all seven clay platelets in each composite block.

Meshing

The most common types of elements used for 3-D FE simulations are hexagonal and tetrahedral elements [28, 29]. Due to the intricate geometry induced by the curvature of the clay platelets and limitations on the number of generated elements which could be employed, the hex element was not used. Tetrahedral elements were used to mesh the composite blocks. Figure 8.7 shows a tetrahedral element with four nodes of $P_1$, $P_2$, $P_3$, and $P_4$. The three directions are $P_1P_2$, $P_1P_3$, and $P_1P_4$, which form a right-handed coordinate system. If the coordinates of the corner points are $P_i(x_i, y_i, z_i)$, then the general tetrahedron can be mapped onto the standard tetrahedron in 3-D special coordinates (Figure 8.8) by means of a the linear transformation.
Figure 8.7. A tetrahedral element with four nodes of $P_1, P_2, P_3, P_4$.

Figure 8.8. Standard tetrahedron in curvilinear coordinates.
The Jacobian of the matrix formed from equations (8.1) to (8.3) is numerically equal to six times the volume of the tetrahedron. This approximation can also be applied to the standard tetrahedron.

A complete linear approximation in three space variables (curvilinear coordinate):

\[ u(\xi, \eta, \zeta) = \alpha_1 + \alpha_2 \xi + \alpha_3 \eta + \alpha_4 \zeta \]  

(8.4)

is uniquely determined by the values of u at the four node points and satisfies the conditions of completeness, symmetry and conformity. The element matrices can be formed from basic matrices. This is applied to the calculation of the stress problems in three dimensions [29].

Tetrahedral elements were used to discretize the composite block and the clay platelets. Each tetrahedral element was translated to a Brick 45 element in the Ansys software (Figure 8.9). The Free Mesh tool in Ansys was used to generate the
unstructured grid. A large number of elements were needed at the corners of the clay platelets and in regions where the curvature of each clay platelet was more significant.

The mesh generation operation produced information about the elements and meshing including the number of elements. 124,800 elements were used for the exfoliated and oriented model (Figure 8.10.a) while 54,600 elements were used for the intercalated model (Figure 8.10b).

![Tetrahedral element translated in Ansys as Brick 45.](image)

Figure 8.9. Tetrahedral element translated in Ansys as Brick 45.

Figures 8.10a and 8.10b show the meshed unit cell of exfoliated and intercalated models. Meshed layers within the exfoliated and intercalated nanocomposite model are demonstrated in Figure 8.11a and 8.11b.
8.10.a. A meshed exfoliated clay/polyDCPD nanocomposite model.

8.10.b. A meshed intercalated clay/polyDCPD nanocomposite model.

Figure 8.10. Meshed Models of Clay/polyDCPD Composites.
8.11.a. Meshed exfoliated clay platelets in the nanocomposite model.

8.11.b. Meshed intercalated clay platelets in the nanocomposite model.

Figure 8.11. Meshed Models of Clay Platelets in the Clay/polyDCPD Composites.
Material Properties

In order to describe the stress-strain behavior of the model, material characteristics and properties must be associated with appropriate groups of elements after the geometry has been meshed. The material properties data were fed into the model. Material model numbers were generated and used to assign elastic bending moduli and Poisson ratio for each platelet group of elements and for each polyDCPD matrix group of elements.

Only linear elastic properties were used in this analysis. Of course, polyDCPD actually has viscoelastic properties. The stress-strain relationship can be linear or non-linear. The stress-strain behavior of many materials is described by a linear relationship when the applied stresses are below their yield point. The linear elastic model (Hook’s law) is an approximation for the present work. Perfect adhesion (continuity displacement) between clay platelet surfaces and the polyDCPD matrix was assumed. The glue command was used to adhere the surfaces of the platelets to the surrounding matrix. This allowed for stress transfer from the matrix to the clay platelet and vice versa. The values for elastic bending moduli and Poisson ratios were put into the model (Table 8.1). The elastic bending modulus of clay platelets was assumed equal to the elastic bending modulus of the clay particles reported by Maseneli-Varlot et al. [30]. The value for the elastic bending modulus of pure polyDCPD (cured in the same manner) was obtained from laboratory measurements on a prepared polyDCPD sample [7].

At this point, the geometry, elements, nodes, and material properties have all been created. Next, the boundary conditions must be applied. It is possible to apply
any stress-strain boundary condition to the geometry which has been constructed. In addition, if the thermal properties of the material have been entered into the model, thermal analysis of the micromechanical model is possible.

Table 8.1. Material properties

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic Bending Modulus, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PolyDCPD</td>
<td>140</td>
</tr>
<tr>
<td>Montmorillonite Clay</td>
<td>0.93</td>
</tr>
</tbody>
</table>
Von Mises Stresses

When the model has only one functional direction of strain and stress, comparison with an allowable value is straightforward. However, when there is more than one component in stresses or strains, the components are normally combined into a single number in order to allow a comparison with an allowable value. This single combined number is the von Mises stress for any given point in the material.

Combined strains are defined as:

\[
\begin{vmatrix}
\varepsilon_x - \varepsilon_0 & \varepsilon_{xy} & \varepsilon_{xz} \\
\varepsilon_{xy} & \varepsilon_y - \varepsilon_0 & \varepsilon_{yz} \\
\varepsilon_{xz} & \varepsilon_{yz} & \varepsilon_z - \varepsilon_0
\end{vmatrix} = 0
\]  (8.5)

where \( \varepsilon_0 \) is the principal strain. The von Mises, or equivalent strain, \( \varepsilon_{\text{eq}} \) is computed using equation (8.6):

\[
\varepsilon_{\text{eq}} = \frac{1}{1+\nu'} \left[ \frac{1}{2} (\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_2 - \varepsilon_3)^2 + (\varepsilon_3 - \varepsilon_1)^2 \right]^{1/2}
\]  (8.6)

where the material’s Poisson ratio is 0.5 for elastic and thermal strains, plastics, creep, and hyperelastic strains.
Combined Stresses

The principal stresses ($\sigma_1, \sigma_2, \sigma_3$) are calculated from the stress components by the cubic equation:

$$\begin{vmatrix}
\sigma_x - \sigma_0 & \sigma_{xy} & \sigma_{xz} \\
\sigma_{xy} & \sigma_y - \sigma_0 & \sigma_{yz} \\
\sigma_{xz} & \sigma_{yz} & \sigma_z - \sigma_0
\end{vmatrix} = 0$$

(8.7)

where $\sigma_0$ is the principal stress.

The three principal stresses are labeled $\sigma_1$, $\sigma_2$, and $\sigma_3$ (Figure 8.12). The principal stresses are ordered so that $\sigma_1$ is the most positive (tensile) and $\sigma_3$ is the most negative (compressive).

Figure 8.12. Primary stress components.
The von Mises, or equivalent, stress $\sigma_e$ is calculated from:

$$\sigma_e = \left[ \frac{1}{2} (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right]^{1/2}$$

(8.8)

When $\nu = \nu'$, the equivalent stress is related to the equivalent strain through the following equation:

$$\sigma_e = E \varepsilon_e$$

(8.9)

Where $E$ is the Young’s modulus [28].

**Finite Element Analysis**

 Structural analysis was performed on the micromechanical model using the finite element software package Ansys 6.1. Results were visualized using the postprocessor tool in Ansys. Distributions of stress and deformation were studied by applying tensile stresses in the transverse and longitudinal directions. A tetrahedral element was used, which was subsequently translated in Ansys to a Brick 45 element.

A uniform tensile stress of 20,000 N/m$^2$ was applied on the surfaces of the micromechanical model and both the deformation and the stress distribution were examined. The first boundary condition is shown in Figure.8.13, in which the bottom surface was stationary and a uniform tensile stress of 20,000 N/m$^2$ was applied to the top surface.
Boundary Condition 1

Constraints were set on the bottom plate \((y = 0)\) as \(U_x = U_y = U_z = 0\). A uniform tensile stress of 20,000 N/m\(^2\) is applied on the top surface \((x=0, z=0, y = 5)\) of the model (Figure 8.13).

Figure 8.13. Applied boundary condition.
Results

Deformation in the y Direction

The results of deformation in the y direction for the polymer, intercalated model, and exfoliated model are shown in Figures 8.14, 8.15.a, 8.15.b., 8.16.a. and 8.16.b. The intercalated nanocomposite model predicted a deformation in the y direction of $0.115 \times 10^{-4}$ m. This is comparable to the deformation of pure polyDCPD ($0.114 \times 10^{-4}$ m) in the y direction under a 20,000 N/m² tensile stress. No improvement in the y direction deformation under load was observed for the intercalated nanocomposite. The y deformation of the exfoliated and oriented nanocomposite was $0.767 \times 10^{-7}$ m and was three orders of magnitude smaller than that of polyDCPD. The model predicted major improvements in the deformation under tensile stress for the fully exfoliated and oriented model.

Figures 8.17.a., 8.17.b., 8.18.a., and 8.18.b. show the deformation vectors of the composite models in the y direction for the intercalated and exfoliated models. A non-uniform deformation distribution in the intercalated model was observed (Figure 8.17.a). Figure 8.17.b shows the deformed and undeformed meshed intercalated model under the tensile stress. The deformation within the exfoliated nanocomposite was uniform (Figure 8.18.a). Figure 8.18.b. shows the deformed and undeformed meshed exfoliated model under tensile stress.

Figure 8.19.a. shows the deformation of platelets in the intercalated system under boundary condition 1. The layers closest to the top surface (where the load was applied) have the highest deformation of $0.971 \times 10^{-5}$ m while platelets closest to the stationary bottom surface have the lowest deformation of $0.227 \times 10^{-5}$ m. Since the
overall deformation of the intercalated model was $0.114 \times 10^{-4}$ m, it appears that the deformation of the layers is smaller than the deformation of the composite.

Figure 8.19.b. shows the deformation of the layers in the exfoliated model. The deformation of the platelets closer to the top surface, where the load is applied, are larger, $0.605 \times 10^{-7}$ m. The lowest deformation was observed in the platelet closest to the bottom stationary surface ($0.101 \times 10^{-7}$ m). In this case, the deformation of the composite model was larger than the deformation of the platelets.

Figure 8.14. Deformation of polyDCPD model in the y direction under a 20,000 N/m² tensile stress, $U_y = 0.114 \times 10^{-4}$ m.
8.15.a. Distribution of the deformations.

8.15.b. Deformed-undeformed geometry of the meshed intercalated geometry.

Figure 8.15. Deformation of the intercalated nanocomposite in the y direction under a 20,000 N/m² uniform tensile stress. $U_y=0.115 \times 10^{-3}$ m.
8.16.a. Distribution of the deformations.

8.16.b. Deformed-undeformed geometry of the meshed exfoliated geometry.

Figure 8.16. Deformation of the exfoliated and oriented nanocomposite in the y direction under a 20,000 N/m$^2$ uniform tensile stress, $U_y = 0.767 \times 10^{-7}$ m.
8.17.a. Overall deformation vectors of the intercalated composite model.

8.17.b. Deformation vector of the clay layers.

Figure 8.17. The deformation vectors of the intercalated model in the y direction.
8.18.a. Overall deformation vectors of the exfoliated and oriented composite model.

8.18.b. Deformation vector of the clay layers.

Figure 8.18. The deformation vectors of the exfoliated model in the y direction.
8.19.a. Deformation of layers in the y direction in the intercalated nanocomposite model.

8.19.b. Deformation of layers in the y direction in the exfoliated and oriented nanocomposite model.

Figure 8.19. Deformation of layers in the y direction in the nanocomposite models.
Stress Distribution

**Stress in the y Direction**

Stress distributions were examined using the postprocessor tool in Ansys. The bottom surface was fixed and a uniform tensile stress of 20,000 N/m$^2$ was applied in the y direction to the top surface of the model. The maximum stresses were found in the bottom of the polyDCPD (Figure 8.20). The maximum overall stress in this model was 26,350 N/m$^2$. Figure 8.20 shows the stress distribution in the y direction for the intercalated composite model. The intercalated model showed higher stress concentrations on and near the surfaces of the platelets. The maximum stress calculated was 292,324 N/m$^2$. In order to improve visualization, the maximum stress was set manually to 25,000 N/m$^2$. The edges of the clay platelets and the surfaces of the platelets (white and gray areas) have the highest stress concentrations. Some degree of reinforcement was found in the bottom left portion of the composite where the stresses are on the order of 12,500 to 15,625 N/m$^2$. If a failure criteria had been considered, clay/polyDCPD debonding would have occurred.

The model’s prediction of the stress distributions in the exfoliated model is illustrated in Figure 8.21. The stress distribution is uniform and is on the order of 17,667 N/m$^2$. Figures 8.22 and 8.23 show the stress distributions on the platelets of the intercalated and exfoliated models, respectively. The maximum stress on the surface of platelets in the exfoliated composite was 22,000N/m$^2$ (Figure 8.24), comparable to the applied stress. However, the maximum stress on the clay platelets in the intercalated composite was 514,837 N/m$^2$, which is orders of magnitude higher than the highest in the stress on the exfoliated composite.
Figure 8.20. Stress distribution in polyDCPD model in the y direction when a uniform tensile stress of 20,000 N/m\(^2\) is applied in the y direction.

Figure 8.21. Stress distribution in the y direction for the exfoliated and oriented model when a uniform stress of 20,000 N/m\(^2\) is applied in the y direction.
Figure 8.22. Stress in the y direction on the platelets for the intercalated model when a uniform stress of 20,000 N/m$^2$ is applied in the y direction.

Figure 8.23. Stress in the y direction on the platelets for the exfoliated models when a uniform stress of 20,000 N/m$^2$ is applied in the y direction.
Figure 8.24. Stress distribution in y direction for the intercalated model when a uniform stress of 20,000 N/m² is applied in the y direction.
Von Mises Stresses

Figure 8.25 shows the distribution of the von Mises stresses in the intercalated model. There are points of stress concentration around the edges of the clay platelets. The maximum stress was $14.5 \times 10^5$ N/m$^2$, which was on the surface of the platelets and around the edges. Some reinforced regions were observed with the maximum stresses in the range of $11,111$ N/m$^2$. These were primarily found in regions rich in clay. Von Mises stresses are more uniformly distributed when the clay platelets are aligned and well exfoliated (Figure 8.26). The maximum stress calculated by the model was $27,000$ N/m$^2$. 
Figure 8.25. The distribution of von Mises stresses in the intercalated model. The points of stress concentration around the edges of the clay platelets were observed.

Figure 8.26. The distribution of von Mises stresses in the exfoliated model. Uniform stress distributions with the model were predicted.
Boundary Condition 2

The left end y-z plane was constrained in this simulation (y=z=0, x = -5), \( U_x = U_y = U_z = 0 \). A uniform tensile stress of 20,000 N/m\(^2\) was applied in the x-direction on the y-z plane at the right end of the model, Figure 8.27, (y=z=0, x = 5).

Constraints: \( U_x = U_y = U_z = 0 \)

Figure 8.27. Applied boundary conditions

Uniform tensile stress of 20,000 N/m\(^2\)
**Deformation in the x Direction**

Figures 8.28 to 8.30 depict the deformation predictions for poly(DCPD), the intercalated model and the exfoliated model. The predicted deformation of polyDCPD under a 20,000 N/m² in the x-direction is \( U_x = 0.212 \times 10^{-4} \) m (Figure 8.28). The x-direction deformation of the intercalated model under the same boundary conditions is \( U_x = 0.256 \times 10^{-4} \) m (Figure 8.29). This deformation is comparable to the deformation predicted for pure polyDCPD. No improvement in deformation was predicted when the clay platelets are in close proximity to one another (intercalated). The x-deformation of the exfoliated composite model (Figure 8.30) was \( U_x = 0.141 \times 10^{-6} \) m, some two orders of magnitude smaller than the deformation of polyDCPD under the same boundary conditions. The model predicts major decreases in x-direction deformation when the clay platelets are more exfoliated within the polyDCPD matrix. The improvement was more significant when the stress was applied in the y direction. The improvement was three orders of magnitude greater versus polyDCPD. The intercalated model exhibits very non-uniform deformations under this boundary condition (Figure 8.29). The model demonstrated that less deformation occurred where the clay platelets were present.

Figure 8.31 shows the platelet deformations within the intercalated composite model. Smaller platelets exhibited larger deformations. The platelets that were closer to the surface where the load was applied exhibited larger deformations. The minimum deformation of the platelets was \( 0.191 \times 10^{-5} \) m while the maximum was \( 0.65 \times 10^{-5} \) m. This maximum deformation was smaller than the overall deformation for the intercalated composite model. Figure 8.32 depicts the exfoliated composite’s x-
Figure 8.28. The deformations of polyDCPD in the x-direction when a tensile stress of 20,000 N/m$^2$ was applied in the x direction ($U_x = 0.212 \times 10^{-4}$ m).
8.29.a. The distribution of the deformations in the intercalated model when a 20,000 N/m² tensile stress was applied in the x direction.

8.29.b. Deformed and undeformed geometry of the meshed intercalated geometry.

Figure 8.29. The deformations of the intercalated model in the x-direction when a 20,000 N/m² tensile stress was applied in the x direction (Uₓ=0.256x10⁻⁴ m).
8.30.a. The distribution of the deformations when a 20,000 N/m² tensile stress was applied in the x direction.

8.30.b. Deformed and undeformed geometry of the meshed exfoliated model.

Figure 8.30. The deformations of the exfoliated model in the x-direction when a 20,000 N/m² tensile stress was applied in the x direction ($U_x = 0.141 \times 10^{-6}$ m).
8.31.a. The distribution of the deformations on the clay platelets when a 20,000 N/m² tensile stress was applied in the x direction on the intercalated composite model.

8.31.b. The deformed and undeformed geometry of meshed clay platelets.

Figure 8.31. Deformations of clay platelets within the intercalated composite model when a 20,000 N/m² tensile stress was applied in the x direction.
8.32.a. Distribution of stresses on the surface of the clay platelets when a 20,000 N/m² tensile stress was applied in the x direction on the exfoliated composite model.

8.32.b. The deformed-undeformed of meshed clay platelets.

Figure 8.32. Deformations of clay platelets within the exfoliated composite model when a 20,000 N/m² tensile stress was applied in the x direction. Deformation of the clay platelets.
The minimum deformations occurred on the platelets close to the fixed surface. These were on the order of $10^{-11}$, which essentially means no deformation. The maximum deformations were predicted for the platelets adjacent to the composite surface where the stress was applied ($0.126 \times 10^{-6}$ m). The deformation of the platelets in the exfoliated model were slightly smaller than the overall deformation.

The intercalated model predictions of the overall deformation vectors of the clay platelets are shown in Figures 8.33 a and b. Here, the clay platelets have the smallest overall deformations. The maximum overall deformation found in this model’s platelets was $0.256 \times 10^{-4}$ m. The minimum overall deformations of the clay platelets were in the range of $0.205 \times 10^{-5}$ m to $0.569 \times 10^{-5}$ m. The deformations of the intercalated model were nonuniform, smaller in the location where the clay cluster is found and larger in the locations without platelets. The overall deformation vectors of the clay platelets within the exfoliated composite model and the overall deformation vector of the exfoliated model are shown in Figures 8.34 a and b. The minimum deformation was calculated as $0.157 \times 10^{-7}$ m and the maximum deformation was predicted to be $0.141 \times 10^{-6}$ m. The clay platelets in close proximity to the surface where the stress was applied have the largest deformation while the platelets in the vicinity of the fixed plate have the minimum deformation. The overall deformations for the exfoliated composite model under this boundary condition were uniform.
8.33.a. Deformation vectors of the platelets when a 20,000 N/m² tensile stress was applied in the x direction on the intercalated composite model.

8.33.b. Deformation vectors of the intercalated model.

Figure 8.33. The deformation vectors of the clay platelets within the intercalated model and the overall deformation vectors of the intercalated model when a 20,000 N/m² tensile stress was applied in the x direction.
8.34.a. Overall deformation vectors for clay platelets in the exfoliated model when a 20,000 N/m² tensile stress was applied in the x direction.

8.34.b. Overall deformation vectors of the exfoliated composite model.

Figure 8.43. The overall deformation vectors of the clay platelets within the exfoliated composite and the overall deformation vectors of the exfoliated model under 20,000 N/m² tensile stress in the x direction.
**Stresses**

**Stress in the x Direction**

A 20,000 N/m² uniform tensile stress was applied to both the intercalated and exfoliated models in the x-direction on the y-z plane at x=5 (right surface) with the y-z plane fixed at x=0 U_x=U_y=U_z=0 (left surface). Figure 8.35 demonstrates the model’s prediction for the stress distribution in the x direction in the pure polyDCPD. The maximum stresses were observed close to the y-z plane x=0 (left surface) where constraints were applied due to reaction forces. The maximum stress was 23,724 N/m², which is in the range of the 20,000 N/m² applied stress. The stress distribution in the x direction for the intercalated model was very non-uniform (Figure 8.36). The maximum stress was 1.06x10⁶ N/m², which is very large. If a failure criteria had been considered, this composite would have failed before reaching this stress. In order to facilitate visualization of the stress distribution within the composite model, the maximum stress was manually set at 25,000 N/m². The stresses around the edges of the platelets (gray area) and on the surfaces of the platelets (white area) well exceeded this manually set limit. The stresses were on in the order of 10⁶ N/m².

A local low stress region was observed in the intercalated composites around the clay platelets. The composite in this region appears to be reinforced by the clay platelets. The stress distribution of the exfoliated composite model is shown in Figure 8.37. The maximum stress, 42,532 N/m², was found on the left surface of the model where constraints were applied. This is due to the reaction forces. The stress distribution within the exfoliated model was uniform and was in the range of 18,000 N/m². These results also indicated that the dispersion of the nanophases had a great
effect on their final mechanical response under stress. Intercalated clay regions within an intercalated clay composite can have reinforcing effects since the low stress regions are found around the clay clusters. These reinforced regions are local, so large clay volume fractions are necessary to reach an overall reinforcement. This is in agreement with the need for high clay volume fractions to achieve reinforcement, when no exfoliation has occurred.

Figure 8.35. The stress distributions in the x direction in the polyDCPD model when a 20,000 N/m² tensile stress was applied in the x-direction.
Figure 8.36.  The stress distributions in the x direction in the intercalated composite model when a 20,000 N/m² tensile stress was applied in the x-direction.

Figure 8.37.  The stress distributions in the x direction in the exfoliated composite model when a 20,000 N/m² tensile stress was applied in the x-direction.
Von Mises Stresses

Von Mises stresses are the most commonly used measure of an overall stress distribution within a mechanical model. Figure 8.38 shows the distribution of the von Mises stress for the intercalated composite model. The maximum stress of $1.2 \times 10^6$ N/m$^2$ was located on the surface of the clay platelets. The polymer regions in the vicinity of clay platelet clusters exhibited reduced stresses. The maximum predicted stress in these regions was 8,333 N/m$^2$. Due to the large stress gradients on the surface of the platelets and low stresses in the polyDCPD in the vicinity of the platelets, failure was predicted to occur at the polymer/clay interface for this model. The distribution of the von Mises stresses in the exfoliated model is depicted in Figure 8.39. This model predicted a more uniform stress distribution. The maximum stress was predicted to be 31,524 N/m$^2$.

The von Mises stresses on the surface of the clay platelets were examined. The stresses on the platelets for the intercalated model were large, with a maximum of $1.83 \times 10^6$ N/m$^2$ (Figure 8.40). The maximum stresses were located in the top layers on all of the platelets and were in the range of $10^6$ N/m$^2$. The platelets in the bottom still exhibited high stresses, but the stresses were predicted to be in the range of 73,375 to 270,530 N/m$^2$. Figure 8.41 shows the distribution of the von Mises stresses on the surface of the platelets for the exfoliated model. The maximum stress was 21,345 N/m$^2$, which was in the range of the 20,000 N/m$^2$ applied stress. The stresses on the surfaces of all platelets were almost in the same range.
Figure 8.38. Von Mises stresses in the intercalated model when a 20,000 N/m² stress was applied in the x direction.
8.39.a. A uniform distribution of stresses within the exfoliated model.

8.39.b. The distribution of stress within the exfoliated composite model and on the clay platelets.

Figure 8.39. Von Mises stresses in the exfoliated model when a 20,000 N/m² stress applied in the x direction.
Figure 8.40. The von Mises stresses on the surface of the clay platelets when the intercalated model is subjected to a 20,000 N/m² tensile stress in the x direction.

Figure 8.41. The von Mises stresses on the surface of the clay platelets when the exfoliated model is subjected to a 20,000 N/m² tensile stress in the x direction.
Summary

Micromechanical models were developed to examine the effect of clay nanodispersion on the final mechanical properties of the composite. Two models were developed. Each model contained exactly seven clay platelets with the same dimensions and geometry. The characteristics of the model were chosen as close as possible to those of the actual composite. The flexibility of the platelets was taken into consideration, in spite of the complexities that this introduced into the model. A polyDCPD control model was developed and composite model results were compared to this baseline case. Clay platelets were assumed to have high aspect ratios, from 200 to 1200. These values were obtained from extensive experimental data, reported in previous chapters of this work. The polyDCPD and clay platelets were assumed to be elastic. This could be a good approximation for the alumina-silicate clay platelets as well. More experiments on the clay platelet’s elastic bending modulus and viscoelastic properties at the nanoscale level are necessary to identify their mechanical properties.

In these computations, it was predicted that:

- When both the intercalated and exfoliated models were subjected to the same boundary conditions, the deformations were reduced in the exfoliated composite when compared to the control polyDCPD model. No improvement in the deformation was observed for the intercalated model. The improvement in the deformation of the exfoliated model was larger when the model was subjected to the same tensile stress in the y direction.
• The overall deformation vectors showed a more uniform deformation of the exfoliated and ordered composite and a more nonuniform overall deformation for the intercalated composite model.

• The intercalated model, when subjected to both transverse and longitudinal stresses, developed a large stress concentration area around the edges of the platelets and on the surface of the platelets. Low stress regions were observed around the vicinity of the cluster of clay platelets (reinforcing effects). This huge stress gradient will lead to catastrophic damage to the composite and platelet/polyDCPD debonding.

• The von Mises stresses showed a uniform stress distribution for the exfoliated and ordered composite model. No point of exceptional stress concentration was observed for either applied boundary condition.

• Von Mises stresses were reduced for the intercalated model around the clay platelet cluster.
REFERENCES


CHAPTER IX

CONCLUSIONS

Highly delaminated montmorillonite clay/polyDCPD nanocomposites were prepared by mixing clay into DCPD monomer (3 hours of sonication) followed by curing. A Ru-based Grubbs’ catalyst was used to polymerize the monomer in these dispersions via ring-opening metathesis polymerization. Three types of commercial clays were employed: Nanomer\textsuperscript{®} I-28 (montmorillonite modified by trimethyloctadecyl ammonium ion), Nanomer\textsuperscript{®} I-44pa (montmorillonite modified by dimethyldecyl ammonium ion), and polyethylene-modified PGW (Polymer Grade Montmorillonite). The degree of clay delamination in the composites was examined by XRD and TEM. The XRD peaks of the I-44pa clay/polyDCPD composites (1-5wt\%) disappeared after simple mixing of the clay into the monomer and curing. TEM studies of the I-44pa clay composites showed that clay remained as particles in the composite. XRD alone can not be used as a criteria for exfoliation and delamination of clay composites. This is more significant when the clay concentration is low and when the tactoids are curved. Fluorescent confocal microscopy using a fluoroprobe was used for the first time to study the state of clay in liquid DCPD.
Flexural moduli and elastic bending moduli of the I-28 clay composites containing low clay weight percentages (0.5 and 1 wt%) were greater than those of the pure polyDCPD. Further increasing the clay concentration did not cause further improvement in the moduli of the composites. The glass transition temperatures of the composites with low clay concentration were increased but further increases in clay concentration did not improve the Tg. If all of the composites were as highly delaminated as the 0.5wt% sample and their spatial dispersions were excellent, the flexural moduli and strengths might continue to increase as the wt% of clay went up. However, as the clay loading increased, the extent of exfoliation/delamination decreased.

Viscosity measurements were performed on the clay/DCPD dispersions. The flow behavior changed from Newtonian to non-Newtonian with increasing clay concentration and upon generating clay platelets and small tactoids. The initial viscosities increased progressively when more platelets and tactoids were produced. Thixotropic flow was observed with delaminated clay dispersions and became more pronounced with increasing clay concentration. Flow behavior showed a yield stress followed by a shear thinning flow behavior with increasing clay concentration and increasing delamination. Alignments of clay platelets and tactoids in the dispersion under shear were captured by fast in-situ polymerization of the monomer in dispersions under shear. A 5wt% I-28 clay composite was subjected to shear in the neutron beam of NIST’s 30m small angle neutron scattering facility. Anisotropic scattering due to the clay alignment was not detected by the SANS instrument. The reason for this is not yet understood.
The surface of a highly delaminated 2wt% clay I-28/polyDCPD composite was subjected to a cold oxygen plasma. The corrosive oxygen plasma oxidized the surface and removed the organic polymer, causing the clay platelets and tactoids to protrude from the surface as nanowalls. These clay platelets and tactoids were randomly oriented and were 90-980 nm apart (highly delaminated).

Both X-ray and neutron scattering were used to characterize clay nanocomposites. The SAXS graphs of $Iq^2$ vs. $q$ for I-28 clay/polyDCPD composites did not show a peak. Thus, ordered structures were not present. SAXS data from the 0.5 and 1wt% I-44pa clay/polyDCPD composites did not exhibit peaks, but the 2 wt% I-44pa/polyDCPD composite showed a shallow peak indicating the presence of tactoids with a wide range of $d$-spacings. The $Iq^2$ SANS graphs of 0.5, 1, 2 wt% I-28 clay composites and 0.5, 1, 2 wt% I-44pa did not exhibit any peaks. Both techniques verified the existence of a highly exfoliated composite containing a mixture of platelets and tactoids. The composite containing 0.5 wt% clay I-28 showed the highest degree of delamination.

The neutron scattering data were fitted to the stacked disk model developed by Ho and co-workers at the National Institute of Standards and Technology. This model predicted the number of platelets per tactoid using parameters obtained from other techniques. The average number of platelets per tactoid was calculated by fitting the neutron scattering data to the stacked disk model. The clay dispersion and distribution in the composites were quantitatively evaluated both by fitting neutron scattering data to the stacked disk model and by the examination of a large number of tactoids (200-400) by HR-TEM. The stacked disk model prediction was consistent with the results
of neutron scattering data for lower clay concentrations. As clay concentration increased, the model predictions showed pronounced deviations from the results of HR-TEM analysis. These deviations could be due to long-range structural factors, which were not taken into consideration by the model and the curvature and bending of the clay tactoids that were not included in the model calculations. HR-TEM is also a local technique and only a mm sized region can be investigated. In contrast, SANS is not a local technique and a cm sized region can be examined. The number of clay platelets per tactoid, the average number of tactoids per unit area, and the average $d$-spacings were obtained from a quantitative HR-TEM analysis. An increase in the average number of tactoids per unit area was not observed when the clay concentration increased. The average $d$-spacings of clay tactoids were in the range of 12-15Å after dispersion of organically-modified montmorillonite in DCPD and curing. These $d$-spacings correspond to unmodified montmorillonite. Degradation of the alkyl ammonium ions at elevated curing temperatures or incomplete ion exchange of the starting clay could account for these $d$-spacings.

Micromechanical finite element models were developed to predict the stress-strain behavior of the intercalated and exfoliated nanocomposites. The same seven platelets were used in both models. The thickness of the clay platelet layers were 1 nm; they were curved, and they had a range of size distributions to mimic the actual clay platelet’s shape and geometry. The clay layers in the intercalated model were in close proximity in the form of a tactoid with some polyDCPD infused. The clay platelets were more dispersed and oriented in one direction in the exfoliated composite model. Two types of boundary conditions were applied. Constraints were set on the $x$-
z plane at y=0, and a uniform 20,000 N/m$^2$ was applied at y=5 to the top plate in the transverse direction, in the first boundary condition. The y-z plane was fixed and a uniform tensile stress of 20,000 N/m$^2$ was applied in the x direction at x=5 in the longitudinal direction for the second boundary condition. Reduced deformations were predicted for the exfoliated nanocomposite model by the model both under longitudinal and transverse tensile stress. Deformation vectors were uniform and the deformation of platelets was almost the same as the overall deformation of the exfoliated composite. No improvement in the deformation of the intercalated nanocomposite model was predicted under the same tensile stress boundary conditions. The deformation vectors were nonuniform. The deformation vectors in the polyDCPD-rich region were larger and the deformation vectors in the clay rich regions were smaller. Stress distributions were more uniform when clay layers were exfoliated and well ordered. The magnitudes of the von Mises stresses were in the range of the applied stress. High stress concentrations were found, both on the surface and around the edges of the clay platelets, for the intercalated model, while the adjacent polyDCPD region did not show such high stresses. These stress gradients could result in crack initiation, and eventually could cause failure. Matrix/clay debonding could occur in these high stress regions. Some low stress regions and reinforced regions were observed when the intercalated model was subjected to the 20,000 N/m$^2$ tensile stress.
APPENDIX A

Fitting SANS Data to the Stacked Disk Model,
Graphs and Tables
Figure A.1. Fitting the experimental SANS data of 0.5wt% I-28 clay/polyDCPD composite to the stacked disk model.

Table A.1. The fitting parameters for the curve fitting illustrated in Figure A.1.

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Figure A.2. Fitting the experimental SANS data of 1wt% I-28 clay/polyDCPD composite to the stacked disk model.

Table A.2. The fitting parameters for the curve fitting illustrated in Figure A.2.

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Figure A.3. Fitting the experimental SANS data of 2wt% I-28/polyDCPD composite to the stacked disk model.

Table A.3. The fitting parameters for the curve fitting illustrated in Figure A.3.

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Figure A.4. Fitting the experimental SANS data of 0.5 wt% I-44pa/polyDCPD composite to the stacked disk model.

Table A.4. The fitting parameters for the curve fitting illustrated in Figure A.4.

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Figure A.5. Fitting the experimental SANS data of 1wt% I-44pa/polyDCPD composite to the stacked disk model.

Table A.5. The fitting parameters for the curve fitting illustrated in Figure A.5.

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Figure A.6. Fitting the experimental SANS data of 2wt% I-44pa/polyDCPD composite to the stacked disk model.

Table A.6.  The fitting parameters for the curve fitting illustrated in Figure A.6.

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Figure A.7. Fitting the experimental SANS data of 0.5wt% PEG-modified PGW clay/polyDCPD composite to the stacked disk model.

Table A.7. The fitting parameters for the curve fitting illustrated in Figure A.7.

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<td>incoh. bkg (cm^2-1)</td>
<td>0.01</td>
</tr>
</tbody>
</table>
APPENDIX B

HR-TEM Micrographs of Clay/PolyDCPD Nanocomposites
Figure B.1. HR-TEM micrograph of 0.5wt% I-28 clay/polyDCPD composite-position 1.
Figure B.2. HR-TEM micrograph of 0.5wt% I-28 clay/polyDCPD composite-position 2.
Figure B.3. HR-TEM micrograph of 0.5wt% I-28 clay/polyDCPD composite-position 3.
Figure B.4. HR-TEM micrograph of 0.5wt% I-28 clay/polyDCPD composite-position 4.
Figure B.5. HR-TEM micrograph of 0.5wt% I-28 clay/polyDCPD composite-position 5.
Figure B.6. HR-TEM micrograph of 0.5wt% I-28 clay/polyDCPD composite-position 6.
Figure B.7. HR-TEM micrograph of micrograph 2wt% I-28 clay/polyDCPD composite-position 1.
Figure B.8. HR-TEM micrograph of micrograph 2wt% I-28 clay/polyDCPD composite-position 2.
Figure B.9. HR-TEM micrograph of micrograph 2wt% I-28 clay/polyDCPD composite-position 3.
Figure B.10. HR-TEM micrograph of micrograph 2wt% I-28 clay/polyDCPD composite-position 4.
Figure B.11. HR-TEM micrograph of micrograph 2wt% I-28 clay/polyDCPD composite-position 5.
Figure B.12. HR-TEM micrograph of micrograph 2wt% I-28 clay/polyDCPD composite-position 6.
Figure B.13. HR-TEM micrograph of micrograph 0.5wt% I-44pa clay/polyDCPD composite-position 1.
Figure B.14. HR-TEM micrograph of micrograph 0.5wt% I-44pa clay/polyDCPD composite-position 2.
Figure B.15. HR-TEM micrograph of micrograph 0.5wt% I-44pa clay/polyDCPD composite-position 3.
Figure B.16. HR-TEM micrograph of micrograph 0.5wt% I-44pa clay/polyDCPD composite-position 4.
Figure B.17. HR-TEM micrograph of micrograph 0.5wt% I-44pa clay/polyDCPD composite-position 5.
Figure B.18. HR-TEM micrograph of micrograph 0.5wt% I-44pa clay/polyDCPD composite-position 6.
Figure B.19. HR-TEM micrograph of micrograph 2wt% I-44pa clay/polyDCPD composite-position 1.
Figure B.20. HR-TEM micrograph of micrograph 2wt% I-44pa clay/polyDCPD composite-position 2.
Figure B.21. HR-TEM micrograph of micrograph 2wt% I-44pa clay/polyDCPD composite-position 3.
Figure B.22. HR-TEM micrograph of micrograph 2wt% I-44pa clay/polyDCPD composite-position 4.
Figure B.23. HR-TEM micrograph of micrograph 2wt% I-44pa clay/polyDCPD composite-position 5.
Figure B.24. HR-TEM micrograph of micrograph 2wt% I-44pa clay/polyDCPD composite-position 6.
Figure B.25. HR-TEM micrograph of 0.5 wt% PEG-modified PGW clay/polyDCPD composite-position 1.
Figure B.26. HR-TEM micrograph of 0.5 wt% PEG-modified PGW clay/polyDCPD composite-position 2.
Figure B.27. HR-TEM micrograph of 0.5 wt% PEG-modified PGW clay/polyDCPD composite-position 3.
Figure B.28. HR-TEM micrograph of 0.5 wt% PEG-modified PGW clay/polyDCPD composite-position 4.
Figure B.29. HR-TEM micrograph of 0.5 wt% PEG-modified PGW clay/polyDCPD composite-position 5.
Figure B.30. HR-TEM micrograph of 0.5 wt% PEG-modified PGW clay/polyDCPD composite-position 6.
Figure B.31. HR-TEM micrograph of 0.5 wt% PEG-modified PGW clay/polyDCPD composite-position 7.