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Shear induced orientation in polymer-clay solutions and their influence on the structure in multilayered films

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SHEAR INDUCED ORIENTATION IN POLYMER-CLAY SOLUTIONS
AND THEIR INFLUENCE ON THE STRUCTURE IN MULTILAYERED
FILMS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
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Doctor of Philosophy

in

The Department of Chemistry

by

Matthew Michael Malwitz
B.S., University of Southern Mississippi, 2000
December 2005
DEDICATION

I would like to dedicate this work to both family and friends who have supported me throughout my academic endeavors. Most importantly I would like to dedicate this work to my wife for providing the support both mentally and physically through the good and bad throughout this project, without her this may have never been possible.

“But true love is a durable fire
In the mind ever burning;
Never sick, never old, never dead,
From itself never turning.”
~ Sir Walter Raliegh
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LIST OF ABBREVIATIONS AND TERMS

AFM – Atomic Force Microscopy

BNL – Brookhaven National Laboratory located in Upton, NY.

CNA – Refers to either polymer-clay solutions or films that contain Cloisite NA+, Montmorillonite clay.

CNR – Center for Neutron Research, the division of NIST in Gaithersburg, MD where our neutron scattering experiments were performed.

DSC – Differential Scanning Calorimetry

Hectorite – A phyllosilicate mineral clay similar in type to bentonite with more negative charges on its surface. These type of clay are used as drilling muds in the oil industry.

KA – Kaolinite clay.

LRD – Laponite RD is a synthetic layered silicate. It also will refer to either polymer-clay solutions or films that contain this type of clay.

NIST – National Institute of Standards and Technology

NSLS – National Synchrotron Light Source the division of BNL in Upton, NY.

PEO – Poly(ethylene oxide) (-CH$_2$-O)$_n$

Phyllosilicate – A mineral with a crystal structure that contains silicon-oxygen tetrahedrally arranged as sheets. Examples are Laponite, Montmorillonite, Kaolinite and Talc.

Rheo-SANS – Refers to the combination of simultaneously shearing a sample while performing a SANS experiment, this allows the user to determine how shear affects the orientation and/or structure of a solution.

SANS – Small Angle Neutron Scattering

SAXS – Small Angle X-ray Scattering

SEM – Scanning Electron Microscopy

Smectite – A class of clay minerals that tend to swell in water. Montmorillonite is in this class of clays.

2D SANS – Refers to the pattern observed on a computer monitor of the counts on the detector.

TGA – Thermogravimetric Analysis
USANS – Ultra Small Angle Neutron Scattering

WAXD – Wide Angle X-ray Diffraction

d or d-spacing – Refers to the spacing between objects in real space as determined by the relationship to the value of q by the relationship $d \approx \frac{2\pi}{q}$.

$\gamma$ - strain

d$\gamma$/dt, $\dot{\gamma}$ - shear rate

$f$ – The Hermans’ orientation function or nematic order parameter. This is a dimensionless number that gives a measure of the degree of orientation in a system with $f = 1$ for a fully oriented system and $f = 0$ for a completely random system.

$G$ – the elastic modulus

$I, I(q)$ – Intensity, referring to the differential scattering cross section.

$\eta$ – viscosity

$\eta_0$ – zero shear viscosity

$\eta_\infty$ - infinite shear viscosity

$K$ – Consistency value, parameter used in the Cross model fit of viscosity vs. shear rate curves. The consistency value is a measure of the characteristic time of the measured material.

$n$ – power law index

$\phi$ - The radial angle of a 2D SANS plot used in calculating the nematic order parameter.

$q, \tilde{q}$ - the scattering vector having both magnitude and direction

$q$ – magnitude of the scattering vector

$\tau$ - stress measured in force per unit area
ABSTRACT

The influence of shear on viscoelastic solutions of poly(ethylene oxide) (PEO) and clay (Cloisite, CNA) was investigated by rheology and small angle neutron scattering (SANS) under shear. These measurements determined the shear-induced orientation of the clay and the polymer as well as their relaxation behavior after cessation of shear. Comparison of PEO-CNA solutions (~100 nm diameter platelets) to previously studied PEO-Laponite gels (~30 nm diameter platelets) found that the orientation of CNA platelets occurs at much lower shear rates. Additionally, the relaxation times were much longer for CNA platelets than for Laponite platelets.

From these solutions and gels, multilayered nanocomposite films were prepared. Shear-induced orientation of polymer-clay solutions is important to the organization of the clay platelets in the films. The structure was determined by scattering and microscopy techniques. Experimental evidence suggests that clay platelets align within multilayers with their surface normal perpendicular to the spread direction. The unusual orientation of the multilayers persists on multiple length scales from nanometer to micrometer.

As part of an independent research project a series of PEO-Kaolinite (~1.5 μm diameter platelets) solutions and films were studied and compared to the results mentioned above. Initial rheological studies of the PEO-Kaolinite solutions showed shear thinning behavior and possible flow irregularities. Preliminary investigation of the films made from the solutions suggests that shear orientation is preserved within the film. Continued optimization of the PEO-Kaolinite solutions leading to improved exfoliation of the platelets will result in a novel class of materials with unique properties.
CHAPTER 1: ORIENTATION OF CLAY IN POLYMER NANOCOMPOSITE MATERIALS

1.1 Introduction

For the past several decades continuing interest has been found in the development of novel polymer nanocomposite materials with synergistic structure and property relationships. Of special interest are nanocomposite materials made from polymer and clay, especially those containing exfoliated and hierarchically ordered clay particles. These materials whether in solution or in bulk have many unexpected mechanical\(^1\), electrical\(^2\), optical\(^2,3\) and thermal properties that can be tuned to the desired application.\(^1,4\) The unique structure and property enhancements are often attributed to the synergistic interaction of the polymer with the nanoparticle and the state of nanoparticle dispersion.\(^1,5,6\) One advantage of nanoparticles over traditional fillers in polymer materials applications lies in the low loadings that lead to great improvements in physical properties. For instance, nylon-Montmorillonite nanocomposites have shown a doubling in the tensile modulus and strength without loss in impact resistance with as little as 2% Montmorillonite.\(^7\) Many of the improved mechanical properties create interest in the automotive and machine industries to produce products such as stronger engine covers, door handles and impellers but also housings for mobile phones and pagers.\(^8\) For example the ability to use polymer nanocomposite materials as under-the-hood automotive applications is due to increased heat distortion temperatures by as much as 100 °C for materials such as nylon-clay nanocomposites.\(^9\)

The use of nano-sized, well dispersed fillers also offers the advantages of transparency and optical clarity of a material as traditional microscopic sized particles do not. This gives the opportunity to develop strong and transparent films, coatings and
membranes with unique gas barrier properties. The food packaging industry is very interested in potential applications of such films for use in both refrigerated and non-refrigerated environments. The pipe industry has expressed interest in nanocomposite films for coatings or membranes on the inside of pipelines, fuel tanks or storage tanks because of the chemical and corrosion resistance of many nanocomposite materials.\textsuperscript{7-11}

Other novel applications for nanocomposite materials lie in the medical, pharmaceutical and biosciences. According to Bizios et al, polymer-nanoceramic materials research may be used for orthopedic implants.\textsuperscript{12} The formation of such polymer-nanoceramic implant materials would allow osteoblasts, bone forming cells, to grow and form bone which would promote the integration of new bone formation. Other bio-related areas that may benefit from innovations in nanocomposite research include the development of dental materials as well as tissue and biodegradable scaffolds engineering.

1.2 Nanotube, Fibers and Rods

Commercial interest in polymer-carbon nanotube composites has been increasing recently due to their conductivity at low loading levels. Recent literature reviews on polymer-carbon nanotubes composites cover varied topics such as the mechanical and electrical properties of the polymer composites\textsuperscript{13,14} as well as approaches to the chemical functionalization of nanotubes to tailor the interactions with polymers\textsuperscript{15} and the attachment of nanotubes to surfaces and polymer matrices.\textsuperscript{16} Andrews et al. have been investigating means to effectively disperse nanotubes into polymer matrices in order to create new and advanced engineering materials.\textsuperscript{17} The development of polymer films and fibers that contain oriented single-walled nanotubes by employing shear orientation at the nanoscale still poses special challenges.\textsuperscript{18,19} Results reported recently by Vigolo et al.
show that flow induced alignment of nanotubes in a polymer matrix can lead to a preferential orientation of the nanotubes into either ribbons or fibers.\textsuperscript{20} According to Raman spectroscopy measurements, performed by Frogley et al., the degree of shear orientation and the polarization direction of the nanotubes in a polymer matrix can be determined.\textsuperscript{21} Research in developing materials that contain nanotubes cover a wide range of polymer matrices, flows and techniques. However, the ability to consistently produce shear-induced supramolecular structures containing inorganic nanotubes, rods or fibers has been proven to be difficult.

According to experiments performed by Wilson et al. polymer films can be produced with tunable colors.\textsuperscript{3} The colors produced are dependent on the size and nature of the nanorod. Metal nanorods are of great interest because they exhibit high electrical capacitance and the color of the colloidal rod is affected by the effective charge on the particle.\textsuperscript{3}

Unique conductive composites can be produced by the solid state polymerization of molecularly oriented silica/monomer matrices. The resulting architecture and the extent of the self-assembly of the conductive silica-polymer hybrid films or fibers is suitable for the integration into various devices and microsystems.\textsuperscript{22} The nanostructured inorganic host alters the monomer polymerization behavior and the resulting nanocomposite displays unusual chromatic changes in response to thermal, mechanical and chemical stimuli. According to Lu et al. the inorganic framework helps to protect, stabilize and orient the polymer and to mediate its function.\textsuperscript{22}

1.3 Polymers and Nanospheres

The development of many new devices can be made possible when combining the ease of processability of an organic polymer with the improved mechanical and optical
properties of an inorganic nanoparticle. Brott et al. developed a method for creating an array of silica spheres on a polymer substrate. To obtain this structure they incorporated a peptide into a polymer hologram. When the nanopatterned structure is exposed to silicic acid an ordered array of biocatalytically formed silica nanospheres is deposited onto the polymer substrate.\textsuperscript{23} Other research describes well structured silica nanospheres with incorporated polymer\textsuperscript{24}, gold nanospheres coated with polymer brushes\textsuperscript{25} or nanoparticle formation within a dendrimer matrix.\textsuperscript{26} Using structures in organogels as a template many different structures can be produced. Fong et al. studied the synthesis of polymer coated silica nanoparticles and the strength of interactions and aggregation in solution.\textsuperscript{27} They contrast the weakness of physical polymer-silica interactions which can be ‘washed away’ versus the covalently attached or strongly adsorbed polymers.\textsuperscript{27} An interplay between rheology, adsorption of polymer and surface charge can affect the viscosity of concentrated dispersions of charged silica spheres.\textsuperscript{28} According to Zaman et al. adsorption studies provided information on the polymer layer density and conformation. They were able to determine if the conformation of the adsorbed polymer on the silica particles was pancake- or brush-like.\textsuperscript{28}

There is also a great deal of interest in the morphological features of composite films and membranes that contain hard inorganic particles in a soft polymer matrix. The ability to enhance membrane separation processes are attractive to industry because they contribute to low cost, energy efficient, green technology where nanoparticles can enhance the selectivity and permeability in glassy amorphous membranes.\textsuperscript{29}

Recently a study by Oberdisse et al. on latex-silica nanocomposite films has shown that the structure and morphology can systematically be controlled by varying the synthetic parameters in solution.\textsuperscript{30} The authors suggest that a competition between the
silica aggregation and film solidification is responsible for the aggregation kinetics. The films demonstrated considerable reinforcement when subjected to small deformations, but when subjected to high elongations the rheology of the films approaches that of a pure latex film.\textsuperscript{31}

Kobayashi et al. recently made measurements on a polymer-colloidal silica film and discovered that the polymer interdiffusion depends on the silica particle size. The high surface area of the silica was found to raise the effective glass transition temperature of the polymer matrix.\textsuperscript{32} Small particles can act as obstacles to increase the tortuosity of the diffusion path or the silica surface can make the adjacent polymer matrix more rigid, which is the traditional ‘filler effect’. The authors suggest that polymer adsorption onto the silicate surface can play an important role in the affecting the diffusion rate of the polymer film.\textsuperscript{32} Nanoparticles may not only raise the glass transition of polymers\textsuperscript{32} but also change the phase behavior of nanocomposite blends\textsuperscript{33}, enhance the selectivity and permeability in glassy amorphous membranes\textsuperscript{29} or lead to new electro-optical properties in polymer films.\textsuperscript{2}

Recent theoretical approaches have examined the chain dimensions in nanosphere-filled polymers.\textsuperscript{34} Molecular dynamic simulations have looked into polymer-nanoparticle interactions as well as the structure and dynamics of polymer melts containing nanoparticles.\textsuperscript{35} According to experiments performed by Lenstra et al. on the flow dichroism of colloidal particle systems, the polymer induces depletion attractions which can give rise to a ‘gas liquid critical point’.\textsuperscript{36} Dichroic behavior was used to test mean field theoretical predictions on the microstructural order of colloidal fluids under shear conditions.\textsuperscript{36}
1.4 Polymer-Clay Interactions

The colloidal and rheological properties of polymer-nanoplatelet composites in bulk and in solution have received considerable attention and good reviews are available. One recent focus has been on the supramolecular organization of surfactants and nanoparticles. For example, a recent study by Castelletto et al. looked at the supramolecular organization of an aqueous mixture of Laponite clay and Pluronic nonionic surfactant. The authors observed a transition from the hexagonal phase to a lamellar phase upon adsorption of the clay by the surfactant. In another study Lal and Auvray performed small angle neutron scattering (SANS) studies examining the affect of adsorbed PEO on Laponite clay at low concentrations. While Lal and Auvray’s results were insensitive to the polymer concentration profile, Smalley et al. and Swenson et al. employed neutron diffraction studies to focus on the interlayer and ordered structure around each clay platelet as well as the mechanism of bridging flocculation.

When the polymer threshold for complete saturation of Laponite particles is kept low enough the possibility of forming a ‘shake gel’ exists. Zebrowski et al. reported that PEO-Laponite solutions underwent dramatic shear thickening under certain conditions. When subjected to shear, these solutions formed a shake gel that was sufficiently strong enough to support its own weight. The shake gels were reversible and would return back to a viscous fluid with a relaxation time dependent on the PEO concentration. It has been proposed that shear induces a bridging between the colloidal particles resulting in a temporary gel network that extends throughout the entire system. When the PEO concentration and molecular weight is increased slightly higher in the same PEO-Laponite system Schmidt et al. found that the polymer chains are in a dynamic adsorption-desorption equilibrium with the clay particles and that a permanent gel
Unlike the gels studied by Zebrowski et al. which were reported to have the consistency of a ‘half-cooled gelatin desert’ the gels formed by Schmidt et al. were found to be highly elastic and behave more like a ‘chewing gum’ than a gelatin. However SANS measurements using contrast matching methods could not distinguish between the intensity contributions of network active PEO, adsorbed PEO or excess PEO inside of the polymer-clay network.\textsuperscript{45-47}

Despite the differences between shake gels and permanent gels, the interactions between polymer and clay remain elusive. A better understanding of the polymer-clay interactions as well as more qualitative knowledge is needed to properly interpret experimental results. Theoretical approaches such as those by Nowicki looked at the conformational properties of polymer chains in the presence of small colloidal particles providing some understanding in the shake gel and permanent gel systems described previously.\textsuperscript{48} Another study attempted to reveal the equilibrium phase behavior of nanocomposite mixtures using a combination of self-consistent field theory with density functional theory.\textsuperscript{49} Simulations performed by Ginzburg and Balazs modeled the phase behavior for a mixture containing polymer and solid thin discs. The models they presented indicate possible nematic ordering of the discs within the polymer matrix.\textsuperscript{50} Recent Monte Carlo and molecular dynamic computer simulations by Hackett et al. were used to determine the atomic scale structure of intercalated polymer-clay composites. The configuration of the polymer within the confined spaces between the clay particles found were significant and interesting.\textsuperscript{51}

1.5 Flow Effects in Polymer-Platelet Systems

In this dissertation we are interested in the novel structure-property relationships that result from nanocomposites materials exposed to shear. Shear-induced structural
changes in fluids containing anisotropic species are often encountered in polymer solutions, liquid crystalline materials, block copolymer melts and in particle solutions. A large body of literature exists on the flow behavior of inorganic particle slurries and solutions as well as polymer solutions. However little is known about the influence of shear on combined polymer nanoparticle systems. One of the great challenges in the fields of science and engineering is to determine the exact interactions between polymers and clays as well as their effect on the structure-property relationships of these materials. The ability to orient clay platelets on the nanometer length scale is an active area of research in materials science. Several different methods have been developed and the techniques span the range from direct manipulation of individual particles to self-assembly in colloidal materials. Clay platelets have large aspect ratios that promote a supramolecular organization similar to other mesoscopic systems such as liquid crystalline polymers, surfactants or block copolymers. Hybrid properties and novel structures can be possible with multicomponent polymer-clay systems. We are especially interested in the shear orientation of the clay particles in solution, in dispersion and in the resulting shear oriented films.

A two dimensional object such as a clay particle can have three possible orientations under flow, commonly referred to as $a$, $b$ and $c$ in the literature (Figure 1.1). In the perpendicular or $a$ orientation the surface normals align parallel to the vorticity direction and the particles lie in the flow-shear gradient plane. In the transverse or $b$ orientation the surface normals align parallel to the flow direction and the particles lie in the vorticity-shear gradient plane. Finally, in the parallel or $c$ orientation the surface normals align parallel to the shear gradient direction and the particles lie in the flow-vorticity plane.
Figure 1.1 Possible shear orientation of clay platelets as detected by SANS. a) Platelets align with surface normals along the neutral direction: vertical streak in the radial pattern (y) and vertical streak in the tangential pattern (x). b) Platelets align with surface normals in the shear plane: horizontal streak in the radial pattern (y) and isotropic tangential pattern (x). c) Platelets align with surface normals along the velocity direction: isotropic radial pattern (y) and a horizontal streak in the tangential pattern (x). Imperfect orientation of the clay platelets has been assumed.

The response of clay particles in a polymer matrix or network is to assume the c orientation. Early studies on nylon based nanocomposites describe this phenomenon nicely as reviewed by Krishnamoorti and Yurekli.\textsuperscript{38} Using in situ X-ray diffraction studies Lele et al. have discovered direct evidence for rheology-microstructure linkages in polypropylene nanocomposites.\textsuperscript{54} In studies using a PEO-Laponite system under shear an unexpected case of a orientation has been observed.\textsuperscript{45, 46} It was proposed that the clay and polymer interact in a dynamic adsorption-desorption equilibrium to form a three dimensional network.\textsuperscript{47} Shear induced orientation of polymer and platelets in D\textsubscript{2}O solution were observed using SANS. Additional experiments using contrast matched samples were performed to observe only the polymer orientation. It was determined that as the polymer-clay solutions were subjected to shear the clay particles aligned initially. After sufficiently high enough shear rates were obtained, the polymer chains would begin to stretch and align. As the shear rate increased it began to distort and rupture the transient gel. Thus coupling between compositions and shear stress lead to the formation
of a macroscopic domain pattern.\textsuperscript{55} It has been suggested by Lin-Gibson et al. that the orientation of clay is a response to the biaxial stress arising from shear and elastic forces.\textsuperscript{55}

In a recent TEM study by Okamoto et al. they discovered that a polypropylene-clay nanocomposite melt under elongational flow adopts a ‘house of cards’ structure.\textsuperscript{56} Strong, strain-induced hardening and rheopexy features at higher deformation originated from perpendicular alignment of the silicate to the stretching direction (\textit{b} orientation). While TEM is not an in situ technique, it demonstrated the difference between shear flow induced versus elongational flow internal structures of the nanocomposite melt. The nanocomposites studied by Okamoto et al. are similar to the polymer-clay solutions studied by Lin-Gibson et al. in that they both display strong interactions between the polymer matrix and the clay platelets.

Changing the focus from other recent explorations, Brown and Rennie studied a dispersion of nickel hydroxide platelets stabilized by polymer.\textsuperscript{57} The object of their research was primarily to observe the flow of dispersions rather than particle-polymer interactions. Adsorption of a low-molecular-weight, charged polyacrylate onto the platelet surfaces provided steric repulsion. They observed a shear-induced phase transition with a change in particle alignment. At low shear rates the particles aligned in the \textit{c} orientation, normals in the flow direction were observed. At higher shear rates a transition occurs and the platelets are observed in the \textit{a} orientation, normals in the gradient direction. The sample was observed to undergo a phase change from columnar to smectic phase at intermediate shear rates. The finite two dimensional particles in this study appear to arrange themselves in response to the subjected shear rate. At low shear
rates the system forms a series of uniaxial particles while at higher shear rates it arranges and performs like a lamellar phase.\textsuperscript{53, 57}

1.6 Kaolinite Nanocomposites

The prevalence of polymer-Kaolinite nanocomposites in the literature is not as well defined when compared to the amount of literature published on polymer nanocomposites containing either Montmorillonite or Laponite. Kaolinite is a natural phyllosilicates mineral composed of a single tetrahedral silicon oxide layer bonded with a dioctahedral (gibbsite type) aluminum oxide layer.\textsuperscript{58} Because of the hydroxyl groups present on the dioctahedral layer of the Kaolinite sheet it allows for hydrogen bonding to occur with adjacent layers which causes the clay platelets to aggregate and form stacks. This property makes it difficult to swell and exfoliate this clay type.

Most research found regarding Kaolinite nanocomposites focused on the intercalation of the clay aggregates.\textsuperscript{10, 59} Komori et al. found retention of the ability to intercalate wet hydrated Kaolinite which was derived from a Kaolinite/methanol compound. Their results indicate that these intercalation reactions may be a precursor to forming unique layered organic nanocomposites. High thermal stability of an intercalated Kaolinite with poly(\(\beta\)-alanine) was discovered by Itagaki et al. suggesting that guest-host interactions with Kaolinite and polymer may be atypical.\textsuperscript{59} Intercalation by small molecules resulting from van der Waals forces and hydrogen bonding within Kaolinite was reported by Kelleher et al.\textsuperscript{60} These studies into the intercalation behavior of Kaolinite seem to suggest that this clay possesses unusual characteristics that are worthwhile for further exploration.

Research using EVOH (polyethylene-vinyl alcohol)-Kaolinite nanocomposites was performed by Cabedo et al.\textsuperscript{10} They formed an EVOH-Kaolinite nanocomposite by
melt blending in order to increase the amount of exfoliation present in the resulting nanocomposite material. Exfoliation was possible in this system as evidenced by their scattering and microscopy studies. Thermal analysis also showed that the nanocomposite films had an increase in the thermal stability over the pure polymer. Additionally, oxygen transmission studies showed a significant increase in the gas barrier properties of the film with clay loadings below 8% by mass. The initial results reported by Cabedo et al. show promise for Kaolinite-based nanocomposites and warrant consideration for developing novel nanocomposites based on this clay type.

1.7 Conclusions

The goal of the research presented in this dissertation is to design new polymer clay nanocomposites from solution and to investigate their structure and properties during and after cessation of shear. The shear-induced orientation of clay platelets in solution is studied as well as the influence of shear on the preparation of multilayered films made from solutions. Another aspect of this work is studying if and how the clay orientation observed in solution can be maintained in the film.

The systems studied here are poly(ethylene oxide) PEO-clay solutions containing synthetic Laponite clay, natural Montmorillonite clay and natural Kaolinite clay. While Laponite and Montmorillonite consist of nanometer sized platelets, Kaolinite platelets are several microns large. In Chapter 3 we examine the orientation of polymer-clay solutions when subjected to shear as well as the relaxation behavior of these materials after the cessation of shear. In Chapters 4 and 5 we examine the ability to maintain the shear orientation of the clay platelets from the solution in the bulk films. Finally, Chapter 6 shows preliminary data on PEO-Kaolinite solutions and films.
From a materials chemistry point of view the fundamental studies provided here may lead to a new class of oriented polymer particle materials. It should be possible in the future to orient particles in any desired way with further understanding of the mechanisms that cause particle alignment. Nanoparticle composites, as they become better understood, can directly contribute to future developments in data storage, optical and electro-rheological materials or display devices.
CHAPTER 2: BACKGROUND THEORY

2.1 Introduction

An outline of basic theory regarding the various techniques used to characterize both the polymer-clay solutions and films is presented as well as some background on the general colloidal properties relevant to the nanocomposite solutions studied. Brief explanations will be given for rheology, small angle neutron scattering (SANS), birefringence and atomic force microscopy (AFM). These will be followed by a description of bridging and depletion flocculation which are important parameters to consider in the design of our polymer-clay solutions. Such colloidal properties strongly influence both the solution behavior as well as the resulting film properties.

Here we briefly discuss the theoretical background necessary to understand this dissertation as it can be found in the following books: William Ferry Viscoelastic Properties of Polymers, Faith A. Morrison Understanding Rheology, and Christopher Macosko Rheology: Principles, Measurements, and Applications. Scattering theory is covered in great detail by Ryong-Joon Roe in Methods of X-ray and Neutron Scattering in Polymer Science, Scattering in Polymeric and Colloidal Systems edited by Wyn Brown and Kell Mortensen and Neutron Scattering: A Primer by Roger Pynn.

2.2 Rheology Basics

Rheology is a study of how a material flows and deforms in response to an applied external force. The study of flow properties is important to understanding a wide range of phenomena observed in other areas such as aeronautics, hydraulics, fluid dynamics and solid mechanics. In practice, rheology deals primarily with the deformation of liquids. A material that undergoes a deformation from an applied external
force can have several different responses. The simplest responses that a material can display are elastic and viscous behavior.

A Hookean or linear solid, is an elastic solid which will exhibit a linear relationship between the stresses and strains. Hook’s law states that the applied force is proportional to the deformation:

$$\tau = G\gamma$$  \hspace{1cm} (2.1)

where \(\tau\) is the force per unit area, commonly called stress, and \(\gamma\) is the relative change in length, referred to as strain. In the simplest of terms \(G\) is a constant of proportionality and has been named the elastic modulus but can be calculated as a function of the material deformation. Materials such as ceramics and most metals at small strains will show Hookean behavior. In other words, a material will recover back to its original state after the applied force has been removed. Hook demonstrated his law by attaching different weights to various springs or long wires. He found that when he doubled the weight the length of the spring or wire would double as well. Hook proposed that the applied force from the suspended weights was proportional to the change in length. However, it was found that by using a different length or gauge of wire made from the same material a change in the constant of proportionality occurred. Therefore, the constant of proportionality is not only a function of the material property but also dependent on the sample geometry.

On the other hand, viscous materials will show complete deformation with no recovery back to its original state. Newton’s law of viscosity has the form:

$$\tau = \eta\dot{\gamma}$$  \hspace{1cm} (2.2)
where $\dot{\gamma} = \frac{d\gamma}{dt}$ which implies that the shear stress is proportional to the rate of strain and $\eta$ is the Newtonian viscosity which is the constant of proportionality. Newtonian fluids such as mineral oil, water, ethanol and air will show a linear relationship between the shear stress and the shear rate. If the shear stress is plotted as a function of the shear rate what will result is a line with a constant slope, this slope is the viscosity of the fluid. Viscous materials can behave quite differently by showing non-ideal Newtonian behavior such as shear thickening and shear thinning. A representative graph of the different types of fluid behavior can be seen in Figure 2.1.

![Graph showing different types of fluid behavior](image)

**Figure 2.1.** Figure shows possible fluid behavior such as a) Dilatent (shear thickening), b) Newtonian, c) Pseudoplastic (shear thinning).

A material that exhibits viscoelastic behavior shows an ‘in between’ state of an ideally viscous or ideally elastic solid. Many everyday materials found in the home demonstrate viscoelastic properties. Silly putty is a very good example of a material with viscoelastic properties. When a ball of silly putty is dropped onto a surface it will bounce behaving like an elastic solid but when left to sit on a surface after a period of time it will
flow like a liquid demonstrating viscous behavior. Other examples of everyday materials that have viscoelastic behavior are liquid soap, shampoo, toothpaste, egg whites, and hand lotion. There are many ways to model viscoelastic behavior, the simplest being the Maxwell model and the Kelvin-Voigt model as well as a combination of these.

2.3 Rheology Experiments

In this dissertation several tests were employed to study some of the physical properties of viscoelastic materials. Because no single test or rheometer can be used to measure all of the rheological properties over an infinite range of parameters a combination of tests and rheometers are generally employed to determine the physical properties that are the subject of interest. The experiments performed on the Kaolinite-polymer dispersion were primarily concerned with the shear rate dependency of viscosity. Steady rate sweep tests were used on polymer-clay solutions to generate flow curves which show the shear rate dependent behavior of viscosity. A plot of the viscosity versus shear rate can then provide a way to determine the flow behavior of the solution. In the steady rate sweep test method, each data point was generated by an individual experiment ensuring that the data collected was at its steady state value. Only the data collected at the steady state region was used by averaging the data and then plotting the average viscosity for a given shear rate. The flow test was also used to determine the solution viscosity dependence on shear rate. The flow test applies a ramped shear rate, or angular velocity, to the sample. This test provides both viscosity and shear stress data as a function of shear rate. The flow curves that are generated can be fit to various models to determine zero shear viscosity ($\eta_0$), infinite shear viscosity ($\eta_\infty$), the characteristic time of the material ($K$) and the power law index ($n$).
In general, a flow curve has three zones which are of the greatest importance. Figure 2.2 is a log-log plot of viscosity versus shear rate demonstrating the various zones that may be observed in a flow curve. Region I is a viscosity plateau where the viscosity remains constant at a given shear and is referred to as the first Newtonian region. Region II is the shear thinning region which can be found to typically model power law behavior. Region III is the second Newtonian region and shows similar behavior to Region I. In addition to these zones a fourth zone, Region IV, can sometimes be observed if the flow curve experiment can reach sufficiently high shear rates. In Region IV the tested sample has a tendency to show shear thickening behavior.

Several models are available for fitting flow curve data. When plotting viscosity versus shear rate, models such as the Power law, Cross and Carreau may be used. If the
data is plotted as viscosity versus shear stress then a model equivalent to the Cross model, the Ellis model, can be used.

The steady state viscosities of the Kaolinite-PEO dispersions described in this dissertation were fitted to a Cross model that describes regions I-III shown in Figure 2.2:

$$\frac{\eta - \eta_0}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\dot{\gamma})^n}$$

(2.3)

Here $\eta_0$ is the zero shear viscosity, $\eta_\infty$ is the infinite shear viscosity, $K$ is the consistency index measuring the characteristic time of the material and $n$ is the power law index which describes the shear thinning behavior of the material. The independent variable in this model is the shear rate, $\dot{\gamma}$.

2.4 Small Angle Scattering

Scattering by different radiation types (light, x-ray or neutron) allows for the determination of objects sizes and their hierarchical organization on length scales ranging from nanometer to micrometer. Each radiation type and scattering method has different advantages. The combination of different techniques allows for structure determination and materials characterization on length scales that one method cannot achieve on its own. The understanding of the material structure and properties at multiple size scales can allow for the manipulation and improvement of properties as well as the adaptation of the scattering methods to the problem to be solved.

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own. The understanding of the material structure and properties at multiple size scales can allow for the manipulation and improvement of properties as well as the adaptation of the scattering methods to the problem to be solved.

Simple elastic scattering theory uses scattering vectors to characterize the scattering geometry from the scattered and incident beam directions. The scattering vector can be related to the scattering angle $2\theta$ and the wavelength $\lambda$ by:

$$s = \frac{2 \sin \theta}{\lambda}$$  \hspace{1cm} (2.4)

The scattering vector $|s|$ was derived from the scattering path length difference and can be related to the scattering vector $|q|$ by the following:

$$|q| = 2\pi |s|$$  \hspace{1cm} (2.5)

or

$$|q| = \frac{4\pi \sin \theta}{\lambda}$$  \hspace{1cm} (2.6)

Scattering can occur in two different ways, elastically or inelastically. In elastic scattering the energy of collision from the neutron or other incident radiation is not significant enough to change the internal energy of the scattering nucleus. With inelastic scattering there is an exchange of energy and momentum between the incident beam and the sample. This causes the incident beam to change in both magnitude and direction after the scattering event.

Figure 2.3 shows how the scattering vector $|q|$ relates to the incident wave vector $|k|$ and the scattered wave vector $|k'|$ for elastic scattering. For elastic scattering the
magnitude of the incident wave vector is equal to the magnitude of the scattered wave vector and we have the following relation:

\[ k_i = k_s = \frac{2\pi n}{\lambda_0} \]  

(2.7)

where \( k_i \) and \( k_s \) are the magnitude of the incident and scattered wave vectors, \( \lambda_0 \) is the wavelength of incident radiation in a vacuum and \( n \) is the optical density. Looking at \( |\mathbf{q}| \) in Equation 2.6 it can be observed that an inverse relationship exists between the scattering vector and the length scales that are being probed in the scattering experiment.

**Figure 2.3.** The elastic scattering triangle that relates the incident (\( \mathbf{k} \)) and scattering (\( \mathbf{k}' \)) wave vectors to the scattering vector \( \mathbf{q} \).

### 2.5 Birefringence\(^{67, 68}\)

According to literature optical birefringence is caused by the double refraction of light of an ordered material (on the micrometer or nanometer length scale) which is the manifestation of the existence of orientation-dependent differences in refractive index of the anisotropic material. Anisotropy is defined as the non-uniform spatial distribution of properties which result in different values being obtained when specimens are probed from several spatial directions within the same material. For the polymer-clay films studied the coin-like clay platelets are anisotropic when viewed from the side. The
diameter of the clay platelets (e.g., Laponite diameter = 30 nm) is much larger than the platelet thickness (Laponite thickness = 1 nm). Thus, birefringence is a result of the non-uniform spatial distribution of size (form birefringence) and refractive index (intrinsic birefringence). In comparison, observation of the clay platelets from the top should not lead to form birefringence because the distribution of isotropic disc-like platelets in is uniform. In a similar manner, a randomly oriented polymer coil will show no birefringence while an oriented or stretched polymer chain will show birefringence.

Birefringence can arise from intrinsic contributions as well as scattering or form effects. The intrinsic contributions are due to the polarizability of the molecules within a polymer chain while the form effects may result from the scattering or orientation of larger domains. Polarized optical light microscopy is a useful tool for identifying birefringent structures formed by liquid crystalline-like materials such as our nanocomposite films. In this work we qualitatively measure the total birefringence of a nanocomposite film by polarized optical microscopy. The total birefringence shown in the micrographs has intrinsic as well as form birefringence contributions and comes from the anisotropy of the clay platelets, the stretched polymer chains, the crystallized polymer chains and the orientation of larger anisotropic domains. The contribution of the birefringence coming from the orientation of the clay particles can be determined by melting the polymer. Above the melt transition the polymer becomes isotropic in shape and its refractive index distribution does not contribute to the total birefringence. The inorganic clay particles remain birefringent at all temperatures when the film is observed from the side. Below the polymer melt temperature the spherulites formed by the polymer contribute to both the form and intrinsic birefringence. The microscopy images shown in this work do not take into account the individual contributions between the
different birefringent types but give us qualitative information regarding the orientation of the polymer and the clay and their average contributions to the total birefringence.

2.6 Atomic Force Microscopy\textsuperscript{69, 70}

AFM or atomic force microscopy is part of a family of microscopy techniques known as scanning probe microscopy which also includes techniques such as scanning tunneling microscopy (STM). The basic operation of scanning probe microscopy is to move a probe across the surface of a sample and monitor the sample tip interactions in order to determine the three dimensional representation of the sample surface. Different modes such as contact, non-contact and tapping can be used to image the sample surface.

In contact mode the AFM tip is in light contact with the sample surface. The force on the tip is repulsive and is set by pushing the cantilever against the sample surface with a piezoelectric positioning element. The deflection of the cantilever is sensed and compared in a feedback loop amplifier to a set deflection value. Differences in deflection of the cantilever cause a change in the voltage of the feedback loop which either raises or lowers the positioning element to restore the cantilever back to the desired deflection value. The voltage change that the feedback amplifier applies to the positioning element is a measure of the “height” features of the surface. The height features are displayed as a function of the lateral positioning of the sample surface.

Non-contact mode is used when the AFM tip may produce subtle alterations of the sample. In the non-contact mode the probe is approximately 50-150 Å above the sample surface. Attractive forces between the tip and the sample due to van der Waals interactions between the tip and the sample are detected. This results in a topographic image formed by scanning the tip above the sample surface. Because the van der Waals forces are significantly weaker than the forces measured in the contact mode the
cantilever is oscillated slightly above its resonant frequency. This allows for the detection of small forces between the tip and sample by measuring changes in the amplitude, phase or frequency of the oscillating cantilever.

Tapping mode is another method employed for observing the surface of a sample. It allows for the imaging of samples that can be easily damaged, those loosely held to their substrate or samples difficult to image using the previously mentioned techniques. In tapping mode, the tip is placed in brief contact with the sample surface and is lifted off to avoid dragging of the tip across the surface. The tip is oscillated near or above its resonant frequency and is slowly brought into contact beginning to tap the sample surface. As the tip is brought briefly in contact with the sample surface, the oscillations of the tip are reduced due to energy loss caused by tip-surface contact. This reduction in the oscillation amplitude is used to determine the surface features. Cantilever oscillation amplitude is maintained by a constant feedback loop. As the tip passes over a rise in the sample the ability for the cantilever to oscillate is reduced and in return the amplitude of the oscillations is reduced. Similarly, as the tip passes over a depression in the sample surface there is more room for the cantilever to oscillate resulting in an increase in the amplitude. The feedback loop uses this information to adjust the tip-sample separation to maintain a constant amplitude and force on the sample.

Phase imaging is an extension of the tapping mode and can provide information about the surface structure on the nanometer scale. Phase imaging is performed by mapping the phase of the oscillations of the cantilever during the tapping mode scans. The phase lag of the cantilever oscillation relative to the signal sent to the cantilever’s piezo driver is simultaneously monitored and recorded. The phase lag is sensitive to differences in properties such as composition, adhesion and viscoelasticity.
The polymer-clay films that were studied by AFM in the tapping mode help reduce sample distortion due to mechanical interactions between the tip and the sample. The “height” images produced by AFM were a highly ordered layer-like structure and were used to directly compare the spacing results found in SANS. A comparison of the anisotropic 2D SANS image was made to a Fast Fourier transform of the AFM height image, which resulted in a similar anisotropic pattern. The AFM results reported herein are found to be in agreement with the SANS results. While SANS provides results in reciprocal space and is a measure of the overall average degree of orientation that occurs in the film, AFM allows for a direct measure of the sample orientation in discrete sections of the sample.

2.7 Colloidal Properties – Bridging and Depletion Flocculation

When designing soft nanocomposite hydrogels, solutions and dispersions the colloidal properties of the components have to be taken into account in to control stability. A dispersion containing Kaolinite clay and polymer can easily lead to bridging or depletion flocculation under proper conditions. Flocculation is defined as the process in which smaller particles, such as clay, begin to agglomerate and form larger aggregates or flocks which then fall out of solution.

Bridging flocculation can occur if the following conditions are met: 1) The presence of a high-molecular-weight polymer with a chain length sufficient to span the interparticle distance and overcome the electrostatic repulsive forces between the particle is present. 2) The colloidal particles must have incomplete surface coverage to have multiple polymer chain segments from different polymer chains adsorb to their surface. The process of forming these polymer bridges between particles causes them to be drawn closer together which can lead to flocculation. Bridging flocculation is an active
mechanism for dispersions at low polymer concentrations and can lead to loosely flocculated structures.

Flocculation or stabilization may also be induced or prevented by polymers dissolved in a good solvent. Depletion stabilization can occur from the reduction in the concentration of free polymer (non-adsorbed) between the colloidal particles surfaces when the particles are in close proximity. In order for the particle surfaces to approach closer further depletion of the free polymer from between the particle surfaces must occur. Because this is an energetically unfavorable situation, in a good solvent, it leads to the depletion stabilization effect. However, if the particle surfaces are able to continue to come closer together it will result in eventually causing a complete exclusion of the polymer molecules from the interparticle spaces. What results is an interparticle space devoid of free polymer but still occupied by pure solvent. This causes the particles to approach further which is energetically favorable due to the polymer concentration gradient present, which is the difference in polymer concentration in the bulk solution versus the interparticle space. This concentration gradient causes the solvent to be squeezed out of the interparticle space in order to mix with the bulk polymer solution. This causes the particles to come into closer proximity and flocculate due to an osmotic pressure mechanism.

Depletion stabilization differs from steric stabilization in that the polymer that provides colloidal stability is free to move about in solution and is not attached to the particles themselves. Also, the stabilization by the free polymer appears to be a kinetic rather than a thermodynamic stability.\textsuperscript{74}
CHAPTER 3. ORIENTATION AND RELAXATION OF POLYMER-CLAY SOLUTIONS STUDIED BY RHEOLOGY AND SMALL-ANGLE NEUTRON SCATTERING*

3.1 Introduction

The large aspect ratio of clay platelets promotes a supramolecular organization similar to that of other mesoscopic systems such as liquid crystalline polymers, surfactants, and block copolymers. Previous studies have considered the influence of nanoparticles on the structure and rheology of lamellar phases. A transition from liquid-crystalline hexagonal phase to a lamellar phase has been observed in aqueous mixtures of a Pluronic-type block copolymer and clay. The formation of the lamellar phase is rationalized by the entropically favored packing of clay discs. A recent small angle neutron scattering (SANS) study described the adsorption of poly(ethylene oxide) (PEO) polymer chains to Laponite (LRD) clay platelets at low polymer and clay concentrations with total concentration < 5%. The gelation of the clay was prevented or extremely retarded due to the influence of the polymer molecular weight and the polymer and clay concentrations. For low concentrations the SANS contributions from bulk and adsorbed polymer chains could be separated with contrast variation methods. Although these results were not sensitive to the shape of the polymer concentration profile, other research groups have used neutron diffraction to address the interlayer and ordered structure around each clay platelet as well as the mechanism of bridging flocculation.

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Below the threshold for the complete saturation of the clay particles by the polymer, shake gels can be generated with the consistency of a half-cooled gelatin dessert. These suspensions undergo a dramatic shear thickening when subjected to vigorous shaking. Our work uses polymer-clay systems at higher concentrations and higher polymer molecular weights. In previous work by Schmidt et al. it was found that the polymer chains were entangled and in a dynamic adsorption-desorption equilibrium with the clay particles forming permanent networks that are highly elastic, behaving more like a soft chewing gum than gelatin. Individual polymer chains can physically absorb to several particles resulting in strong bridging effects. In this case SANS contrast matching methods cannot distinguish between the intensity contributions of network active PEO, adsorbed PEO (just adsorb PEO not necessarily network active), and excess PEO (the PEO that is not attached to the clay because the clay surface is already covered) inside the network. Despite this large body of work polymer-clay interactions remain complex and poorly understood phenomena requiring much more investigation.

Small angle neutron and X-ray scattering is a powerful technique for characterizing the structure and provides a measure of nanoparticle orientation under shear. Scattering from an anisotropic distribution of platelets directly leads to an anisotropic scattering pattern.

The expected response of flat objects in a flow field is to align in the c orientation. This has been seen in a number of systems of clay platelets in polymer matrices and solutions. Some of these systems have been nicely described by earlier studies on nylon based nanocomposites reviewed by Krishnamoorti and Vaia. Recent studies by Lele et al. with in situ X-ray diffraction experiments have provided direct evidence for rheology-microstructure linkages in polypropylene based nanocomposites.
Recently Schmidt et al. reported an unexpected case of a orientation for aqueous solutions of synthetic LRD clay and PEO. SANS for samples in D$_2$O measured the shear-induced orientation of the polymer and platelets. SANS for samples with the solvent contrast matched to the clay detected the orientation of the polymer alone. When a shear field was applied the clay particles oriented first. With increasing shear the polymer chains started to stretch and began to contribute to the anisotropy. As the shear distorted and ruptured the transient gel, coupling between the composition and shear stress led to the formation of macrodomains. It has been proposed that the clay orients in response to a biaxial stress arising from shear and elastic forces.

A recent transmission electron microscopy (TEM) analysis by Okamoto et al. have revealed a house-of-cards structure in polypropylene-clay nanocomposites subjected to elongational flow. Strong strain-induced hardening and rheopexy features at higher deformation originated from the perpendicular alignment of the silicate to the stretching direction (b orientation). Although TEM is not an in situ technique it did reveal the difference in clay orientation caused by shear flow versus elongational flow. Similar to the polymer-clay solutions discussed by Schmidt et al., Okamoto’s nanocomposites had strong interactions between the polymer matrix and the silicate layers.

The goal of this study is to probe microscopic and nanoscopic changes in PEO-Cloisite NA+ (CNA) solutions under shear. The combination of rheology and SANS provides a more complete physical picture of the shear response and relaxation behavior of these suspensions. We compare this work on PEO-CNA networks and focus on the differences and similarities in the shear orientation as well as the polymer-clay interactions.
3.2 Experimental

We prepared viscoelastic solutions of a natural smectite clay, Montmorillonite (CNA, Southern Clay Products)†, and PEO (Polysciences, Inc., weight average molecular weight \( M_w = 5 \times 10^6 \text{ g/mol, } M_w/M_n \approx 1.5 \), and radius of gyration \( R_g \approx 200 \text{ nm in } H_2O \). All the CNA results reported here are for a solution containing mass fractions of 3% CNA and 5% PEO at ambient temperature. The reference LRD samples contained 3% LRD and 2 or 5% PEO (Table 3.1).

The CNA clay produced an opaque suspension of predominantly exfoliated platelets. There were no peaks at high scattering vector \( q \) values in SANS\(^82\) that ranged in size from 700 to 1500 Å across and were about 10 Å thick, according to atomic force microscopy.\(^*\) The quiescent or equilibrium structure was that of a homogeneous solution with a nearly ideal polymer and clay dispersion and good adhesion between the polymer and clay.

Table 3.1. PEO-Clay Solution Characteristics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Clay (%)</th>
<th>PEO (%)</th>
<th>PEO ( M_w )</th>
<th>Power Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO5-CNA-6</td>
<td>3</td>
<td>5</td>
<td>600,000</td>
<td>-0.03</td>
</tr>
<tr>
<td>PEO5-CNA-10</td>
<td>3</td>
<td>5</td>
<td>1,000,000</td>
<td>-0.03</td>
</tr>
<tr>
<td>PEO5-CNA-50</td>
<td>3</td>
<td>5</td>
<td>5,000,000</td>
<td>-0.03</td>
</tr>
<tr>
<td>PEO5-LRD-10</td>
<td>3</td>
<td>5</td>
<td>1,000,000</td>
<td>-0.07</td>
</tr>
<tr>
<td>PEO2-LRD-10</td>
<td>3</td>
<td>2</td>
<td>1,000,000</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

\(^a\) Relative mass error < 1%

Because of the relatively high polymer and clay concentrations, we expected randomly oriented domains of oriented polymer covered clay particles to be present. Both the pH

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\(^†\) Estimated polydispersity ca. 30% according to manufacturer.
and ionic strength of the solutions were controlled by the addition of $3.34 \times 10^{-4}$ mol/L NaOH (for a pH of ca. 10) and $3.5 \times 10^{-3}$ mol/L NaCl, respectively. The sample preparation was reduced to 3 weeks when the samples were mixed/sheared and centrifuged daily. Simply dissolving the polymer and the clay in water was not sufficient to completely exfoliate our samples. Extensive mixing and shear were necessary to guarantee the reproducibility of the rheological experiments. All the CNA-PEO solutions used in this study were exfoliated, homogeneous, and stable for more than half a year.

![Graph](image.png)

**Figure 3.1.** Steady-state viscosities of several polymer-clay solutions as a function of shear rate.

Rheological experiments were performed on a Rheometrics Scientific ARES rheometer (transducer range = 0.2 – 2000 g·cm) with either parallel plate (38 mm diameter and 1 – 2 mm gap) or Couette type geometry. The Couette cell had a 2 mm gap between the cup and the bob with an approximate volume of 8 mL. The shear rate dependence of the viscosity (Figure 3.1) was obtained with individual, time dependent and constant rate experiments. Once the samples equilibrated after cessation of shear
another time dependent and constant rate experiment was performed. Constant shear rates were applied for about 200 s at low shear rates \((d\gamma/dt < 5 \, \text{s}^{-1})\) and for about 100 s at higher shear rates \((d\gamma/dt > 5 \, \text{s}^{-1})\). These intervals were sufficient to reach steady state as determined from the time dependent viscosity measurements. Duplicate measurements with a new sample showed the reproducibility of steady state values within a relative error of about 7%.

![Figure 3.2](image)

**Figure 3.2.** 2D SANS profiles (raw data) of PEO5-CNA-50 solutions obtained with the radial beam (x-z plane observed; left) and the tangential beam (y-z plane observed; right) at a shear rate of 70 s\(^{-1}\). The anisotropy in the gradient direction is slightly influenced by reflections due to the empty Couette shear cell in the tangential beam configuration. The two profiles do not have the same scaling. The figure at the right is a top view of the Couette cell.

SANS measurements were performed on the 30 m NG7 SANS instrument at the Center for Neutron Research (NCR) of the National Institute of Science and Technology (NIST).\(^{83}\) SANS spectra were recorded simultaneously while the sample was being sheared at a constant rate. The shear cell had a Couette geometry (as described previously)\(^{84, 85}\) with an inner diameter of 60 mm and a gap of either 0.5 or 1 mm for a total path length of either 1 or 2 mm through the sample. To study the three-dimensional (3D) clay orientation we carried out SANS measurements with two configurations of the sample with respect to the beam (Figure 3.2). In the standard configuration, called radial
beam geometry, the incident beam was parallel to the shear gradient and transverses the center of the annular cell. In the second configuration, called tangential beam geometry, the incident beam was parallel to the flow direction and tangential to the cell annulus. Sample to detector distances of 11.2 and 1.5 m with an incident wavelength of \( \lambda = 9 \, \text{Å} \) were used to give a total \( q \) range of \( 0.003 \, \text{Å}^{-1} < q < 0.2 \, \text{Å}^{-1} \). The scattering vector \( q \) is defined as \( q = 4\pi/\lambda \sin(\theta) \), where \( 2\theta \) is the scattering angle. The scattered intensities were corrected for background and parasitic scattering.\(^{86}\)

3.3 Results and Discussion

Our current understanding of the previous rheology and present SANS results is that the polymer chains are in a dynamic adsorption-desorption equilibrium with the clay particles and thus form a network.\(^{47, 54}\) When clay particles strongly absorb to the surrounding polymer chains the polymer does not provide a continuum medium for particle support any more. Individual polymer chains can physically absorb to several clay particles resulting in strong bridging effects. All polymer-clay solutions (Table 3.1) consist of a network between clay platelets and PEO chains, with the polymer chains crosslinked between the platelets.

The steady-state values of the viscosity for two reference PEO-LRD solutions (PEO \( M_w = 10^6 \, \text{g/mol} \)) and three PEO-CNA solutions (PEO \( M_w = 300,000, 10^6, \) or \( 5 \times 10^6 \, \text{g/mol} \)) are shown in Figure 2.1. All CNA solutions have the same polymer (5%) and clay (3%) concentrations and show shear thinning. The two reference PEO-LRD solutions contain 2 or 5% PEO and 3% LRD clay each (Table 3.1). At low shear rates a power law exponent \([m = -0.03, \text{viscosity} = (d\gamma/dt)^m]\) can be obtained for PEO5-CNA-10 (\( M_w = 1 \times 10^6 \, \text{g/mol}, 5\% \text{PEO} \)) and a change in the slope and curvature can be observed at \( d\gamma/dt > 3 \, \text{s}^{-1} \); whereas, a reference PEO5-LRD-10 solution (\( M_w = 1 \times 10^6 \, \text{g/mol}, 5\% \))
PEO) previously studied by us\textsuperscript{46} had higher viscosity and $m$ values [$m = -0.7$, viscosity = $(d\gamma/dt)^m$].

As Figure 3.1 shows for similar concentrations of the polymer and clay and a given polymer molecular weight, the viscosities of the solutions with larger clay platelets (CNA) are much lower than those of LRD solutions with smaller clay platelets, indicating weaker interactions. Thus, it seems that the polymer-clay interactions become stronger as the particle size is reduced. PEO-LRD (30 nm diameter particles) solutions (Table 3.1) do not flow when a vial containing the solution is turned upside down, whereas almost all PEO-Montmorillonite solutions (100 nm diameter particles) except PEO5-CNA-5 and comparable PEO-Kaolinite solutions (micrometer diameter particles) do flow. However, there are additional parameters such as the polydispersity, surface effects, and chemistry that may contribute to enhanced interactions. Nonetheless, this suggests that nanoscale interactions are essential for the enhancement of rheological properties at these relatively low particle concentrations.

As the polymer $M_w$ (at a fixed polymer concentration) increases so does the viscosity of the PEO-CNA solutions. This might be expected because of the longer and more entangled chains. However, in addition to entanglement effects the longer individual polymer chains contain more adsorption points (crosslinks) which result in stronger bridging effects and enhanced viscosity. Given the effect of pure entanglements evidenced by the rheology of a pure PEO solution described in the literature\textsuperscript{87} with viscosities an order of magnitude below what is observed in these polymer-clay mixtures, it is reasonable to assume that the polymer molecular weight strongly influences the density and strength of the polymer-clay bridges.
The PEO5-CNA-50 samples were shear-oriented while being loaded into the SANS shear cell, as shown by the anisotropic SANS patterns observed at rest. Shear is necessary to reorient clay platelets in one direction. Steady-state viscosity experiments showed reproducible results when we switched from low to high or high to low shear rates demonstrating that although pre-shearing affects startup viscosities it has no influence on steady-state values. All SANS data were obtained from samples in the steady-state regime. When clay particles and polymer chains are aligned in a flow field (real space) the resultant scattered intensity distribution (reciprocal space) also becomes anisotropic. The resultant anisotropy will manifest itself as an anisotropic pattern on a 2D SANS multidetector oriented parallel to the plane of anisotropy.

Representative SANS results obtained from polymer-clay solutions in the radial and tangential beam configurations are shown in Figure 3.2 and Figure 3.3. All radial SANS patterns show isotropic intensity distributions [e.g. Figure 3.2(b)], whereas all tangential SANS patterns show anisotropy parallel to the gradient axis of the flow field [Figure 3.2(a)]. As shown in Figure 3.3, the intensities in the radial and tangential configurations do not change significantly within the measured major shear-thinning (Figure 3.1) range of shear rates (0.5-90 s\(^{-1}\)) indicating that the orientation of the PEO-CNA system as detected by SANS occurs at shear rates below 0.5 s\(^{-1}\). The shear thinning then must come from some other mechanism than the usual orientation effect and must instead reflect changes in more subtle polymer-clay interactions with shear. This is similar to a later discussion on relaxation times in the PEO-LRD system and demonstrates the complementarities of the techniques. In any event, this PEO-CNA

\[^{1}\] Preliminary flow-birefringence experiments also support these results. Depending on the orientation and size domains as well as sample history during filling, birefringence from a “new” sample is always slightly different and non-zero. Due to strong birefringence, probably going over orders, we can not determine the sign of the birefringence. Birefringence can also be visualized using a microscope and cross polarizers.
alignment saturates at a much lower point than that observed with the PEO-LRD systems of which the alignment did not saturate until above 90 s$^{-1}$. Thus, the data indicate that a very low flow is strong enough to orient this polymer-clay system.$^{45-47}$

![Figure 3.3. PEO5-CNA-50 SANS intensity averaged in 10° sectors for all three directions in space. The isotropic SANS data have been circularly averaged. In this case the intensities in the z and x directions are the same. The SANS data have not been corrected for incoherent. This may cause larger relative errors at high q values. Some error bars are smaller than the plotting symbols.

The form factor for randomly oriented discs is well known to have a $q^2$ dependence, as does the form factor for an unperturbed Gaussian coil for example.$^{88}$ Thus, a plot of the logarithm of the intensity ($I$) versus log $q$ from a system of randomly oriented, non-interacting thin disks, such as clay platelets, would be expected to have a
slope of -2 over a wide $q$ range, as observed by many other research groups. For the $q$ range shown in Figure 3.3(a) [radial beam, radial averaging of $l(q)$ versus $q$], we note that $l(q)$ scales with $q^{-1.6}$ (high $q$) and $q^{-2.8}$ (low $q$). In our case, the deviations from $q^{-2}$ are probably due to contributions from the scattering of polymer chains, especially at high $q$ values, from the clay polydispersity, possible clustering, and clay orientation. Hanley et al. attributed deviations from $q^{-2}$ toward $q^{-3}$ to clustering and polydispersity in Montmorillonite suspensions. In the tangential beam configuration gradient direction [$y$ direction; Figure 3.3(d)], $l(q)$ scales with $q^{-1.9}$ and this is attributed to the disk form factor. Future experiments with contrast variation techniques and partial structure factor analyses will help to separate out the individual contributions of the clay and polymer in the mixtures.

In radial beam configuration, perfectly shear aligned platelets in the expected $c$ orientation would be oriented with their surface normals parallel to the neutron beam and their projection in this plane ideally would be seen as 2D discs with no anisotropy. In the tangential beam configuration, their surface normals would be perpendicular to the neutron beam correctly being seen edge on with the projection looking like a rigid rectangle (or a needle) and the scattering intensity would be predominantly in the horizontal (gradient) direction. The orientation of the platelets in the $a$ orientation would lead to anisotropy in both the tangential and radial configurations. Thus, the small required shear field appears to align the platelets in the flow direction in the expected $c$ orientation rather than the $a$ direction observed for PEO-LRD, Figure 3.4. These orientations were also observed in lamellar liquid-crystalline phases, block copolymer solutions, and melts.
The orientation of the platelets is a competition between (1) flow alignment and (2) orientation and configurational relaxation. At a given shear rate, the relaxation processes must be hindered by a coupling between the polymer and clay.

Figure 3.4. Model for the real space orientation of CNA clay platelets and corresponding reciprocal space SANS patterns (x = flow direction, y = gradient or velocity direction, and z = vorticity or neutral direction). As the CNA platelets align with the surface normal along the velocity direction we can observe an isotropic radial SANS pattern (beam in y direction) and a horizontal streak in the tangential SANS pattern (beam in x direction). An imperfect orientation of platelets is assumed.

With arguments similar to those of Ramsay and Lindner and Hayter and Penfold, competing effects can be characterized by the dimensionless Weissenberg parameter ($\Gamma = g\tau$, where $g$ is the shear rate and $\tau$ is the relaxation time). Full alignment will occur for $\Gamma \gg 1$. In this study, the alignment of the PEO-CNA system starts at shear rates $\ll 0.5 \text{ s}^{-1}$, whereas the PEO-LRD systems containing smaller LRD particles studied previously begin to align at shear rates of about $5 \text{ s}^{-1}$. This corresponds to characteristic relaxation times of $\tau \gg 2 \text{ s}$ for the PEO-CNA system and $\tau \approx 0.05 \text{ s}$ for PEO-LRD. Although Hayter and Penfold studied micellar solutions 20 years ago, our polymer-clay
solutions and gels pose different challenges because the polymer and clay orientation relaxation times can be very different. Future contrast matching studies should be able to help separate these components. If the shear becomes large enough to disrupt the clay-polymer interactions it is possible for phase separation to occur. Effects similar to shear banding have been observed within rheology and microscopy experiments for both PEO-LRD and PEO-CNA solutions at very high shear rates and over long shear times. The relaxation of PEO-CNA after the cessation of shear is slow, as would be expected from very low shear rates for alignment, and on the timescale of the experiments (> 2 h) is incomplete, with the anisotropic peaks in the SANS patterns (discussed later) relaxing to only about half their original height in 70 minutes.

There are a variety of ways of characterizing the anisotropy in sheared SANS data. Dadmun and Han, 76 for example, characterized anisotropy in scattering patterns in terms of peak heights and widths of azimuthal intensity scans. They used the peak height to characterize changes in the molecular orientation. With this procedure, the azimuthal trace of PEO-CNA data fit with a Lorentzian curve and the width and peak height were plotted as functions of the time that elapsed after the cessation of shear. Data obtained from azimuthal averaging at (1) $q \approx 0.07 \text{ Å}^{-1}$ and $d \approx 90 \text{ Å}$ ($d = \text{characteristic dimension}$ $d = 2\pi/q$) are shown in Figure 3.5, and data obtained at (2) $q \approx 0.007 \text{ Å}^{-1}$ and $d \approx 900 \text{ Å}$ are shown in Figure 3.6. The SANS relaxations for 1 and 2 indicate that after 120 minutes there is still some anisotropy visible. The results displayed in Figure 3.7 show that the PEO-CNA samples relax back to a much lower degree of orientation but do not randomize completely as PEO-LRD solutions do.
Figure 3.5. Plot of peak height and half-width versus relaxation time after cessation of shear of the azimuthal intensity distribution from a Lorentzian fit. The insert shows a SANS pattern with an azimuthal ring ($q \approx 0.07 \text{ Å}^{-1}$ and $d \approx 90 \text{ Å}$) used to calculate the anisotropy.

Figure 3.6. PEO-CNA relaxation of anisotropic SANS patterns (tangential beam configuration). Peak intensity plot versus time. Data was azimuthally averaged at $q \approx 0.007 \text{ Å}^{-1}$ and $d \approx 900 \text{ Å}$. From the plot it can be seen that after 120 minutes the relaxation is not complete.
The Hermans’ orientation function \( f \) or nematic order parameter can be used to quantitatively assess the degree of orientation at any point in the relaxation process as follows:\textsuperscript{100-102}

\[
f = \frac{3\langle \cos^2 \phi \rangle - 1}{2} \] (3.1)

\[
\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I \sin \phi d\phi} \] (3.2)

Where \( \langle \cos^2 \phi \rangle \) is the average cosine squared weighted by \( I \) as a function of the radial angle (\( \phi \))\textsuperscript{8}. Thus, \( f \) varies between \( f = 1 \), corresponding to a perfect orientation, and \( f = 0 \), corresponding to a random orientation. With azimuthally averaged data for \( q = 0.07 \text{ Å}^{-1} \) (SANS configuration = 1 m), the PEO-CNA solution yields \( f = 0.85 \) at a shear rate of 90 sec\(^{-1} \); this decreases to \( f = 0.74 \) within 70 minutes after the cessation of shear indicating that complete randomization (\( f = 0 \)) would probably take weeks and thus, is experimentally inaccessible to SANS.

Anisotropic SANS data from PEO-LRD solutions, on the other hand, relax to completely isotropic patterns within 50 s (Figures 3.5, 3.6 and 3.7). This makes it hard to quantify the relaxation time. To provide some measure of this fast relaxation a time-slicing procedure\textsuperscript{103} was used to obtain better time resolution. To maximize the signal from this relatively time intensive and inherently low intensity measurement, we used a PEO2-LRD-10 solution to eliminate the large background signal from unaligned excess PEO. The change in the alignment with time was quantified by plotting of the total

\textsuperscript{8} Vectors at 0 and 90° have between them angle \( \phi \).
SANS intensity versus the time in Figure 3.8.** These data indicate that regardless of the initial degree of alignment, the time constant for orientation relaxations is approximately 7 seconds. However, better time resolution is clearly needed to obtain an accurate value.

![Diagram of SANS intensity relaxation for PEO-CNA and PEO-LRD](image)

**Figure 3.7.** Tangential SANS data for PEO5-CNA-50 and PEO2-LRD-10 at a shear rate of 90 s\(^{-1}\) and the relaxation of the SANS intensity after the cessation of shear (similar q range).

** Although ideally we would like to limit the number of parameters being altered this is often impossible in large part because of the very complicated phase diagrams of these complex systems. For example, although PEO2-LRD-10 (Table 2.1) is the sample with the most network active PEO it is not possible to prepare anything exactly comparable to CNA because under similar conditions [e.g. same polymer M\(_{\text{w}}\) and same polymer (2%) and clay (3%) concentrations] a PEO-CNA solution or mixture will strongly phase separate. On the other hand, PEO5-LRD-10 appears to have a considerable amount of excess PEO, the isotropic scattering signal of which provides a large background signal that is very difficult to handle here. This is not the case for PEO-CNA-10. Thus, the choice of samples is limited by the phase diagrams and the limitations of the technique involved. However, the relaxation times for the various LRD samples are the same order and are much faster than those of the CNA solutions. Here we are roughly able to quantify that.
with the PEO5-LRD-10 solution. Despite this very rapid orientation relaxation in PEO-LRD solutions, stress-relaxation measurements show that full relaxation requires much longer times (ca. 30 min). As mentioned earlier this is another example of the synergism between SANS and rheology. Nonetheless, the relaxation behavior after the cessation of shear is currently poorly understood.

To understand the PEO-CNA results, we propose that as the polymer chains adsorb to the clay particles they build a connected 3D network, much as we proposed for a similar network-like polymer-clay system containing much smaller platelets (30 nm diameter LRD).\textsuperscript{45-47} The polymer chains are envisioned to be entangled and in adsorption-desorption equilibrium with the clay particles exhibiting characteristics of soft, reversible crosslinkers. Several studies besides our own work have shown that PEO polymer chains are very silicatophilic making our model reasonable.\textsuperscript{104-106} Further evidence for such connectivity is the fact that long, strongly birefringent fibers (up to 8 m long and 2 μm in diameter) can be manually drawn from PEO-CNA and PEO-LRD solutions; this is not possible with either pure clay or a pure percolated polymer solution on its own. Polymer molecular weights of $10^6$ g/mol ($R_g \approx 100$ nm in aqueous solutions) or higher are necessary to produce the fibers. A pure reference PEO solution with up to 2% ($M_w = 10^6$ g/mol) at the same pH and salt concentration has been found to produce no anisotropic SANS patterns at shear rates of up to about 100 s\textsuperscript{-1}.\textsuperscript{45,46} Pure reference PEO solutions discussed in the literature behave like shear-thinning viscous fluids with a Newtonian plateau at low shear rates.\textsuperscript{55} It is not possible to completely dissolve larger amounts (5%) of high molecular weight PEO in water without phase separation affects and aggregation. However, the polymer-clay absorption and interactions increase the solubility of polymer in water, stabilizing our solutions. Finally, as another indication of
a strong polymer-clay network, we note that our PEO-CNA and PEO-LRD samples could not be diluted without flocculation and macroscopic phase separation.

**Figure 3.8.** PEO-LRD relaxation with time-slicing procedures: total SANS intensity (y axis) versus time after cessation of shear (time slicing procedure as described in ref. 63). Shear rates used before shear stop are: 90 s\(^{-1}\) (○), 50 s\(^{-1}\) (□) and 10 s\(^{-1}\) (◊).

### 3.4 Conclusions

The two PEO-clay systems clearly have very different dynamics. Under comparable conditions (similar polymer concentration, pH, and salt), large CNA clay platelets (diameter = 100 nm) align much more readily under flow than smaller LRD clay platelets (diameter = 30 nm)\(^{45-47}\) and relax from that alignment much more slowly as well. This is a new and unexpected result that we need to explain with further rheological studies. The size of the clay may play an important role in the relaxation
processes and the nanoscale interactions influence the macroscopic behavior. Finally, the interactions between the polymer and clay may be somewhat different because of the nature of the clay. These interactions and the kinetics of the adsorption-desorption equilibrium of the polymer chains to the clay surfaces influence the strength of the network. The dispersion and stabilization of the clay platelets in an aqueous polymer solution occur because of hydrogen bonding as well as strong dipole interactions between PEO chains and charged clay surfaces. Polymer-clay interactions depend on many parameters, such as the polymer and clay concentration, clay chemistry, clay size distribution, surface treatment, solvent type, pH, and salt.

Our unexpected results pose many open questions and more experiments are necessary for a quantitative evaluation. Planned SANS measurements may help us to determine the thickness and density of the polymer-clay interfacial region, the average number of contacts per chain and per particle for the different sizes of clay particles, and the different molecular weights. Once we have obtained this information, we can determine how the polymer-clay interactions influence the macroscopic behavior. Planned dynamic testing will lead to further elucidation of the rheological behavior for a better understanding of the viscoelasticity, relaxation, and interaction-based phenomena. This information will be important for better controlling the fluidity of nanocomposite systems and thus changing their mechanical and electronic properties. Further experiments are required to fully and quantitatively characterize the polymer-clay interactions in these fascinating and extremely complex systems.
CHAPTER 4. ORIENTATION OF PLATELETS IN MULTILAYERED NANOCOMPOSITE FILMS

4.1 Introduction

In this chapter, we focus on the preparation and structural characterization of polymer-clay films prepared by a layer-by-layer approach from polymer-clay solutions. Efficient nanoparticle dispersion in solution combined with good polymer-particle interfacial adhesion allows the exciting possibility of developing strong and transparent films, coatings, and membranes. Hybrid films such as the ones described within this chapter may offer opportunities for a wider range of applications.

The effect of shear on the orientation of polymer-clay nanocomposites has been examined by a number of groups, and in some cases, the three dimensional (3D) orientation of the polymer and clay has been determined. The two dimensional (2D) clay may align in three primary directions under shear, often referred to as $a$, $b$, and $c$ orientations.

Polymer nanocomposite multilayered films were prepared with a defined orientation from network-like solutions as previously described by Schmidt et al. Next a determination whether was made to see if and how the shear orientation in the solution can be maintained when the solvent is evaporated. The multilayered structures that have been developed and examined may be important for many applications, such as microelectronics, optical devices, or chemical sensors. Scattering and diffraction measurements were used to investigate the shear-induced orientation of polymer and platelets in nanocomposite films. First, examination of films derived from well-dispersed

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synthetic Laponite clay and then a comparison of the results with those derived from Montmorillonite dispersions.

4.2 Experimental

Synthetic and natural clay, Laponite and Montmorillonite respectively, were used in this study. The clay platelets were comprised of three layers with a center magnesium layer ion layer sandwiched between two silicate layers. The synthetic hectorite-type clay, Laponite RD (LRD), provided by Southern Clay Products,\textsuperscript{117, 118} consists of platelets of high purity and uniform crystalline size.\textsuperscript{119, 120} The natural smectite Montmorillonite clay is Cloisite NA+ (CNA). The platelet diameter, platelet dimension in the plane of the platelet, is on the order of 300 Å for Laponite and 700 to 1500 Å for Montmorillonite. Both clay types have an average thickness of 10 Å. The smaller Laponite diameter results in a smaller aspect ratio, 30:1, than for Montmorillonite, 100:1. Under the appropriate conditions, Laponite and Montmorillonite platelets may completely exfoliate in aqueous solutions.\textsuperscript{121, 122} Poly(ethylene oxide) (PEO), molecular weight average, $M_w$, $10^6 \text{ g/mol}$, molecular mass distribution: ca. 1.5, was purchased from Polysciences, Inc. All reagents were used as received.

PEO-clay films were prepared from exfoliated polymer-clay solutions via a layer-by-layer spreading approach. PEO and various concentrations of LRD were prepared in distilled, deionized water, mixed for at least 4 weeks until optimally exfoliated and transparent dispersions were obtained.\textsuperscript{47} The solution pH and ionic strength were controlled by the addition of NaOH and NaCl respectively. A pH value of 10 and a NaCl concentration of $10^{-3} \text{ M}$ were used for all samples. Under these conditions, flocculation due to the dominance of van der Waals attraction over electrostatic repulsion of the clay as well as degradation of the clay particles is avoided. Solutions were spread on glass
slides layer by layer and dried at 25 °C in desiccators and in vacuo. More detailed film preparation is described in the literature.‡‡ During the drying process there is no sedimentation of the clay particles. Transparent single films with an average layer thickness of 5 to 7 μm were obtained by manually spreading the polymer-clay gel on a glass substrate with a blade.

For comparison, nonoriented bulk samples prepared by simply drying PEO-LRD solutions without spreading and therefore without any mechanical orientation were also investigated. Although the bulk samples have the same characteristics as those prepared by the layer-by-layer approach they are significantly thicker, between 2 and 3 mm, than the multilayer films, between 5 and 7 μm, see Table 4.1.

**Table 4.1.** PEO/Clay Film Characteristics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass Fraction, % Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRD15</td>
<td>15</td>
</tr>
<tr>
<td>LRD40</td>
<td>37</td>
</tr>
<tr>
<td>LRD60</td>
<td>60</td>
</tr>
<tr>
<td>CNA40</td>
<td>33</td>
</tr>
</tbody>
</table>

Relative mass error < 1%

SANS measurements were performed on the 30 m SANS NG7 instrument at the Center for Neutron Research, National Institute of Standards and Technology (NIST).83

In a standard γ-beam configuration the incident beam is perpendicular to the spread direction of the film and the SANS intensity is obtained in the x-z plane. In the z-beam

‡‡ In Single films with an average layer thickness of few microns were obtained by manually spreading the filled polymer gel on a glass substrate with a blade. Every few hours one film was spread and dried, which gives ca. 7-10 layers a day. During the drying process the films were manually oriented by re-spreading the already half dried films. Samples were dried in desiccators over night. Films with the same spread direction were dried layer by layer onto each other until a total multilayer film of ca. 1mm was obtained. Then the total thickness was measured with a caliper and divided by the number of layers. This procedure was done for several samples giving thicknesses of 5-7 microns for each single film. The film uncertainty is ca. 20% and was calculated as an average from several samples. A mechanical spreader could not be used due to high viscosity and chewing gum like sample behavior.
configuration the incident beam is parallel to the spread direction of many stacked PEO-clay films (see Figure 4.1 and Figure 4.2). The neutron beam in the z-beam configuration provided SANS intensities in the $x$-$y$ plane. Sample to detector distances of 15 and 4 m and incident wavelengths ($\lambda$’s) of 8.44 and 5 Å were used to give $q$ ranges ($q = 4\pi/\lambda \sin (\theta/2)$ of $0.0008221 \text{ Å}^{-1} < q < 0.01515 \text{ Å}^{-1}$ and $0.00898 \text{ Å}^{-1} < q < 0.08621 \text{ Å}^{-1}$).

Because of the longer wavelength, neutron scattering probes structures at longer length scales than typical X-ray scattering. The primary contrast in the SANS experiments is between the silicate and PEO. This allows SANS experiments to detect the overall orientation of the clay platelets in the polymer matrix.

Time resolved SAXS and wide angle X-ray diffraction (WAXD) measurements were performed at the Advanced Polymers Beamline (X27C) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength of the X-ray beam was 1.366 Å. The beam size was 0.4 mm in diameter at the sample position. Synchrotron X-rays were collimated with a three 2° tapered tantalum pinhole collimator. The sample to detector distance used was 1.73 m for SAXS. The SAXS scattering angle was calibrated with silver behenate and the intensity was normalized by incident beam fluctuations. The relative uncertainty associated with the X-ray measurement was ±5%.

There is a possibility that voids and porosity may influence the total scattering intensity. Thermogravimetric analysis (TGA) on representative films and differential scanning calorimetry (DSC) detected the presence of about 0.5% water in our films. Research by other groups has demonstrated that composite films prepared by alternate adsorption of polymer and exfoliated sheets of a synthetic Laponite may respond in a dramatic way to changes in ambient humidity. Residue water molecules in our films
should be distributed homogeneously and do not affect the structure and orientation of clay platelets in the film.

![Diagram]

**Figure 4.1.** (a) With the clay platelets aligned in the spread direction of the film (x-z plane), we observe an anisotropic SANS pattern with the neutron beam in the z configuration and an isotropic SANS pattern with the beam in the y configuration. (b) SANS intensity averaged from 10° sectors in the horizontal (x) and vertical directions (y or z) of the 2D SANS patterns. This procedure allowed us to obtain SANS intensities for each of the three directions in space.

### 4.3 Results and Discussion

Polymer-clay solutions were used to prepare nanocomposite films with well-defined clay-platelet orientations through a layer-by-layer approach. The orientation of polymer and/or clay platelet will greatly affect various properties, such as mechanical and barrier properties, of the nanocomposite films. Our previous work focused on determining the polymer-clay solution orientation; in this study, we determine the orientation of the polymer-clay films that have been prepared with polymer-clay solutions.
Figure 4.2. 2D SANS patterns from samples described in Table 2.1. The neutron beam in the \( z \) configuration gives SANS patterns in the \( x-y \) plane and with the beam oriented in the \( y \) configuration we obtain SANS intensity in the \( x-z \) plane.

There has been new technology of adsorption from solution for the fabrication of molecularly ordered nanocomposite films to expand and replace the well-known Langmuir-Blodgett techniques and to open the field of molecular self-assembly to materials science.\textsuperscript{124-126} For example, an atomic force microscopy (AFM) study on multilayered clay films revealed that polymer-Laponite films are characterized by significantly higher surface coverage than natural clays.\textsuperscript{124} Similar to systems that have
been investigated, the films used in our work were prepared by sequential adsorption of a polymer-clay gel. The preparative method used by us offers a powerful strategy to building ordered films by shear orientation from solution. One major motivation to use the spreading and drying procedure for PEO-clay nanocomposites containing 40-60\% clay by mass fraction is the ability for preparing well-dispersed and oriented nanocomposites which would otherwise be nearly impossible to prepare with conventional bulk mixing. Spin-casting of polymer-clay solutions was also problematic because of high-solution viscosity and elasticity as well as difficulties in removing the impurities.

The surface morphology and roughness of similar but one-layer films (5 \( \mu \)m thick) has been characterized by AFM. Although strong concentration dependence was observed on film morphology, no anisotropy could be detected. Because our nanocomposite films were prepared by spreading a thin layer of polymer-clay solution followed by drying and then repeating this process in the same spread direction several times until a multilayer film of approximately 1mm thickness was obtained, it was important to examine whether any interface exists between each layer. Our preliminary scanning electron microscopy (SEM) studies could not detect boundaries between single-spread micrometer-thick film layers but surprisingly showed a highly ordered and layered structure in the \( x-y \) plane and fractal-like structures in the \( x-z \) plane. Additional SEM studies also suggested that the exact thickness of one dried layer is not important to the overall orientation of platelets.

Various scattering and diffraction techniques can be used to analyze the clay orientation. Figure 4.1 depicts 2D SANS patterns obtained in the \( y \)- and \( z \)-beam configurations for LRD40. The orientation of the clay platelet can be deduced from these
results, and the physical picture is illustrated in the schematic (See Figure 4.1(a)) in which the predominant orientation of the clay platelets is the $c$ orientation with a surface normal perpendicular to the film plane. As shown in detail, the orientation of clay observed in solution, the $a$ orientation, was preserved only to a small degree in some compositions when the solvent was evaporated.

SANS results obtained for PEO-LRD nanocomposite films with various clay contents and a PEO-CNA nanocomposite film in the $y$- and $z$-beam configurations are shown in Figure 4.2. 2D scattering patterns obtained in the $y$-beam configuration show slight anisotropy for LRD60 and LRD40 but not for LRD15 and CNA40. Scattering patterns obtained in the $z$-beam configuration reveal a strong anisotropy for all samples with the LRD40 sample exhibiting the most distinct features. The relatively isotropic pattern observed in the $y$-beam configuration and the relatively large anisotropy observed in the $z$-beam configuration suggest that the clay platelets orient with their surface normal perpendicular to the film plane ($x$-$z$ plane) for all compositions.

From 2D SANS patterns obtained in the two beam configurations, the intensity as a function of $q$ can be calculated in the $x$, $y$, and $z$ directions. The SANS intensity is averaged in $10^\circ$ sectors in the horizontal ($x$) and vertical directions ($y$ or $z$) of the 2D SANS pattern with the intensity averaged in the horizontal $x$ direction overlapping perfectly. This procedure allows the SANS intensities in all three directions to be compared (see Figure 4.3). All SANS intensities were without incoherent scattering corrections. For all PEO-LRD films, a maximum at $q_{\max} \approx 0.01$ Å$^{-1}$ corresponding to a $d$-spacing, $d = 2\pi/q_{\max}$, on the order of 600 Å was observed and this was most pronounced in the $y$ direction. It is difficult to determine the exact peak positions because of smearing from the form factor. The maximum is observed best in the $y$ direction for
LRD40 at \( d = (644 \pm 15) \) Å. Intensities in the \( y \) direction are significantly stronger than those observed in the \( x \) direction. A visual inspection of data obtained in the \( z \)-beam configuration suggests that the composition strongly influences the degree of clay orientation and the film morphology.

It is of interest to compare the orientations in polymer-clay solutions determined in our previous study\(^{45}\) with those in the films. This could offer insight into the origin and mechanisms for the orientation in the nanocomposite films. The LRD fully exfoliates in PEO solution with the polymer keeping the clay platelets apart at a specific correlation length. From solution orientation measurements under shear, we know that during the spreading process, the polymer chains stretch and restrict the mobility of the platelets. In addition, an unusual alignment of the clay platelets along the flow direction with the surface normal in the vorticity direction (\( a \) orientation) was observed.\(^{45}\) The relaxation after cessation of shear is not well understood. Although SANS studies on PEO-LRD solutions observed very fast relaxation of anisotropy, stress-relaxation measurements showed that full relaxation occurs at very long times. Upon drying, the predominant clay orientation is the \( c \) direction. Those studies suggested that during the drying process, the network collapses and the concentration changes significantly. Thus, relaxation as observed in solution is slowed down. Although manual spreading continues with incompletely dried films,\(^{\text{88}}\) platelets orient and do not randomize as they would in solution.

\(^{88}\) In single films with an average layer thickness of few microns were obtained by manually spreading the filled polymer gel on a glass substrate with a blade. Every few hours one film was spread and dried, which gives ca. 7-10 layers a day. During the drying process the films were manually oriented by respreading the already half-dried films. Samples were dried in desiccators over night. Films with the same spread direction were dried layer by layer onto each other until a total multilayer film of ca. 1 mm was obtained. Then the total thickness was measured with a caliper and divided by the number of layers. This procedure was done for several samples giving thicknesses of 5-7 microns for each single film. The film uncertainty is
Figure 4.3. SANS intensity as averaged in 10° sectors for all three directions in space. Isotropic SANS data such as Figure 4.2(e and g) are circularly averaged. In this case, intensities in the $z$ and $x$ directions are the same. Intensities in the $x$ direction or circularly averaged data cover a larger $q$ range than intensities in the $y$ or $z$ direction. This is due to an off centered beamstop (see Figure 4.2). Data were place on the same arbitrary scale.

Scattering patterns from films in the $y$-beam configuration demonstrate some anisotropy for LRD40 and LRD60 (See figure 4.2(a, b)). This suggests that even with the collapse of the network a small amount of solution-like orientation is preserved in the films. This may be attributed to strong concentration changes during the drying process which reduce the rate of relaxation or randomization of the platelets. SANS patterns obtained in the $y$-beam configuration from LRD15 and CNA40 multilayer films were ca. 20% and was calculated as an average from several samples. A mechanical spreader could not be used due to high viscosity and chewing gum like sample behavior.
isotropic. The LRD15 and CNA40 samples showed the c orientation in both solution and in films. The LRD60 and LRD40 samples exhibited different orientation in solution (α orientation) and in films (c orientation) (see Table 4.2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Orientation in Film</th>
<th>Orientation in Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>LRD15</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>LRD40</td>
<td>c (α)</td>
<td>a</td>
</tr>
<tr>
<td>LRD60</td>
<td>c (α)</td>
<td>a</td>
</tr>
<tr>
<td>CNA40</td>
<td>c</td>
<td>c</td>
</tr>
</tbody>
</table>

Figure 4.4 portrays the intensity versus q plot from the PEO-LRD films with the various LRD contents averaged in the y direction. A maximum or shoulders occurs at (614 ± 50) Å for LRD15, (644 ± 15) Å for LRD40, and (630 ± 70) Å for LRD60, suggesting that spacing is relatively independent of the clay concentration. From solution studies, we know that excess polymer chains remain free in the solution and do not contribute mechanically once the clay platelets are saturated with the polymers. The network in solution consists of clay-rich and clay-poor domains. The critical concentration occurs at 3% LRD by mass fraction and 2% PEO by mass fraction in solution comparative to 60% LRD by mass fraction in the film. The shoulder or maximum observed in this SANS data on films relates to correlation in the lateral packing domains consisting of clay sequestered in polymer. A larger polymer composition should result in higher d-spacing, but this was not observed in our system. The LRD40 sample appears to have the optimal polymer to clay ratio that leads to the most pronounced SANS anisotropy and stronger correlation than for LRD15 and LRD60. Parameters that may contribute to higher SANS anisotropy for LRD40 are concentration of the clay combined with strong polymer-clay interactions, polymer molecular mass and
chain flexibility of PEO, the type of deformation, and crystallization of the polymer. The relationship between clay orientation and orientation of other structural units such as polymer unit cells and polymer lamellae remains unclear but will be the subject of future investigation.

Figure 4.4. (a) LRD series: concentration dependence for I(q) versus q as averaged in the y direction. An estimated relative error for maxima or shoulders is given in the text. (b) Azimuthal scans of scattered intensity at q = 0.0031 Å⁻¹ (SANS configuration: 15 m) and Lorentzian fit. (c) Half-width of azimuthal intensity as a function of clay concentration. (d) Peak height of azimuthal intensity as a function of clay concentration.

For comparison CNA40 (d = 628 ± 70 Å) and LRD40 (d = 644 ± 15 Å) films that have similar polymer to clay ratios but differ in clay type and aspect ratio were examined. At the same clay mass fraction the LRD sample will contain more particles than the Montmorillonite sample. The SANS measurement showed that the orientation is stronger
for the LRD sample than for the Montmorillonite sample. This is counterintuitive because we expected the larger particles to align more preferentially than the smaller ones at a similar concentration. Rheological experiments in solution suggested that the network structure formed by PEO and LRD is stronger than the network formed by PEO and Montmorillonite.\textsuperscript{128} The strength of the polymer-clay network in solution may strongly influence the alignment of clay during the film-spreading process.

The anisotropy in scattering patterns has been characterized in terms of peak heights and widths of azimuthal intensity profiles in which the peak height was used to assess the changes in molecular orientation.\textsuperscript{76} With the same approach data such as those presented in Figure 4.4(b) were fit with a Lorentzian curve and the width and peak height are plotted as a function of clay concentration. The half-width at half-maximum decreased with increasing LRD concentration indicating that the degree of order increased with clay concentration. The half-width of CNA40 is also included for comparison. The peak height versus clay concentration shows a surprising behavior for LRD40.

The Hermans’ orientation function \((f)\textsuperscript{100-102}\) or nematic-order parameter was also used to assess the degree of orientation:

\[
f = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (4.1)
\]

\[
\langle \cos^2 \theta \rangle = \frac{\int_0^{\pi/2} I \cos^2 \phi \sin \phi d\phi}{\int_0^{\pi/2} I \sin \phi d\phi} \quad (4.2)
\]
\( f \) was calculated with the azimuthally averaged data shown in Figure 4.4, where \( \langle \cos^2 \phi \rangle \) is the average cosine squared weighted by intensity \( I \) as a function of the radial angle, \( \phi \).

A system is completely aligned when \( f = 1 \) and random when \( f = 0 \). For \( q = 0.0031 \text{ Å}^{-1} \) (SANS configuration: 15 m), \( f = 0.41 \) for LRD15, \( f = 0.46 \) for LRD40, \( f = 0.38 \) for LRD60, and \( f = 0.51 \) for CNA40. On the basis of these calculations, the degree of alignment was significantly greater for LRD40 than for LRD15 and LRD60 which are comparable. In addition, the PEO-LRD film was considerably more aligned than the PEO-CNA film with the same clay mass fraction (See Figure 4.2).

Figure 4.5 displays combined SANS and USANS\( ^{***} \) intensity profiles for bulk samples LRD40 and LRD60 over a large \( q \) range. LRD60 is characterized by \( I(q) \propto q^{-2.7} \) in the low USANS \( q \) range and a shoulder at about 0.02 \( \text{ Å}^{-1} \) which corresponds to the spacing between polymer-covered clay platelets. This structure can be observed by AFM. Because of the special experimental data collection of USANS, it is not easy to explain these data (desmeared USANS data were used here).\( ^{†††} \) A qualitative interpretation of the data allows some speculations. The collapse of a 3D network from solution leads to fractal structures in three dimensions. In an oriented film, however, fractal structures are observed in two dimensions (\( x-z \) plane) as observed with SEM.\( ^{123} \) Fractal structures influence the total scattering intensity and the scaling behavior. Scattering data on the LRD40 showed onsets for at least two maxima. The maximum at high \( q \) can be correlated with the spacing between clay platelets. The maximum at very low \( q \) originates from individual large micrometer-sized clusters. The shapes of SANS

\( ^{***} \) In USANS is only a minor part of this paper, therefore the experimental setup and data collection is not explicitely defined. Here we show only preliminary results.

\( ^{†††} \)USANS is only a minor part of this chapter therefore the experimental setup and data collection is not explicitly defined. Only preliminary results are shown.
intensities versus $q$ from manually oriented micrometer thick films ($x, z$ plane, anisotropic pattern) and millimeter thick bulk samples ($x, z$ plane, isotropic pattern) were significantly different (See Figures 4.2, 4.3, and 4.5). This demonstrates that manual spreading influences the orientation of clay platelets strongly.

![Graph showing SANS and USANS data](image)

**Figure 4.5.** LRD40 and LRD60 reference bulk samples: circularly averaged $I(q)$ versus $q$ from SANS and USANS data obtained over a large $q$ range. An estimated relative error is about 4%.

Preliminary SANS annealing studies on LRD40 and LRD60 (not shown here) indicated that SANS intensities did not change with increasing temperature up to 100 °C. At very high temperatures (>200 °C) polymer degradation was observed and once transparent samples turned slightly yellow.

SAXS and WAXD were also used to examine the orientation in PEO-LRD nanocomposite films. Figure 4.6 shows 2D SAXS and WAXD profiles for a LRD40 film measured perpendicular and parallel to the spread direction. Both SAXS and WAXD profiles measured perpendicular to the spread direction were isotropic; whereas, those measured parallel to the spread direction were highly anisotropic. Although a small
degree of anisotropy was detected by SANS measurement probing a much lower $q$ range, SAXS did not detect anisotropy in the $z$ direction.

Perhaps the more interesting profiles are those obtained with WAXD in which the PEO crystal structures as well as interplatelet spacings can be assessed. The typical crystalline structure of pure PEO is a well-known monoclinic lattice with WAXD showing several orders of diffraction [many observed diffraction peaks are numbered in Figure 4.7 and 4.8]. The relative intensity versus 20 obtained in WAXD for LRD40 was calculated in the $x$, $y$, and $z$ directions (Figures 4.7 and 4.8).

**Figure 4.6.** SAXS and WAXD for LRD40 measured parallel and perpendicular to the spread direction: (a) SAXS perpendicular to the spread direction, (b) WAXD perpendicular to the spread direction, (c) SAXS parallel to the spread direction, and (d) WAXD parallel to the spread direction. The stripe in (c) is an experimental artifact.
Interestingly, the diffraction profiles obtained in the x and z directions exhibited signatures for PEO crystallites but lacked peaks 4 and 5 as would be expected in pure PEO. The scattering profile obtained in the y direction was significantly different from those profiles obtained in the x and z directions, indicating that this sample is highly oriented. The peaks observed in the y direction corresponded to distances between the clay platelets. These results suggested that the clay platelets are oriented with their surface normal to the film spread direction, and this agreed with our SANS results. In addition, the results obtained in the x direction suggested the crystalline PEO is also oriented and is orthogonal to the orientation of the clay platelet.

![Graph](image)

**Figure 4.7.** WAXD pattern of LRD40 measured in the x, y, and z directions.

The WAXDs of PEO-LRD nanocomposites with 15, 40, and 60% LRD by mass fraction measured in the x and y directions are shown in Figure 4.8(a, b), respectively. Comparisons of diffraction patterns showed mostly PEO crystalline structures in the x direction, but the diffraction pattern was more complex in the y direction. In the x direction [Fig. 4.8(a)], PEO-LRD with the lowest LRD mass fraction (15%) showed a
number of distinct PEO diffraction peaks. Surprisingly LRD40 did not show peaks 4 and 5 but the relative intensity for peak 3 was significantly stronger than that measured for LRD15. The disappearance of peaks 4 and 5 may be attributed to the high orientation of PEO crystal structures. At even higher clay composition, LRD60, the sample becomes mostly amorphous as all crystalline peaks essentially disappear.

![Figure 4.8](image.png)

**Figure 4.8.** WAXD pattern of PEO-LRD nanocomposites with various clay contents measured in the (a) \( x \) direction and (b) \( y \) direction.

The diffraction profiles in the \( y \) direction exhibit a number of peaks not associated with PEO crystal structures, but with interparticle spacing for all clay compositions. The relative intensity was highest for LRD40 indicating that this composition exhibits the strongest orientation, in agreement with the SANS data.

The orientation of the clay particles and possibly the presence of voids that were generated during the drying process may influence the total scattering intensity as well as the position of intensity peaks. The onset for a second maximum cannot be explained at this moment (Fig. 4.5(a)). This will be investigated in the future.
LRD40 and LRD60 are hygroscopic transparent and strongly birefringent films that have to be stored in a dry environment. Crystallinity of representative films, determined by DSC, changed within 0.5 year from about 0 to 2.8% for LRD60 and from 40.1 to 40.4% for LRD40, showing that the sample structure did not change significantly over time. Extensive crystallinity and birefringence studies are not the scope of this article but will be discussed in the future.123

4.4 Conclusions

The orientation of platelets in micrometer thick PEO-clay nanocomposite films with various clay contents was investigated with scattering and diffraction measurements. Polymer-clay solutions were used to prepare nanocomposite films with defined clay orientations and high clay contents (60% by mass fraction) which are difficult to prepare by other methods. The mechanism for the observed clay orientation follows. During the drying process the polymer-clay network collapses and the clay platelets are shear-oriented preferentially in the spread direction. Some solution LRD orientation is maintained in the film during the drying process at high clay concentration. Surprisingly, large Montmorillonite particles aligned less than the smaller LRD particles at a similar concentration. We concluded that the strength of the polymer-clay network strongly influences the alignment of the clay during the film-spreading process. As the solvent leaves clay-clay interactions which should be very strong above 5-10% will play a dominant role in determining the orientation of platelets with their surface normal perpendicular to the plane of the film.

We have shown that the presence of oriented and dispersed nanometer sized clay particles in a PEO film strongly affects the structure but material properties such as mechanical, optical, and permeability are also influenced. Some of the films discussed
above were transparent and showed strong birefringence which made them suitable for optical components. These properties will be presented in a future article.\textsuperscript{123} Because the clay as well as the polymer component are hygroscopic, the reversible absorption of water by a multilayered polymer-clay film makes the material interesting as a humidity sensor.\textsuperscript{116} Although PEO was the only polymer study here, some of the nanocomposite films do not significantly degrade at temperatures up to 200 °C suggesting they have good thermal properties. Preliminary results have suggested that at very high clay concentrations rheological experiments with conventional rheometers are not possible because of excessively high moduli and sample toughness. Films containing 60\% of silicate by mass and higher may be used as precursors for future ceramic materials, microelectronics, and anisotropic electric insulators. These are all issues that will be addressed in future research.
5.1 Introduction

Polymer clay nanocomposites are hybrid materials that exhibit a change in composition, structure and properties over the scale of nanometers. Small and wide angle scattering and microscopy are powerful techniques used to characterize structure and orientation. For example, poly(ethylene oxide) PEO-clay blends have been investigated and accelerated crystallization and clay induced orientation of PEO crystallites have been observed. Earlier work has found that intercalation of PEO within galleries of clay resulted in hybrid structures that can accommodate a maximum of ratio of polymer to clay and any excess polymer leads to the formation of two phases: either polymer-clay intercalates or pure polymer phases. More recent transmission electron microscopy (TEM) has revealed a house of cards structure in nanocomposite melts under elongational flow. Strong strain induced hardening and rheopexy features at higher deformation originate from perpendicular alignment of the clay to the stretching direction. TEM can reveal the difference in the shear flow induced versus elongational internal structures of the nanocomposite which is important in making films.

There are several different nanocomposite fabrication techniques that vary from intercalation to exfoliation in solution as well as the polymer melt. The structural and mechanical properties of PEO in aqueous solutions have been found to penetrate into Montmorillonites and strongly promote the exfoliation process. In a few cases an
interlayer helical conformation was reported for polymer molecules such as PEO.\textsuperscript{5, 133} When polymer solutions are added to exfoliated clay dispersions the strong interactions between the two components often leads to re-aggregation which is difficult to overcome.\textsuperscript{134} In the “wet state” of an exfoliated polymer clay gel or after air drying, the silicate layers remain trapped in the gel-like polymer film.\textsuperscript{5} The film quality can be improved by slow evaporation of the solvent where the clay platelets have time to assemble under gravitational and osmotic forces before the viscosity of the system impedes particle realignment.\textsuperscript{130, 135} An industrial more promising way is the melt intercalation of PEO into Montmorillonites where polymer chains were found to be more effectively intercalated than via solution.\textsuperscript{131, 136, 137} The reason was water is a good solvent for PEO and the polymer water interactions impede complete intercalation.\textsuperscript{131, 136, 137}

There has been new technology of adsorption from solution\textsuperscript{124} for the fabrication of molecularly ordered multicomposite films in order to expand and replace the well known Langmuir-Blodgett techniques and to open the field of molecular self assembly to materials science.\textsuperscript{125, 126} For example, atomic force microscopy\textsuperscript{124} on multilayered clay films revealed that polymer Langmuir films are characterized by significantly higher surface coverage than clays such as Montmorillonite. These films as well as those studied by Kleinfeld et al.\textsuperscript{127} were prepared by sequential adsorption of polymer and clay.

Previous work relevant to this chapter describe rheological and small angle neutron scattering (SANS) on network like solutions of clay and poly(ethylene oxide).\textsuperscript{45-47} The polymer and clay interact in a dynamic adsorption/desorption equilibrium to form a 3D network.\textsuperscript{47} The mesh size of this 3D network and the orientation in solution is important to the structure of dried films. Our work also focused on the orientation of
platelets in multilayered polymer-Laponite films as studied by small and wide angle scattering.\textsuperscript{138}

The objective in this chapter is to use network-like polymer-Montmorillonite solutions to prepare nanocomposite films with a defined orientation of the clay platelets and determine how the shear orientation in the solution influences the film structure after the solvent has evaporated. Only completely dried films were investigated. Efficient nanoparticle dispersion in solution combined with good polymer/particle interfacial adhesion allows the exciting possibility of developing network-like films, tissues or very porous membranes. Porosity strongly depends on sample preparation conditions. On a nanometer length scale, SANS and AFM are complimentarily used to study the structure and shear induced orientation of the polymer and platelets after a film was spread and dried from a network-like polymer clay solution. SEM and microscopy were used to investigate the morphology and porosity of the films on a micrometer length scale. Hybrid films, such as those described in this chapter, offer a range of challenges and opportunities.

5.2 Experimental

Natural clay Montmorillonite (Cloisite NA+, CNA) provided by Southern Clay Products was used in this study. The clay consists of platelets that range in size from 700 to 1500 Å across and ca. 10 Å in thickness. The clay polydispersity was reported to be approximately 30% according to the supplier. Poly(ethylene oxide) ($M_w = 10^6$ g mol$^{-1}$, molecular weight distribution about 1.5) was purchased from Polysciences Inc. Films were prepared via solution exfoliation. All the results reported here are from multilayered films that have been made from a solution containing mass fractions of 3% CNA clay and 5% PEO at ambient temperature. The CNA clay produces an opaque
suspension of predominantly “exfoliated” platelets with no peaks observed at high $q$ in SANS. The quiescent or equilibrium structure is that of a homogeneous solution with near ideal polymer and clay solution and good adhesion between the polymer and the clay. Due to the relatively high polymer and clay concentrations we expect that randomly oriented domains or oriented polymer covered clay particles are present. Both the pH and the ionic strength of the solution were controlled by the addition of NaOH (pH = 10) and NaCl (3 mM) respectively. Under these conditions flocculation and degradation of the clay particles were avoided. Sample preparation can be reduced to approximately 3 weeks when samples were mixed/sheared and centrifuged daily. Simply dissolving the polymer and the clay in water is not sufficient to completely exfoliate the samples. Extensive mixing and shearing are necessary to assure sample reproducibility. All solutions used for making films were confirmed to be exfoliated, homogeneous and stable.

Solutions were spread on glass slides layer by layer and dried at 25 °C in desiccators and under vacuum. Multilayered films containing ca. 33% clay and 67% PEO were obtained. Preliminary annealing studies and Thermogravimetric analysis indicate that water is dried out of the films («0.5%).

Single films with an average layer thickness of a few microns were obtained by manually spreading the filled polymer gel on a glass substrate with a blade. Every few hours one film was spread and dried, giving about 7 to 10 layers per day. During the drying process the films were manually oriented by re-spreading the already half dried films. Samples were dried in desiccators over night. Films with the same spread direction were dried layer by layer onto each other until a total multilayer film with a thickness of approximately 1 mm was obtained. The total thickness of the film was then
measured by a caliper and divided by the number of layers to obtain the average layer thickness of the film. This procedure was done over several different films giving an average thickness per layer of 5 to 7 microns for each film. The uncertainty in layer thickness for each film is ca. 20% as it was calculated from the average from several different films. A mechanical spreading process was not possible due to the high viscosity and chewing gum like behavior of the sample. Additional information on the film preparation has been previously published. The simple preparative method we have used offers a powerful strategy to build ordered films by shear orientation from solution. One reason this method was used is because the spreading and drying procedure, due to the high modulus of the 33% clay polymer nanocomposite, made shear orientation in the bulk with conventional rheological instrumentation difficult. Spin coating or dipping of the gum like hydrogel was problematic due to high viscosity and elasticity, as well as impurities which are difficult to remove.

SANS experiments utilized the 30 m SANS instrument NG7 at the Center for Neutron Research at the National Institute of Standards and Technology. In a standard configuration, referred to as the y-beam configuration, the incident beam is perpendicular to the spread direction of the film and we obtain SANS intensity in the x-z plane. In the second configuration, referred to as the z-beam configuration, the incident beam is parallel to the spread direction of many stacked films. The neutron beam in the z-beam configuration gives SANS intensities in the x-y plane (Figure 5.1). The effective q range for this experiment was $0.0008221 \, \text{Å}^{-1} < q < 0.08621 \, \text{Å}^{-1}$ ($q = 4\pi/\lambda \sin (\theta/2)$). The primary contrast in the SANS experiments was between the silicate and PEO. This allows SANS experiments to detect the overall orientation of the clay platelets in the
polymer matrix. Voids and porosity of the network like film structure may influence total scattering intensity.

Figure 5.1. With the clay platelets aligned in the spread direction of the film (x-z plane) we observe an anisotropic SANS pattern with the neutron beam in the z-configuration and an isotropic SANS pattern with the neutron beam oriented in the y-configuration.

Optical microscopy was performed with an Olympic BX51TF microscope under crossed polarizers. A small section of a single layer film was removed by scratching to expose both the x-z and x-y plane and to compare results with those obtained from complementary techniques.

SEM experiments were performed with a Cambridge 260 Stereoscan Electron Microscope. Several bulk film samples were first frozen in liquid nitrogen then fractured attached to an SEM stub and sputter coated with gold/palladium in an Edwards S-150
sputter coater. Fractures in all three planes have been investigated and only representative images are shown.

Sample preparation for AFM included cryo-fracture and cryo-ultramicrotome slicing. Samples from both methods showed the same morphology and structure when investigated. Representative AFM images from dried and cryo-fractured samples are shown. All AFM experiments have been carried out in air at room temperature using a Nanoscope III Multimode Microscope from Digital Instruments. The AFM was operated in the tapping mode to minimize the sample distortion due to mechanical interactions between the AFM tip and the sample surface. Integrated silicon tips with a radius of curvature of about 10 nm and cantilevers with a nominal spring constant of 30 N m\(^{-1}\) were used. In the tapping mode, the cantilever oscillates vertically at a drive frequency close to its resonance frequency and contacts the sample surface briefly in each cycle of oscillation. As the tip approaches the surface the vibrational characteristics of the cantilever oscillation (e.g. amplitude, resonance frequency and phase angle) change due to tip-sample interactions. The surface can be imaged in different ways. For instance “height” images are obtained by using the feedback loop which keeps the amplitude at a constant value \(A_{\text{sp}}\) by translating vertically the sample with the piezoelectric scanner. The feedback loop is controlled by the set-point amplitude ratio \(r_{\text{sp}} = A_{\text{sp}}/A_0\) where \(A_0\) is the amplitude of free oscillation. The recorded “height” images are the vertical displacements of the piezoelectric scanner. AFM images were recorded with the highest sampling resolution, 512 \(\times\) 512 data points. Duplicate measurements on all instruments show exact reproducibility.

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5.3 Results and Discussion

The overall properties of the dried polymer clay nanocomposite films depend on structural features such as morphology, polymer-clay interaction, and orientation on the nanometer length scale. In a previous work on solutions, we found the polymer chains to be entangled with the clay particles to form a network. Individual long polymer chains can physically absorb to several particles in solution resulting in strong bridging effects and thus enhanced properties in the dried film. When clay particles strongly absorb to the surrounding polymer chains in solution, the polymer does not provide a continuum medium for particle support anymore. The network character of the solution can be described as water-rich and nanocomposite rich regions which can be visualized by freeze fracture SEM. Preliminary SANS data over a large $q$ range confirm that polymer-clay solutions have large scale structures that could be described as interconnected networks on several length scales. The structure in solution strongly influences the morphology of the dried film when the water is evaporated and these networks collapse. The complexity of the nanocomposites makes them extremely tunable through small changes in the chemistry and structure of the polymers. The polymer molecular weight strongly influences the density and the strength of the polymer clay bridges and makes shear orientation during the spreading process easy. The orientational alignment of clay platelets is a competition between flow alignment and configurational relaxation during shear. At a given shear rate the relaxation process is hindered by a coupling between the polymer and the clay. Rheological experiments on PEO-CNA solutions (those used for making films) have shown that the CNA clay platelets already align at shear rates below $5 \text{ s}^{-1}$ and after cessation of shear relax from that alignment very slow (within many hours). Evaporation of the solvent at ambient temperature combined with shear
orientation strongly improved the film quality and increased the orientation of clay platelets that are layered between polymer.

The orientation of the clay platelets in the dried film can be deduced from SANS results and a simple physical picture is illustrated in Figure 5.1. The isotropic pattern in the x-z plane and the relatively large anisotropy observed in the x-y plane suggest that the predominant orientation of platelets is with the surface normal perpendicular to the plane of the film (x-z plane) (See Figure 5.2). The SANS intensity is averaged from 10° sectors in the horizontal (x) and vertical (y or z) direction of the 2D SANS pattern with the intensity averaged in horizontal x-directions overlapping (Figures 5.1 and 5.2). This procedure allows the SANS intensities in all three directions to be compared. A shoulder at \( q_{\text{max}} \approx 0.01 \, \text{Å}^{-1} \) corresponds to a \( d \)-spacing, \( d_{\text{SANS}} = 2\pi/q_{\text{max}} \), on the order of ca. 63 nm and is related to a distance between clay rich areas and polymer rich areas (SANS contrast between polymer and clay). The collapsed network structure from solution must lead to highly oriented layers in the dried film. The \( d \) spacing obtained from SANS \( (d_{\text{SANS}} \approx 63 \, \text{nm}) \) is more or less consistent with the spacing of the striped texture measured from AFM \( d_{\text{AFM}} \approx 56 \, \text{nm} \) (average over many measured spacings from several AFM images, see Figure 5.3). It is very important that the films are completely dry. The clay, as well as the polymer component, are hygroscopic and the reversible absorption/desorption of water leads to swelling/shrinking of the polymer thus increasing/decreasing layer spacing. This is a property that makes the material applicable as a potential humidity sensor.\textsuperscript{116}

The anisotropic SANS pattern (Figure 5.2) can be well correlated with the fast Fourier transform AFM data (Figures 5.3 a, b, and c) showing that a broad anisotropic
Isotropic SANS data are circularly averaged. In the case, intensities in the $z$ and $x$ directions are the same. Intensities in the $x$ direction or circularly averaged data cover a larger $q$ range than intensities in the $y$ or $z$ directions. This is due to an off-centered beamstop. Data were placed on the same arbitrary scale.

Figure 5.2. SANS intensity as averaged in 10° sectors for all three directions in space. Isotropic SANS data are circularly averaged. In the case, intensities in the $z$ and $x$ directions are the same. Intensities in the $x$ direction or circularly averaged data cover a larger $q$ range than intensities in the $y$ or $z$ directions. This is due to an off-centered beamstop. Data were placed on the same arbitrary scale.

streak in the diagonal (Figure 5.3, right) is perpendicular to the striped texture (Figure 5.3, left). On similar length scales both methods complement each other. While SANS yields reciprocal space information and an average degree of orientation, AFM visualizes real space structures within discrete sections of the sample. Therefore, slight differences in $d_{AFM}$ and $d_{SANS}$ spacing are to be expected. The existence of the high ordered and layered structure observed with AFM is unusual and unexpected. The orientation and size of the clay platelets, ca. 100 nm in a diameter and 1 nm thick, does not explain the highly ordered layers and their thickness of ca. 56 nm (Figure 5.3). We note, however, that the clay can absorb a maximum amount of polymer until all the clay surfaces are covered. Any excess polymer in solution as well as in the bulk leads to formation of two nanocomposite phases—network like polymer-clay intercalates and pure polymer phases. We assume that during the drying process these two phases lead to the
layered structure observed with AFM and SANS. Also of note, this interpretation is consistent with similar behavior reported by Vaia, Wu, and Schmidt.

Figure 5.3. Representative AFM data from the x-z plane of multilayered films. (a) 952 × 952 nm AFM "height" image of the x-z plane of a multilayered film. The AFM experimental conditions were: $A_0 = 54$ nm, $f_0 = 179$ 788 Hz, $A_{sp} = 52$ nm, $f_{sp} = 179$ 572 Hz, $z$-range = 90 nm; (b) FFT spectrum of Fig. 5.3a; (c) cross section of Fig. 5.3a.

The anisotropic SANS scattering pattern can be characterized in terms of peak heights and widths of azimuthal intensity profiles in which the peak height is used to assess the changes in molecular orientation using Hermans’ function to calculate $f$, the degree of orientation. A system is completely aligned when $f = 1$ and random when $f = 0$. For multilayered films studied in this paper a value of $f = 0.49$ was obtained. At this time SANS contrast of our samples is between the polymer and the clay and cannot distinguish between the orientation of each component, thus limiting the usefulness of
shear simplified analysis of form factors. Planned contrast matching studies with
deuterated polymer will help interpret these differences and separate scattering
contributions from clay and polymer.

Figure 5.4. SEM images of freeze fractured surfaces: (a) view on top of the x-y plane; (b)
view on top of the x-z plane; (c) view on top of the x-y plane and fracture. Planes are
described in Figure 5.1. Fracture of the film shows part of the network like structure
which holds layers together suggesting strong interconnectivity between layers and
between the polymer and clay.

SEM determined morphology on a micron length scale. A nanometer scale
resolution as obtained with AFM is not achievable with the SEM instrument. As
mentioned before, the polymer clay solutions have works fractal structures that can be
described as interconnected networks on several length scales. When the solvent is
evaporated the network collapses (like a squeezed sponge) and we obtain layered
structures that can be observed on several length scales (nm resolution given by AFM and
micrometer size observed by SEM). In the y-z plane (Figure 5.4a) SEM was used to
examine whether an interface exists between each layer. No boundaries between
spreading layers could be detected by SEM, indicating substantial intermixing of spread
layers while preserving the platelet orientation. Surprisingly, a highly ordered and
layered structure of the films has been observed in the $x$-$y$ plane and porous structures in the $x$-$z$ plane. The porous structure in the $x$-$z$ plane (Figure 5.4b) appears to consist of interconnecting areas of film and fibers that form a porous mesh or network. From the $x$-$z$ image we observe polymer fibers that, on average, are about $2050 \pm 280$ nm in length and approximately $170 \pm 10$ nm in width with random orientation. These fibers contain both polymer and nanoclay and no such fibers could be obtained with either pure PEO or clay. The clay particles serve as cross linking points within the polymer nanocomposite and lead to improved properties. The layered texture of the $x$-$y$ SEM image was calculated to have an average dimension of $d_{\text{SEM}} = 394 \pm 42$ nm per layer or roughly two times the width of a fiber observed in the $x$-$z$ plane. According to AFM and SANS measurements, each of the 390 nm thick layers (measured by SEM) must consist of a bundle of smaller layers which are, on average, 55 nm thick. One has to investigate several AFM images in horizontal and vertical distances to observe these bundles. The layers observed by SEM are considerably smaller than the calculated width of a single layer spread to form the nanocomposite film. Further SEM studies suggest that the exact thickness of one dried layer is not as important to the overall orientation of polymer and platelets as, for example, the “shear rate” during the spreading process and the drying procedure. Fracture of the film (Figure 5.4c) shows part of the network-like structure which holds layers together suggesting strong interconnectivity between layers and between the polymer and the nanoclay. During the drying and spreading process the polymer clay network collapses and the clay platelets are shear-oriented preferentially in the spread direction. We conclude that the strength of the polymer network in solution strongly influences the alignment of polymer and clay during the spreading process. In solution, a high degree of porosity is available between the polymer-clay matrix and
water filled channels. The collapse of the network during the spreading and drying process of films reduces the pore sizes and the shear leads to orientation and anisotropy. The spreading and drying procedure influences both the micro and macrostructure.

Polarizing microscopy showed differences in birefringence in each plane, $x$-$z$ and $x$-$y$ (Figure 5.5). A small section of a one layer film was removed (by scratching) to expose the $x$-$y$ plane. Observation of the $x$-$z$ plane shows a lightly speckled pattern. This speckling is primarily due to the birefringence observed from PEO crystallites present in the sample. With increasing temperatures in a range from 25 to 200 °C the birefringence gradually disappears due to the melting of the polymer crystallites. Observation of the exposed edge of the film, the $x$-$y$ plane, shows a highly birefringent pattern even after annealing an hour at 200 °C. The total birefringence of the film is dominated by the orientation of the clay platelets and the polymer within the sample. At high temperatures we believe that the birefringence comes from the clay alone while at low temperatures both polymer and clay contribute to the total birefringence. Previous work on PEO nanocomposites have shown that it is difficult to significantly increase the intergallery distances by adding more polymer to the system and excess polymer will phase separate upon removal of water. With our polymer nanocomposites, both the pH and ionic strength of the solutions were controlled by the addition of NaOH and NaCl respectively. As the water evaporates during the film preparation, the electrolyte concentration increases causing separation of PEO at higher concentrations. The presence of salt may be in part responsible for the development of the layered structure. Optical microscopy data suggest that our nanocomposites do contain PEO crystals that may have been phase separated during the drying and spreading process. Neither high molecular weight polymer nor shear was sufficient to completely overcome phase separation and
crystallization of PEO. We also note that there is time required for crystallinity to be observed (ca. 3 weeks). However, after some time (0.5 years) crystallinity of 55% does not change any more. The crystallinity of PEO various nanocomposites has been studied in the past.\textsuperscript{129, 130, 142} The confinement induced crystallinity is very important in controlling the structure in our multilayered films, an aspect that will be investigated in more detail elsewhere.

![Optical micrograph of a spread nanocomposite film with a scratched surface. A small section of a one layer film was removed to expose the x-y plane. Crossed polarizers and a magnification of 20x were used.](image)

**Figure 5.5.** Optical micrograph of a spread nanocomposite film with a scratched surface. A small section of a one layer film was removed to expose the x-y plane. Crossed polarizers and a magnification of 20x were used.

### 5.4 Conclusions

Nanocomposite multilayered films were studied with a combination of scattering and microscopy. The length scales covered by these techniques provide information about short range packing as well as long range correlations. The multilayered films were formed by a layer by layer spreading method from a network like solution. No boundaries between spreading layers could be detected by SEM indicating substantial intermixing of spread layers while preserving the platelet orientation. During the drying
process the polymer clay network collapsed and the clay platelets oriented inside the network with the clay surface normal perpendicular to the spread direction. On a nanometer scale the clay can absorb only a maximum amount of polymer until all the clay surfaces are covered. Any excess polymer in solution as well as in the bulk leads to formation of two phases- network like polymer-clay intercalates and pure polymer phases. We assume that these two phases lead to the unusual and unexpected layered structure observed with AFM and SANS. We also note that this interpretation is consistent with similar behavior reported in literature.

Our unexpected results pose many open questions and more experiments are necessary for better understanding the origin and nature of the layered structures for a more quantitative evaluation. Planned SANS measurements may help determine the thickness and density of the polymer-clay interfacial regions as well as the average number of contacts per chain and per particle. Once we have obtained this information we can determine how the polymer-clay interactions influence the macroscopic behavior and quantify the origin of observed layers. Future X-ray, AFM, and SEM investigations in the wet state will help to determine how the layered structure developed when solvent is evaporated slowly. Planned dynamic testing will lead to further elucidation of the rheological behavior in order to better understand viscoelasticity, relaxation, and interaction based phenomena.
6.1 Introduction

The natural clay Kaolinite falls under the classification of phyllosilicates clays and is similar to the mineral talc in that it forms sheets or platelets. These platelets aggregate and form stacks similar to pages in a book or a deck of cards. Unlike the previous clays studied, Laponite and Montmorillonite which are a 2:1 layered structure, Kaolinite is a 1:1 layered structure. This ratio refers to the number of silicon oxide tetrahedral layers to the number of aluminum oxide octahedral layers that make up an individual clay platelet. Kaolinite shows a pseudo-hexagonal shape and can have average diameters in the plane of the platelet in the micron range with a platelet thickness of approximately 5 Å. This provides an average aspect ratio of 2000:1, based on an average platelet diameter of 1 μm. Unlike the structure of Laponite and Montmorillonite which have surface exposed oxygen atoms on both sides of the platelet, Kaolinite has exposed oxygen atoms on the silicon oxide layer and hydroxyl groups on the aluminum oxide side of the platelet. This configuration for Kaolinite makes swelling of the clay stacks very difficult in aqueous solution causing both intercalation and exfoliation to be a challenging process.

The polymer chosen for this study, poly(ethylene oxide) (PEO), is the same as used in previous Laponite and Montmorillonite studies. The PEO was purchased from Polysciences, Inc. The molecular weights used were $1 \times 10^6$, $5 \times 10^6$, and $8 \times 10^6$ with molecular weight distributions reported by the company to be 1.5 for all polymer molecular weights.
There were three main reasons for pursuing this project. First, it allows for size dependence study in nanocomposite solutions and films as the clay platelet size is larger than the previously studied Laponite and Montmorillonite clays. Second, is how the influence of salt ionic strength has an affect on the exfoliation of clay particles. We hypothesize that the ionic strength may influence polymer intercalation in aqueous solution. Finally, it provides the opportunity to develop new nanocomposite materials with unique properties.

6.2 Experimental

Stock salt solutions were prepared using distilled water. The concentration of the salt solution, NaCl and NaOH, varied from no salt added (0X) to forty times (40X) what has been used for a Laponite-based system (1X) (see Table 6.1).\(^{128}\)

Table 6.1 PEO-Kaolinite Stock Salt Solution Concentrations

<table>
<thead>
<tr>
<th>Solution</th>
<th>NaCl conc. (g/mL)</th>
<th>NaCl conc. (M)</th>
<th>NaOH conc. (g/mL)</th>
<th>NaOH conc. (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0X</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.25X</td>
<td>1.463×10(^{-5})</td>
<td>2.50×10(^{-4})</td>
<td>1×10(^{-6})</td>
<td>2.5×10(^{-5})</td>
</tr>
<tr>
<td>0.5X</td>
<td>2.925×10(^{-5})</td>
<td>4.996×10(^{-4})</td>
<td>2×10(^{-6})</td>
<td>5×10(^{-5})</td>
</tr>
<tr>
<td>1X</td>
<td>5.85×10(^{-5})</td>
<td>1×10(^{-3})</td>
<td>4×10(^{-6})</td>
<td>1×10(^{-4})</td>
</tr>
<tr>
<td>3X</td>
<td>1.755×10(^{-4})</td>
<td>3×10(^{-3})</td>
<td>1.2×10(^{-5})</td>
<td>3×10(^{-4})</td>
</tr>
<tr>
<td>5X</td>
<td>2.925×10(^{-4})</td>
<td>5.01×10(^{-3})</td>
<td>2×10(^{-5})</td>
<td>5×10(^{-4})</td>
</tr>
<tr>
<td>10X</td>
<td>5.85×10(^{-4})</td>
<td>1×10(^{-2})</td>
<td>4×10(^{-5})</td>
<td>1×10(^{-3})</td>
</tr>
<tr>
<td>20X</td>
<td>1.17×10(^{-3})</td>
<td>2×10(^{-2})</td>
<td>8×10(^{-5})</td>
<td>2×10(^{-3})</td>
</tr>
<tr>
<td>40X</td>
<td>2.34×10(^{-3})</td>
<td>4×10(^{-2})</td>
<td>1.6×10(^{-4})</td>
<td>4×10(^{-3})</td>
</tr>
</tbody>
</table>

This approach was utilized to find ways of better swelling the Kaolinite clays and to help determine the optimal salt concentrations needed to form homogeneous polymer-clay

\(^{128}\) Solution names of 1X, 3X, etc. refer to the solution concentrations based on the stock solution used for the PEO-Laponite studies. For example, 1X would refer to the solution concentration used in the PEO-Laponite study and 40X would be a solution that contains forty times more NaCl and NaOH in solution.
gels, that have similar properties to previously published PEO-Laponite and PEO-
Montmorillonite gels. The calculated salt concentrations used in this study can be
seen in Table 6.1.

Samples were prepared as 15 g total weight samples. The samples consisted of 1
%wt Kaolinite and 2, 5, 8, and 10%wt PEO, the balance was the NaOH/NaCl/H₂O
solution. Table 6.2 shows the calculated weights for the samples used in this study.

After the salt solution was added to the combined polymer and clay powder the samples
were placed on a wrist-action shaker for 24 hours.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Clay Amount (g)</th>
<th>Polymer Amount (g)</th>
<th>Solution Amount (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ka 1-1</td>
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<td>0.15</td>
<td>14.7</td>
</tr>
<tr>
<td>Ka 1-3</td>
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<td>0.45</td>
<td>14.4</td>
</tr>
<tr>
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<td>0.75</td>
<td>14.1</td>
</tr>
<tr>
<td>Ka 1-8</td>
<td>0.15</td>
<td>1.2</td>
<td>13.65</td>
</tr>
<tr>
<td>Ka 1-10</td>
<td>0.15</td>
<td>1.5</td>
<td>13.35</td>
</tr>
</tbody>
</table>

During this time as the polymer begins to dissolve the samples become highly viscous.

Additional shaking can no longer ensure complete mixing. Samples were then
centrifuged in the cap down position for 30 minutes, and then placed in the cap up
position for an additional 30 minutes. This centrifuging procedure was carried out for a
total of 2 hours. In addition to centrifuging, the samples were also mixed by hand using a
metal spatula. This was done to make sure any large agglomerates of undissolved
polymer or clay could be broken up and mixed into the overall system. Ideally, with
daily mixing and centrifuging of the sample they can be ready in as little as 3 to 4 weeks.
Samples were deemed ready when they appeared homogenously mixed with no visible
clumps of undissolved polymer or clay present. Samples were also inspected by optical
microscopy which showed the clay was mostly homogeneously suspended throughout the polymer/water matrix (see Figure 6.1).

![Image of optical microscopy](image)

**Figure 6.1.** Optical microscopy image of a representative Ka 1-5 $8 \times 10^6$ 0.25X sample (1%wt Kaolinite, 5%wt $8 \times 10^6$ MW PEO, 94%wt 0.25X concentration salt solution). Sample shows that the clay is homogeneously mixed throughout the sample but there is still the presence of clay agglomerates even after samples have been mixed for longer than 2 months. Approximate platelet diameter of 1-2 $\mu$m.

Rheological experiments were carried out on a series of PEO-Kaolinite solutions that consisted of 1%wt Kaolinite and either 5, 8 or 10%wt $8 \times 10^6$ MW PEO. According to the manufacturer, the polydispersity index (PDI) of the polymer used in this study was 1.5. All experiments were carried out using samples that were homogeneously mixed and validated by optical microscopy.

Experiments were performed using a TA Instruments AR1000 strain controlled rheometer and a TA Instruments ARES series stress controlled rheometer. Experiments performed on the AR 1000 used a parallel plate configuration with a peltier bottom plate and an anodized 40 mm diameter aluminum upper plate. A 1 mm gap was used for all
experiments. In order to prevent solvent loss during the experiment, a solvent trap was placed around the sample which can be seen in Figure 6.2.

**Figure 6.2.** An image of the AR1000 with solvent trap in place. The solvent trap consists of three pieces, a bottom piece with a small reservoir for solvent and two acrylic top pieces to keep the solvent trap closed to minimize solvent loss during the time frame of the experiment.

After loading the sample, it was allowed to reach the experimental temperature (25 °C) and remain at rest with no preshearing, other than shearing experienced by the sample when loading, for a minimum of 4 minutes.

Experiments performed on the ARES rheometer used two different parallel plate configurations. The first configuration consisted of a 38mm diameter quartz glass upper plate paired with a 45 mm diameter quartz glass bottom plate. In order to prevent solvent loss in this configuration a small amount of low viscosity silicon oil was floated over the top of the sample. The viscosity of the silicon oil is considerably lower than the sample viscosity and should have negligible affect on the overall rheological experiment. A second configuration consisted of a pair of stainless steel 25 mm diameter parallel plates, no solvent trap was present. A gap of 1mm was used in this first configuration while gap
values of 0.5, 0.8 and 1mm were used for the second configuration. Samples after loading were allowed to reach the experimental temperature (25 °C) and remain at rest, no sample preshearing, for a minimum of 4 minutes before the experiment proceeded.

PEO-Kaolinite films were formed on clean borosilicate glass microscopy slides from well dispersed Kaolinite-PEO solutions (Ka 1-10 1×10^6 MW PEO salt concentrations 1, 3, 5 and 10X). Samples were prepared using a layer by layer approach until a total of 27 layers were obtained with average film thickness of 0.998±0.07 mm Ka 1-10 1×10^6 1X, 1.04±0.07 mm Ka 1-10 1×10^6 3X, 1.157±0.06 mm Ka 1-10 1×10^6 5X and 1.043±0.06 mm Ka 1-10 1×10^6 10X. These samples were used in preliminary SEM and SAXS experiments. Additionally, a small amount of 5×10^6 MW PEO and PEO-Kaolinite solution (Ka 1-10 5×10^6 PEO series) was placed on microscopy slides with a cover slip placed over the solution to observe the solution under cross polarized light microscopy. After the initial observation of the solutions under microscopy, the samples were then placed in a desiccator and allowed to dry. The dried single layer that is now sandwiched between the glass slide and cover slip was observed again by cross polarized light microscopy.

6.3 Results and Discussion

A series of Kaolinite-PEO solutions were prepared for numerous solution and film studies. Samples were made with PEO which had molecular weights of 1×10^6, 5×10^6 or 8×10^6. The polymer concentrations varied from 1%wt to 10%wt as outlined in Table 6.2, with salt concentrations outlined in Table 6.1. This approach allowed for determining what polymer molecular weight, polymer concentration and salt solution concentration would give the best solutions with viscoelastic properties similar to previously published PEO-Laponite and PEO-Montmorillonite solutions studied by
Schmidt et al.\textsuperscript{46,47} and Malwitz et al.\textsuperscript{128} It was observed in the PEO-Kaolinite series that consisted of $1 \times 10^6$ and $5 \times 10^6$ MW PEO that the clay could not be kept suspended in solution unless the polymer concentration was at 10\%wt. A possible explanation for this occurrence could be strong interactions between the polymer and the clay that leads to flocculation. Another interpretation suggests that the polymer chains are not sufficiently long enough to create “bridges” between clay particles because the clay particles are not completely exfoliated and the aggregates are too far apart. A “network” as it is found in other polymer-clay systems\textsuperscript{45-47,128} is then not possible. The polymer chains would effectively only be able to cover the clay particles and aggregates but not prevent them from settling out. When the polymer concentrations are high enough (10\%wt) the clay particles can remain suspended because the polymer builds a viscous matrix. With enough polymer present, the clay particle surface may become completely covered allowing excess polymer left in the solution to counteract the gravity of the clay. Interactions between the polymer covered clay particle and the free polymer through other mechanisms such as chain entanglements are also possible. This phenomenon, however, is not seen in a Kaolinite-PEO system where the polymer molecular weight is $8 \times 10^6$. It may be possible that a minimum viscosity is needed to achieve a network-like structure within the system to prevent the clay particles from settling.

Rheological experiments were performed on a Kaolinite-PEO series containing $8 \times 10^6$ MW PEO, the samples were made according to Table 6.2 and solutions from Table 6.1. Both stress controlled (AR1000) and strain controlled (ARES) rheometers were used to check the data for reproducibility and consistency of results. The flow curve presented in Figure 6.3 was from a Ka 1-5 $8 \times 10^6$ 0.25X sample (1\%wt Kaolinite, 5\%wt $8 \times 10^6$ MW PEO, solution type 0.25X). The stress controlled data were obtained
from a “flow test” where a single continuous curve was generated for a given set of shear rates (0.02 – 500 sec\(^{-1}\)). The strain controlled data was collected as a series of individual steady state shear measurements and each data point was the average of the steady state data collected for a given shear rate. Comparison of the data from both testing methods show the data between instruments and experiment types are in good agreement (relative error ± 10%).

![Steady state viscosity as a function of shear rate obtained from two different rheometers. Flow curve and steady state shear data. The flow curve data was produced as a single continuous test on the AR1000. The steady state shear data was generated from individual tests and each data point was the average of the steady state data for the given shear rate. The relative error between the two experimental methods was ±10 %. Error bars are smaller than the data points.](image)

**Figure 6.3.** Steady state viscosity as a function of shear rate obtained from two different rheometers. Flow curve and steady state shear data. The flow curve data was produced as a single continuous test on the AR1000. The steady state shear data was generated from individual tests and each data point was the average of the steady state data for the given shear rate. The relative error between the two experimental methods was ±10 %. Error bars are smaller than the data points.

The flow curve tests for the Ka1-5 solution series (1%wt Kaolinite, 5%wt PEO 8 × 10\(^6\) MW, all solutions types from Table 6.1) can be seen in Figure 6.3. Initial observations show that the polymer-clay solutions are shear thinning. The initial viscosity appears to not be linearly related to the salt concentration and no increasing or decreasing trend is
observable. The shear thinning region of the curve has a power law behavior of 0.8.

Power law exponents of 0.9 and 0.94 were determined for Ka1-8 $8 \times 10^6$ and Ka1-10 $8 \times 10^6$ respectively. In all series, the value of the power law index is independent of salt concentration. A Cross model fit was attempted on all sample data to provide an estimated initial zero shear viscosity ($\eta_0$), power law index ($n$) and infinite shear viscosity ($\eta_\infty$) values. The Cross model has the following form:

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + (K\dot{\gamma})^n} + \eta_\infty$$

(6.1)

Also included in Figure 6.5 is the consistency value ($K$) which is a measure of the characteristic time of the material, the greater the value of $K$ the more the curve shift to the left. Figure 6.5 is a representative Cross model fit and Table 6.3 shows the data fitting results for all samples. The values for the power law index were found to show no linear dependence on the salt concentration, no observable trend, and were generally higher than the straight line fits of the shear thinning region of the flow curve.

Differences in the power law index and the slope value for a) straight line fit versus b) Cross model fit could be caused by possible errors in the model fit. Error in the Cross model fits ranged from 5% to 20% suggesting that the choice in models to fit the data may not be perfect. Another explanation for the high error in the Cross model fit could be insufficient data in the very low and high shear rate ranges and a lack of a definite viscosity plateau in the first and second Newtonian regions of the curve. Figure 6.6 compares the flow curves for Ka-PEO 0X and Ka-PEO 10X solution concentrations with polymer concentrations of 5, 8 and 10%wt. From these flow curves it can be seen that the PEO-Kaolinite solutions are strongly dependent on the polymer concentration as opposed to the salt concentrations indicated by the increase in the viscosity of
Figure 6.4. a) Flow curve series for Ka 1-5 (1%wt Kaolinite, 5%wt $8 \times 10^6$ MW PEO).
b) Inset of the initial viscosities of each sample that shows that the initial viscosity follow no trend with increasing salt concentration. The shear thinning region of the flow curves in a) were also found to be more or less independent of the salt concentration with a power law value of $\sim 0.8$. Similar results were found for the Ka 1-8 and Ka 1-10 series (not shown).
Figure 6.5. Cross model fit of Ka 1-5 8×10⁶ MW PEO 0.25X solution. Sample shows shear thinning behavior and the fit values for the zero shear viscosity ($\eta_0$), power law index ($n$), infinite shear viscosity ($\eta_\infty$) and consistency ($K$).

the samples with increasing polymer content. Figure 6.6 also shows flow irregularities that have repeatedly occurred during the flow tests and are more pronounced at the higher polymer concentrations. Possible reasons for these irregularities may occur:

1) The occurrence of wall slip. According to Walls et al\textsuperscript{144}, colloidal gels and other solution suspensions are believed to have a thin layer of fluid that exists between the tool geometry and there may be an absence of particles or weak particle interactions near the tool geometry surface. When sufficiently high shear rates are obtained, the velocity of the fluid near the geometry surface is higher than that of the bulk material. In the worse case scenario, the particle-lean fluid near the tool surface can flow and deform while the bulk material does not experience any deformation.

2) Flow irregularities due to rupture of the sample. Rupture can occur when a critical edge velocity is reached for a given material.\textsuperscript{61} The critical edge velocity for a
material appears to decrease with an increase in the sample viscosity and decreasing surface tension. A possible method to correct for this phenomenon would include using different tool geometries or smaller sample gaps. Another cause for the sample to rupture at the edge is due to the gas-liquid interface of the sample creating a hardening effect. In an attempt to correct for this, a layer of light silicon oil can be spread over the exposed surface.

3) A third reason for the discrepancies in the flow curves is caused by the delamination of the clay agglomerates during shear. This would amount to a type of internal wall slip within the sample itself. Initially as the agglomerates delaminate a reduction in viscosity could be caused. As the newly delaminated clay particles begin to align in the flow field they may increase the viscosity until the next delamination occurs. Finally, it is reasonable to expect that a combination of one or more of the previously mentioned effects could occur within the sample during the rheological testing procedure causing the flow curve to show irregularities.

Single layer films of neat $5 \times 10^6$ MW PEO in a 1X salt solution were compared to a Ka-5 $5 \times 10^6$ 1X sample (1%wt Kaolinite, 5%wt PEO $5 \times 10^6$ MW, 1X salt solution) to see if the addition of clay affects the sample crystallinity. Figure 6.7 shows cross polarized optical microscopy images of the pure PEO and the PEO-Kaolinite samples.

Initial observations suggest that the spherulite size is significantly smaller in the presence of clay compared to the pure PEO sample. Additionally, the spherulite density appears to be much higher in the PEO-Kaolinite sample than in the pure PEO. Clay strongly influences the nucleation and growth of PEO crystals. Our results are very similar to those reported by Strawhecker and Manias for PEO-Montmorillonite
nanocomposites. Additional more quantitative studies to determine crystallization behavior may be performed in future studies.

Table 6.3 Data Obtained from Cross Model Fit

<table>
<thead>
<tr>
<th></th>
<th>$\eta_0$</th>
<th>$\eta_\infty$</th>
<th>Power law index $(n)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ka 1-5</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0X</td>
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<tr>
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</tr>
<tr>
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<td>0.807±0.001</td>
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<tr>
<td>3X</td>
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<tr>
<td><strong>Ka 1-8</strong></td>
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<tr>
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</tbody>
</table>

Preliminary SEM and X-ray scattering studies were performed on a series of Ka1-10 1×10^6 MW PEO films, salt concentrations of solutions were 1X, 3X, 5X and 10X. Table 6.4 shows the film composition as a function of weight percent. Figure 6.8 shows SEM images of a) pure Kaolinite clay and b) Ka 1-10 1×10^6 MW 10X film.
The flow curves show that as the polymer viscosity is more sensitive to polymer content than salt content. The stacking of individual clay sheets to form a large clay agglomerate are shown in Figure 6.8a and consists of approximately 42 individual sheets covering a distance of 5.9 μm. Figure 6.8b is an image of a PEO-Kaolinite film and shows that there may be
some imperfect orientation of the clay platelets parallel to the plane of the film.

Additional work on solution optimization will be needed to produce better films for SEM analysis.

![Figure 6.7](image.png)

Figure 6.7. Polarized optical microscopy images of a) neat PEO (5×10^6 MW) and b) Ka1-5 5×10^6 1X. From the images it can be seen that spherulite size is significantly decreased in the presence of clay and the spherulite density has increased. Magnification bar is 140 μm.

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>Polymer %wt</th>
<th>Clays %wt</th>
<th>NaCl %wt</th>
<th>NaOH %wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1X</td>
<td>90.82</td>
<td>9.10</td>
<td>0.06</td>
<td>0.0034</td>
</tr>
<tr>
<td>3X</td>
<td>90.71</td>
<td>9.11</td>
<td>0.16</td>
<td>0.0083</td>
</tr>
<tr>
<td>5X</td>
<td>90.66</td>
<td>9.07</td>
<td>0.25</td>
<td>0.016</td>
</tr>
<tr>
<td>10X</td>
<td>90.16</td>
<td>9.01</td>
<td>0.47</td>
<td>0.034</td>
</tr>
</tbody>
</table>

Table 6.4 Ka 1-10 1×10^6 Film Content

Initial X-ray scattering (SAXS) measurements suggest that the films show some degree of clay orientation within the film (see Figure 6.9). These results are expected and similar to PEO-Laponite and PEO-Montmorillonite films investigated by Malwitz et al. The preliminary scattering data suggests that there is orientation of
Figure 6.8. SEM micrographs of a) pure Kaolinite clay and b) Ka 1-10 1×10^6 MW PEO film made from 10X solution. a) Shows the typical stacking associated with the individual clay platelets to form an agglomerate. b) Incomplete exfoliation of the solution lead to a film that shows clay agglomerates of differing sizes and possibly some individual clay particles. The bars in b) were used to highlight possible clay platelet orientation parallel to the film. (SEM by Avinash Dundigalla)

View parallel to spread direction
(x-y plane)  
View perpendicular to film plane

Figure 6.9. SAXS images of Ka 1-10 1×10^6 MW PEO 5X solution. a) The anisotropic pattern observed indicates that there is orientation within the polymer-clay film. b) The isotropic pattern observed perpendicular to the film plane shows there is no clay orientation. From these images it can be determined that the clay platelets are oriented parallel to the plane of the film. (SAXS images by Elena Loizou)
clay in the film and also some degree of intercalation and/or exfoliation occurring within the films when analyzing the data. Additional scattering studies will be needed to determine the exact extent of intercalation/exfoliation.

6.4 Conclusions

A series of PEO-Kaolinite solutions were investigated by rheology and films were investigated by optical microscopy, SEM and X-ray scattering. Initial rheology studies suggest that solutions show similar shear thinning behavior regardless of salt concentration but the power law of the shear thinning region of the flow curve increases with increasing polymer concentration. One would expect that increased polymer concentration leads to increased viscosity. It was also observed that the initial viscosity of a sample within a series is random with increasing salt concentration.

Flow curve irregularities may be attributed to wall slip, rupture or delamination of clay aggregates within the sample during shear. Each of these interpretations is not mutually exclusive and a combination of one or all three could be the case. Further rheological studies using other tool geometries or optical microscopy to see if delamination is occurring would be needed to help further understand this flow phenomenon.

Optical microscopy of samples used in this study showed homogenously dispersed clay particles within a polymer solution matrix but clay aggregates still remained even after samples had been mixed for 2 months. Cross polarized optical microscopy showed that the presence of clay has a tendency to reduce the size of the spherulites of PEO when compared to a neat sample. Nucleation and growth of PEO spherulites is strongly influenced by the clay. Similar results were reported by Strawhecker and Manias for a PEO/Na\textsuperscript{+} MMT system\textsuperscript{145} Additional studies such as
DSC would elucidate the affects on the degree of crystallinity and crystallization behavior. Preliminary SEM and X-ray scattering studies on PEO-Kaolinite films are promising but more analysis is necessary to better understand the results. SEM studies remain inconclusive on the orientation of clay particles in the bulk films at the micrometer scale. However, initial X-ray scattering studies suggest that there is possible clay orientation within the film on the nanometer scale as well as intercalation and exfoliation occurring. These initial results are very promising in development of novel materials and orientating large clay particles within a polymer film.

Future work for this system requires further optimization in order to decrease the presence of clay agglomerates and increase the degree of intercalation and exfoliation within the solution. Several approaches could be made to try and achieve this goal. A first approach would be to continue adjusting the polymer, clay, and salt concentrations and exploring the phase diagram. A series of solutions has already been investigated in this initial study where only the salt and polymer concentrations were adjusted. Fine tuning of the viscoelasticity of these gels and solutions may also require an adjustment to the clay concentration in order to determine a well defined phase diagram for this very complex fluid. A second approach to controlling and improving the viscoelasticity of the polymer clay solutions would be the direct treatment of the clay surfaces themselves. This would allow for the tailoring of the specific interactions between polymer and clay. Surface treatment may lead to better intercalation and/or exfoliation.

Ultimately, if the polymer-clay solutions can be optimized to provide a minimum amount of clay aggregates thereby maximizing the amount of intercalation/exfoliation within the solution, a class of novel materials with exciting properties may be generated.
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