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Fabrication, Characterization and Properties of Hierarchically Ordered Nanocomposites

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FABRICATION, CHARACTERIZATION AND PROPERTIES OF HIERARCHICALLY ORDERED NANOCOMPOSITES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College
In partial fulfillment of the requirements for the degree of Doctor of Philosophy

In

The Department of Chemistry

By
Avinash Dundigalla
Bachelor of Pharmacy, 2000
University College of Pharmaceutical Sciences, Warangal, India.
December, 2006
Dedication

This dissertation is dedicated to my parents, Vijayalakshmi Dundigalla and Amarnath Dundigalla and to my sister, Suman Dundigalla. This dissertation is also dedicated to my grandfather, Vanama Satyanarayana. I also dedicate this dissertation to all my friends and relatives for their love and support.

“Be Good, Do Good”
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List of Abbreviations and Terms

AFM - Atomic force microscopy

CNA - Refers to natural clay, cloisite Na⁺

DSC - Differential scanning calorimetry

EM - Electron microscopy

ESEM - Environmental scanning electron microscopy

FTIR - Fourier transform infrared spectroscopy

LRD – Laponite clay

PEO - LRD - Refers to a gel or film containing Poly (ethylene oxide) and Laponite clay.

PEO - MMT - Refers to a gel or film containing Poly (ethylene oxide) and Montmorillonite clay.

POM - Polarized optical microscopy

SEM - Scanning electron microscopy

MMT - Montmorillonite clay

NaCl - Sodium chloride

NaOH - Sodium hydroxide

PEO - Poly (ethylene oxide)

SANS - Small angle neutron scattering

SAXS - Small angle x-ray scattering

TEM - Transmission electron microscopy

Tₐ - Glass transition temperature

USANS - Ultra small angle neutron scattering

WAXS - Wide angle x-ray scattering
Abstract

The objectives of this research are to study the structure, morphology and properties of poly(ethylene-oxide) (PEO)-clay nanocomposites using various imaging techniques. Optical Microscopy, Scanning Electron Microscopy, Environmental Scanning Electron Microscopy and Atomic Force Microscopy are used to image structures on all length scales. Complementary scattering experiments are discussed along with preliminary differential scanning calorimetry and Fourier Transform Infrared spectroscopy results.

In particular we investigated the multilayered structures of PEO-Laponite and PEO-Montmorillonite multilayered films made from solution. The shear orientation of a polymer-clay network in solution combined with simultaneous solvent evaporation leads to supramolecular multilayer formation in the film. The resulting films have highly ordered structures with sheet-like multilayers on the micrometer length scale. The polymer covered clay platelets were found to orient in interconnected blob-like chains and layers on the nanometer length scale. Inside the blobs, scattering experiments indicate the polymer covered and stacked clay platelets orient in the plane of the film. The effect of clay on polymer crystallinity in multilayered films containing different concentrations of clay is inferred from preliminary DSC studies.

Overall our results suggest the re-intercalation of clay platelets in films made from exfoliated polymer-clay solutions as well as the supramolecular order and hierarchical structuring on the nanometer, via micrometer to the centimeter length scale.
Chapter 1

Research Objectives

The overall objective of this research is to develop methods for fabrication of hierarchically structured nanocomposite films and to characterize the resulting structures via microscopy, scattering and other techniques. Beginning with exfoliated but random nanocomposite morphologies in solutions and gels, regular and predictable structures in films are generated. Properties of conventional polymer-clay nanocomposites such as mechanical strength, barrier properties and thermal conductivity are expected to be improved significantly by hierarchical structuring of the material on all length scales. With supramolecular organization of anisotropic clay platelets, minimized structural defects are anticipated. Of particular interest are the supramolecular structures of nanocomposite multilayered films that are prepared from the corresponding PEO – Laponite (LRD) and PEO – Montmorillonite (CNA) gels and solutions. We have found that the properties of the resulting films are dependent on the composition, concentration and molecular weight of the polymer, the salt content as well as the type and size of the clay. The structure of the films is characterized on a micron length scale by scanning electron microscopy (SEM) and polarized optical microscopy (POM). Atomic force microscopy (AFM) is used to study the structure on a nanoscale. Complementary scattering techniques such as small angle neutron scattering (SANS) and small angle x-ray scattering (SAXS) are used to study the orientation of the clay platelets in the films. Polymer crystallinity is characterized by differential scanning calorimetry (DSC).

Since the structure in solution is important for understanding the formation of supramolecular multilayers in the films we have investigated these solutions and gels in more detail. In Chapter 3, results from soft nanocomposite PEO-LRD hydrogels are presented. The
clay particles are exfoliated in solution and the large scale structures in these hydrogels are studied by examining SANS and ultra small angle light scattering (USANS) patterns and electron microscopy. These techniques indicate that LRD clay platelets covered by polymer coating are tethered together to form a very open fractal-like aggregate up into the micron regime.

The structural formation and characterization of multilayered films made from PEO-LRD gels is discussed in Chapter 4. Highly oriented and layered structures can be fabricated on all length scales. The orientation of the clay platelets in the film and the structure of the polymer are characterized by SAXS and WAXS. The high clay content of the PEO-LRD film has a significant impact on the crystallization of polymer and the crystallinity is found to be strongly suppressed. Anisotropy of the clay platelets on larger length scales can be inferred from the SAXS data and from birefringence results.

It is often difficult to compare structural features of PEO-LRD and PEO-CNA nanocomposites at the same composition because of the very complicated phase diagrams of these complex systems in solution. Solution stability is often dependent on salt concentration but also on many other unknown parameters. In a first attempt to fabricate multilayers from PEO-CNA solutions we have chosen those solutions that were stable over time (did not flocculate) and were easy to prepare. In Chapter 5, we describe the structure and morphologies of multilayered films made from one representative PEO-CNA solution. We have succeeded in producing multilayers but the structure and composition is not the same as the PEO-LRD multilayers described in Chapter 4.

In Chapter 6, we characterize the supramolecular structures from PEO-CNA multilayered films that can be compared to the PEO-LRD films discussed previously. The same
concentrations of the polymer and clay have been used as for the PEO-LRD system and only the size, type and the chemistry of the CNA clay is different. The resulting structure and properties differ significantly. For example, large CNA platelets produce more disordered layers than small LRD platelets and the results suggest re-intercalation of clay platelets in films made from exfoliated polymer clay solutions.

Finally, **Chapter 7** summarizes the research completed and gives an outlook on future directions.
Chapter 2
Theory

2.1 Introduction

In this chapter, the theory and instrumentation necessary for characterization of the nanocomposite polymer-clay solutions, gels and multilayered films is briefly discussed. Microscopic techniques such as optical microscopy, scanning electron microscopy, transmission electron microscopy and environmental scanning electron microscopy are used to characterize the polymer clay solutions, gels and films on all length scales. Atomic force microscopy is used to characterize the films on a nanometer length scale. Scattering techniques such as small angle neutron scattering, small angle x–ray scattering and wide angle x-ray diffraction are briefly described and are used to deduce the orientation of the clay platelets and the polymer on a nanoscale.

2.2 Light and Electron Microscopy

2.2.1 Theory

Light is used as a source of illumination in an optical microscope. The wavelength of the visible light ranges between 400 – 700 nm. A light microscope mainly consists of an objective and an eye piece. The image formed by the objective is further magnified by the eye piece and the final image formed is a virtual image. Magnification in light microscopes depends on the focal length of the lenses. The shorter the focal length, the greater is the magnification. The total magnification in a light microscope is given by the product of the magnifying power of the eyepiece and objective.

The resolving power of a light microscope is limited by the wavelength of visible light. The resolving power of an electron microscope is much higher as compared to a light microscope because it depends on the wavelength of the electron. Shorter wavelength radiations
give a better resolution. Resolution is defined as the ability to distinguish between closely located points, as clearly as possible. Chromatic aberrations are minimized in an electron microscope by using an electron beam of a single wavelength. The wavelength is maintained constant with a constant accelerating voltage in the chamber of an electron microscope.

The resolving power of a light microscope\(^3\) is given by the formula:

\[
D = \frac{0.612 \lambda}{nsin \alpha}
\]  

(2.1)

\(\lambda\) = wavelength of light

\(n\) = refractive index of the medium,

\(\alpha\) = aperture angle

In an electron microscope, the resolution can be improved by increasing the negative high voltage, which leads to the production of electrons with a shorter wavelength. Shorter working distance also improves the resolution because a greater number of secondary electrons reach the detector.

The wavelength of the moving particle according to de Broglie,\(^3\) is given by the following equation:

\[
\lambda = \frac{h}{mv}
\]  

(2.2)

and the relationship between the wavelength, \(\lambda\) of an electron and the accelerating voltage, \(V\) in an electron microscope\(^3\) is given by:

\[
\lambda = \frac{12.3}{\sqrt{V}} \text{Å}
\]  

(2.3)

\(\lambda\) = wavelength of the moving electron

\(V\) = accelerating voltage in an electron microscope.
Electrons are accelerated to high velocities in the chamber of an electron microscope and at such high velocities, there is a relative change in the mass of an electron, according to the equation:

\[ m = \frac{m_0[1 - v^2]}{c^2} \]  \hspace{1cm} (2.4)

- \( m_0 \) = rest mass of an electron
- \( v \) = velocity of an electron
- \( c \) = velocity of light

The depth of field can be increased by increasing the working distance, as this decreases the aperture angle, \( \alpha \). This also leads to poor resolution, as few secondary electrons reach the detector. A better signal-to-noise ratio would lead to better resolution. Magnification in SEM is the ratio of the length displayed on screen to the length scanned on the specimen. High vacuum is required to remove air from the chamber of an EM and to prevent the ionization of the gas. A series of pumps is used to create a very high vacuum up to \( 10^{-5} \) Pascal in the chamber of an EM.

### 2.2.2 Instrumentation

A Scanning Electron Microscope mainly consists of the following parts:

a. Electron gun
b. Electron Optical System
c. Specimen stage
d. Secondary electron detector
e. Vacuum system

Metals like tungsten, with low work function and high melting point are used as an electron source that serves as a cathode in the assembly of an electron gun. Electrons are produced by thermionic emission. A very thin tungsten metal wire is bent in the form of a ‘V’
shape (see figure 1). An abrupt change in the direction leads to an increased resistance, and easy emission of electrons. When the electrons move from the cathode to the anode, the emission of electrons from the tungsten filament depends on the current passing through it. As the current is increased, the electron emission is increased until a saturation point is reached. The filament is made negative relative to the anode by the application of a negative high voltage to the cathode. The cathode is surrounded by a cap called the Weynelt shield, to prevent the electrons bypassing the anode. The cap or shield is made up of a material with high work function and is flat, so that electrons are not emitted by the cap. The cap is maintained at a higher voltage (by 200 V) than the filament. Electrons hitting the cap from the filament are repelled because of the relatively higher negative charge of the cap. A space charge is created away from the filament and this

![Diagram of electron gun assembly in an SEM](image)

**Figure 2.1** The electron gun assembly in an SEM
serves as a source of electrons. A homogeneous supply of electrons is thus maintained by the space charge.

The electron beam emanating from the electron source is ca. 50 µm in diameter. Combinations of condenser lenses are used to further demagnify the electron beam. Usually,

![Figure 2.2 Schematic representation of an SEM](image)

three condenser lenses are used in a typical electron microscope. The first two condenser lenses mainly demagnify the electron beam and the final condenser lens reduces the beam spot size to 2 nm. Peripheral electrons are lost while the electron beam is demagnified. This results in fewer
electrons and poorer resolution. The focal length can be changed by varying the current passing through the electromagnetic lenses.

The interaction of the electrons with the sample leads to elastic and inelastic scattering. Elastic scattering of electrons from the sample surface leads to the production of backscattered electrons. Backscattered electrons are of high energy and are detected by a backscattered electron detector. Inelastic scattering of electrons leads to the production of secondary electrons from the sample surface. The energy of secondary electrons range from 0 to 50 eV. Higher atomic weight elements produce more secondary electrons. In a polymer-clay sample, the presence of inorganic clay (silicate) leads to production of a high number of secondary electrons and hence the clay rich areas are brighter compared to clay poor areas or polymer areas which are darker in color. Secondary electrons are primarily used for three dimensional topographical contrast. The number of secondary electrons ejected mainly depends on the topography of the sample.

Secondary electrons are detected by a secondary electron detector (SED). The SED is maintained at a positive potential of 200 V. Since, electrons are negatively charged; they are attracted towards the anode. The inner cap of the detector is maintained at a very high positive potential of 12 kV. Once the electrons reach the outer surface of the detector, they are attracted towards the detector, due to a very high potential of 12 kV. Electrons reach the photomultiplier tube present in the secondary electron detector and are amplified by a series of dynodes before finally reaching the cathode ray tube. The image is recorded as a series of pixels. The brightness of the pixel is directly proportional to the number of secondary electrons generated from the specimen surface.

The sample is usually sputter-coated with gold and palladium using an Edwards S-150 sputter coater. Phosphorus pentoxide is placed inside the chamber of the sputter coater and is
used as a dehydrating agent. Coating is done in order to increase the conduction and thus to produce more secondary electrons. Sputter coating for 1 min at a current of 10 mA and at a pressure of 0.1 Torr will deposit roughly a 100 Angstrom layer. In our procedure, sputter-coating was done for 2 minutes which is sufficient to achieve good conduction.

2.3 Environmental Scanning Electron Microscopy, ESEM

Hydrated samples can be imaged at low pressures using environmental scanning electron microscopy (ESEM). The pressure and temperature conditions inside the specimen chamber can be amenably controlled by using a Peltier cooling stage. This allows for imaging non processed, unstained wet samples in their natural state. ESEM offers appreciable spatial resolution at micron and sub-micron levels. The requirements of high vacuum conditions and the conducting sample surfaces are precluded by ESEM.

An ESEM consists of a differential pumping system. The electron gun and the upper part of the chamber column are maintained at high vacuum by means of rotary pumps and diffusion pumps. The lower part of the column is maintained at low vacuum. A gradient in the pressure is maintained along the length of the column by using a series of pressure limiting apertures. These apertures aid in a proper isolation of various chambers, but enable the electrons to pass through. The specimen chamber is provided with an inlet for water or a gas, for controlling the pressure inside the chamber. The temperature is controlled using a Peltier cooling stage. A 100% relative humidity can be maintained by a proper choice of pressure and temperature conditions. Additional amounts of water droplets can be placed around the sample in the specimen chamber to ensure complete saturation of the sample environment. The secondary electrons emitted by the sample are amplified by interactions with the gas in the chamber. The gas molecules are ionized on interaction with the secondary electrons and lead to the production of more secondary
electrons and these further collide with additional gas molecules in the chamber, leading to a cascade process of secondary electron emission. The negative surface of the sample is neutralized by the positive ions produced from the cascade process. The detector used for ESEM is gaseous secondary electron detector.\textsuperscript{9}

\textbf{2.4 Atomic Force Microscopy}

Atomic force microscopy consists of a cantilever that is scanned over the sample surface. A topographical image of the sample is obtained from the signals sent by the feedback loop.\textsuperscript{12} The interactions between the tip and the sample leads to the formation of a spatially resolved image of the surface.\textsuperscript{13} Improved resolution is dependent on various factors such as the scanning rate, tip shape and resonant frequency of the cantilever.

A laser beam is deflected from the back of the cantilever onto a photodiode. Different types of probes can be used to measure a wide range of forces such as Van der Waals forces, electrostatic forces and adhesive forces. Atomic force microscope (AFM) can be operated in various modes such as contact mode, non-contact mode and tapping mode. The tip is in direct contact with the sample in the contact mode AFM. Contact mode is also called constant force mode, in which the deflection of the cantilever is kept constant by the feedback loop.\textsuperscript{12} In the non–contact mode of AFM, the tip is scanned very close to the sample, but does not touch the surface during imaging. A frequency shift is caused in the resonant frequency of the cantilever, which is maintained constant by controlling the amplitude of oscillation.\textsuperscript{12} In the tapping mode of AFM, the cantilever is vibrated at its resonant frequency. The tip sample interactions lead to a change in the resonant frequency and amplitude of vibrations. Height images are obtained by keeping the amplitude constant and the vertical displacements of the piezoelectric scanner are recorded. The frequency of the cantilever is changed upon interactions with the sample surface
due to a change in the attractive or repulsive forces. This frequency change leads to a change in the position of the laser on the photodiode. Van der Waals attractive forces operate at the angstrom level.

2.5 Scattering and Diffraction

Scattering and diffraction studies are only a small part of this thesis and will be described only briefly. Interaction of inhomogeneous systems with electromagnetic radiation leads to oscillatory motion of the electric charges present in matter. Some of the incident radiation is radiated in the form of scattering and the rest of it is transmitted into other forms. Two types of scattering are possible, elastic and inelastic scattering. The frequency of the incident radiation remains unchanged in elastic scattering. The frequency changes, and may be lower or higher than the incident frequency in inelastic scattering. Energy absorption takes place when the frequency of the incident radiation matches the natural frequency of the particle. Here we are interested only in elastic scattering which gives us structural information at the nanometer length scale.

Techniques like small angle neutron scattering (SANS), small angle x-ray scattering (SAXS) and wide angle x-ray diffraction (WAXD) are used to deduce structural information. Exposure of a substance to a high energy radiation like X-rays causes the electric field of the incoming wave to induce dipole oscillations and the electrons are excited. The scattering efficiency of X-rays increases linearly with the atomic number of the element.

While X-rays interact with the electron density of atoms, neutrons are neutral and interact with the nuclei of the atom. For both neutron and x-ray scattering, the relationship between the wave properties and particulate properties are related by de Broglie’s equation:

\[ \lambda = \frac{h}{mv} \]  

(2.5)
The velocity and the wavelength of the particle are inversely proportional to each other. The scattering vector or momentum transfer \( q \), wavelength of the incident radiation \( \lambda \), and the scattering angle \( \theta \), are related to each other by the following relation,

\[
q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}
\]  

(2.6)

Structural information can be deduced by plotting the intensity as function of the scattering vector ‘\( q \)’. In the ideal case, scattering intensity is directly proportional to the number of particles present in the sample and is strongly dependent on the scattering angle.\(^{15}\)

Scattering of X-rays and neutrons by structured matter may lead to the formation of a periodic array of scattering sites, in which, the incident wave plane scatter in a constructive or destructive manner.\(^{16}\) The peaks formed in X-ray diffraction are the summations of constructive scattering amplitudes of the incident wave. Structural information is obtained by studying peak positions, intensities and shapes.

The wavelength of the incident radiation \( \lambda \), the diffraction angle \( \theta \), and the interplanar spacing \( d \), are related by Bragg’s law.\(^{17}\)

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

(2.7)

From equations 2.6 and 2.7, it can be shown that \( q \) and \( d \) are inversely proportional:

\[
\frac{2\pi}{q} = \frac{d}{n}
\]  

(2.8)

The term “\( q \)” stands for momentum transfer in reciprocal space and “\( d \)” stands for “characteristic dimension” in real space. This means that large scale structures (large \( d \)) can be probed at low \( q \) values and vice versa.
2.6 Birefringence

Anisotropy in a substance is caused by non-uniform distribution of properties.\(^{18}\) The properties of the anisotropic crystal are orientation dependent and the refractive index of the anisotropic crystal change with direction. Isotropic crystals have a uniform and periodic arrangement of elements.\(^{19}\)

Whether a crystal is isotropic or anisotropic is determined by the length of the crystallographic axes and their interaxial angles.\(^{20}\) Differences in the lengths of the crystallographic axes and their interaxial angles in a crystal lead to anisotropy. Anisotropic crystals possess two or more refractive indices depending on their axial geometry.\(^{20}\) Crystals having a uniaxial symmetry possess two refractive indices, one along the major axis and the other along the minor axis. Crystals having a biaxial symmetry possess two optical axes and three refractive indices, namely \(n_\alpha, n_\beta\) and \(n_\gamma\).\(^{20}\)

Anisotropic substances exhibit a property called birefringence or double refraction. Birefringence may be defined as a variation in refractive index with a change in direction.\(^{1,21}\) Birefringence in our nanocomposite films is characterized qualitatively using polarized optical microscopy with crossed polarizers consisting of polarizer and analyzer. Plane polarized light passing through the polarizer interacts with the birefringent sample and the incident light ray is split into an ordinary ray and extraordinary ray. The two rays travel in mutually perpendicular directions with each other and with different velocities. The refractive index of the material in a particular direction determines the velocity of the particular ray. Birefringence can be defined by the following relation,\(^{21}\)

\[
B = n_e - n_o \tag{2.9}
\]

\(n_e\): Refractive index of the extra-ordinary ray,
As the two rays emerge from the analyzer, one of the waves is retarded. The retardation between the ordinary ray and the extraordinary ray is given by the following equation,

\[
\text{Retardation} = (\text{thickness of the sample}) \times (\text{difference in refractive index values})
\]  

(2.10)

Asymmetry present in a crystal structure leads to intrinsic birefringence. Form birefringence is caused by orientation of the particles within a medium of different refractive index. Isotropic substances when subjected to any kind of deformation by external forces may become anisotropic and show birefringence. Naturally occurring fibers, proteins and polymers exhibit structural birefringence due to structural anisotropy. Alignment of particles in a shear flow leads to flow birefringence.

The Laponite and Montmorillonite clay platelets used in this work are anisotropic objects when viewed from the side and appear as isotropic objects when viewed from the top. In solution, the clay platelets are randomly oriented and hence a well dispersed solution is on average not birefringent. The PEO polymer is highly crystalline and builds birefringent spherulites when observed between crossed polarizers. In solution the PEO dissolves into random coils which are not birefringent. A polymer clay solution with exfoliated clay and fully dissolved polymer chains is not birefringent as well.

Shear deformation can orient the clay particles and stretch the polymer chains in solution as well as in the multilayered film. Shear-orientation of the polymer and clay during film preparation leads to anisotropy and birefringence because the clay particles orient in one direction and the polymer is stretched and sometimes crystallized. Poly(ethylene-oxide) in the crystalline form is ordered, anisotropic and birefringent. The total birefringence in the multilayered films comes from the PEO crystallites, oriented and stretched polymer chains,
oriented clay platelets and possibly clay clusters and defects. With so many components contributing to the total birefringence we cannot distinguish between intrinsic birefringence and form birefringence. We can however distinguish between the birefringence coming from the polymer and that coming from the clay. When the polymer is melted, spherulites dissolve and the polymer becomes isotropic so that birefringence is dominated by the oriented clay particles. In the following chapters we will discuss these effects in more detail.

2.7 Fourier Transform

A Fourier transform is used to convert images from the spatial domain into the frequency domain. A spatial domain is the normal image space which is decomposed into its sine and cosine components. The output of the Fourier transformation represents the image in the frequency domain while the input represents the spatial domain. Each point in the frequency domain image represents a particular frequency contained in the spatial domain image. A Fourier spectrum denotes the summation of all the frequency components present in the spatial domain. A process called windowing is used to suppress some frequencies obtained from the edges of the image. The two-dimensional Fourier transformation of the image is represented by spatial frequency which refers to the periodicity with which the image intensity value changes. The magnitude and phase of the Fourier image are required to reconstruct the spatial image. In scattering experiments, the reverse Fourier transformation is not possible because the phase information is lost.

A Fourier transform of a function $f(t)$ is given by the following formula:

$$ F(\omega) = \int_{\infty}^{\infty} f(t)e^{-i\omega t} dt $$

Where $e^{-i\omega t} = \cos \omega t - i \sin \omega t$
The function $f(t)$ is the time domain or spatial domain.

In Nuclear Magnetic Resonance spectroscopy, phase corrections$^{24}$ are applied to the Fourier transformed signal in order to detect the real and imaginary components of the signal. This is because the NMR spectrometer cannot detect the components. Such phase corrections are not required for AFM data. Phase can be defined as the time relationship between the signals.$^{26}$ It is the frequency coherence of a signal.$^{27}$ Phase information is important in reconstructing the spatial image from the Fourier image.

2.8 References


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3.1 Introduction

The colloidal properties of nanocomposite polymer-clay gels and solutions have received considerable attention in the literature. Unusual properties are induced by the physical presence of the nanoparticle and by the interaction of the polymer with the particle and the state of dispersion. Approaches developed range from manipulation of individual particles to exploitation of self assembly in colloids.\textsuperscript{1,2} The large aspect ratio of platelets promotes a supramolecular organization similar to other mesoscopic systems such as liquid crystalline polymers, surfactants or block copolymers.

The presence of the nanosized clay and its interactions with the polymer lead to a class of novel properties\textsuperscript{3-6} that are dependent on the structure and arrangement of the individual particles and their interactions with the polymer. Poly (ethylene-oxide) (PEO) absorbs onto clay platelets. Low molar mass polymers thus inhibit aggregation by classic steric hindrance, while higher molar mass polymers, particularly at higher concentrations of clay, bridge between particles and lead to the formation of large clusters\textsuperscript{7} or smart gels with novel properties.\textsuperscript{3-6} The adsorption of PEO onto the laponite clay platelets studied by Lal et al\textsuperscript{8,9} showed that at low concentrations of polymer and clay, the thickness of each polymer layer is 1.5nm on each face of the clay platelet, independent of the polymer molecular weight.. Contrast variation methods were used to separate the scattering contributions from the bulk and the adsorbed polymer.
SANS studies on polymer clay solutions with no excess polymer showed that the layer thickness of the adsorbed polymer is higher on the edges of the clay platelets than on the face of the clay platelets. Other research groups have used neutron diffraction to look at the local segmental, salt, and water structure around each clay platelet and to understand the mechanism of bridging flocculation.

Below the threshold for complete saturation of clay particles by sufficiently large molecular weight polymers, “shake gels” can be generated which undergo a dramatic shear thickening when subjected to vigorous shaking. Above this threshold we showed in our previous work that the systems form strong shear thinning gels. In that case, we postulated a dynamic adsorption-desorption equilibrium of the entangled polymer chains with the clay particles to form “permanent” networks. Those preliminary data suggest that it is possible to tune gelation as well as kinetics, however more studies are necessary to quantify results. The purpose of this article is to describe and correlate microscopic and nanoscopic structures in a polymer clay hydrogel. Several methods have been applied to examine the polymer-clay interactions. Among them, microscopy and light, x-ray, and neutron scattering have proven to be powerful techniques for revealing their structure and providing a measure of size, shape and interfacial polymer conformation. Here we use microscopy techniques such as Transmission Electron Microscopy (TEM) and Environmental Scanning Electron Microscopy (ESEM) to provide a complete physical picture of the large scale structure and explain some of the unique behavior observed previously.

3.2 Experimental

In this study aqueous solutions of the synthetic hectorite type clay, (Laporte Industries Ltd), Laponite RD (LRD), and poly (ethylene-oxide) (PEO) were used. The clay particles are
composed of platelets of high purity and relatively uniform size (30±5 nm in diameter and ca. 1 nm thick) and have a specific surface of 370 m²/g as estimated by the supplier. PEO with a $M_w = 100 \times 10^3$, $300 \times 10^3$, $600 \times 10^3$ and $10^6$ g/mol was purchased from Polysciences Inc. For all samples in this study a pH value of 10 and a NaCl concentration of $10^{-3}$ mol/L were used. The results reported here were obtained from gels containing mass fractions of 3 % LRD and 2 % PEO at room temperature. At equilibrium, the clay surfaces are covered by adsorbed PEO segments with the diffuse polymer chains serving to “bridge” neighboring clay particles, leading to a macroscopically homogeneous transparent hydrogel with clay relatively complete exfoliation as evidenced by a lack of peaks at high q in SANS. TEM samples from the polymer clay gel were prepared by the Freeze Fracture (FF) technique, resulting in a carbon-platinum replica of the fractured sample surface. Environmental Scanning Electron Microscopy was performed with a FEI Quanta 200 Environmental SEM instrument. ESEM, which operates under low pressures, was used to study the structure on a micron length scale. PEO-Laponite gels freeze fractured in Freon were used to avoid the formation of ice crystals. ESEM facilitates the observation of the samples in their natural state, by a precise control of the operating variables in the specimen chamber. Evaporation of the solvent is precluded by maintaining appropriate pressure and temperature conditions. Selected ESEM experiments were performed on pure solutions of PEO and pure laponite clay. The solvent evaporation was too fast to control and made it difficult to monitor any real and reproducible structures. ESEM on PEO-LRD gels seems to work because the solvent evaporation is much slower and can be controlled easier. This may be due to synergistic polymer-clay interactions or / and the resulting overall gel structure that is capable of retaining water easier than each component on its own.
3.3 Results and Discussion

A combination of microscopy techniques are used to probe structures on various length scales. Transmission Electron Microscopy (TEM) is used to study the structure on a nanometer length scale and to provide direct visualization. TEM was performed by Ella Kesselman\textsuperscript{13}. Environmental Scanning Electron Microscopy is used to provide structure on a micrometer length scale. Our current understanding of present and previous results is that the polymer chains are in a dynamic adsorption/desorption equilibrium with the clay particles to form a network. Since there is more polymer available than necessary to cover all the clay platelets we expect the presence of excess polymer may influence the network structure. The microscopy results presented here confirm that polymer-clay gels contain structures on multiple length scale.

\textbf{Figure 3.1} TEM: a) Freeze fracture replica of the polymer-clay hydrogel with polymer Mw= \(10^6\)g/mol, showing a network like structure on a nanometer length scale. Arrows point to areas with network-like structure and white asterisks indicate smooth areas.

Figure 3.1 shows Freeze Fracture TEM images, from the network like polymer clay gel. The network like gel is characterized by an extremely fine texture of interconnected thin strings.
The mesh size of the network is ca. 50-80nm, in good agreement with the SANS results obtained by Loizou et al.\textsuperscript{13} The thickness of these strings is ca 4 nm while the thickness of single clay platelets is ca 1nm. Interpreting these lines as polymer coated platelets viewed from the side leads to an adsorbed layer thickness of 1.5nm on each side in perfect agreement with the values obtained from dilute solutions below the gel transition mentioned before.\textsuperscript{10}

\textbf{Figure 3.2} Representative SEM image of freeze fractured surfaces of a polymer-clay hydrogel with polymer Mw= 10\textsuperscript{6}g/mol, showing the network-like structure on a micron length scale. Bright lines are clay rich areas.

One should take care to overcome the natural tendency to overinterpret real space images. For example for these freeze fracture samples we cannot see any platelets which don’t happen to be sitting normal to the fracture plane, nor can we easily tell at what depth the observed platelets are. With these caveats however, we may cautiously note that the platelets seem to lie within a network area adjacent to areas with no platelets. While there may be several interpretations for this, one consistent with conservation of volume arguments would be that in fact at these lengths scales the polymer coated platelets form a relatively tight network with hundreds of nanometer
pockets of solution. Figure 3.1 also provides evidence that the clay platelets can interconnect by network-active polymer through their edges with many strings being much longer than the 30nm nominal platelet diameter.

Although all samples are completely transparent to the eye and to optical microscopy, as are multilayered nanocomposite films made from the same polymer and clay components,\textsuperscript{14} structures can be observed on a micron length scale using Environmental Scanning Electron Microscopy. Optical transparency of samples with micron size texture is usually possible when refractive index matching of the large scale structures is present. SEM on the other hand “sees” by reflection from the electron density and thus will clearly show areas of high electron density form the clay as bright areas while the low, and nearly equal (H$_2$O and H$_2$C are fairly similar in density), electron density will show up as darker regions (LRD contains many electron rich atoms).

In Figure 3.2, SEM reveals an exquisite, lacey, sponge like texture on a micron length scale with on average 5 micron large clay poor regions (dark areas) and ca. 1.5 micron thick interconnected membranes of clay rich areas (bright lines). An interconnecting network like structure of the polymer clay gel, consisting of light and dark regions is clearly seen. Several areas show fine network structures within the 5 micron size pores. Assuming the SEM and TEM interpretation is correct, this network like structure on the micron length scale, is self similar to that on the nm length scale observed by TEM (fig 3.1). Such an interpretation would be in excellent agreement with the open self similar structure implied by the fractal dimension of 1.55 from the USANS\textsuperscript{13} data which covers the same spatial range. SANS studies performed by Loizou et al\textsuperscript{13} on similar PEO-laponite gels show that the adsorption of PEO chains onto the laponite clay platelets is independent of the polymer molecular weight. SANS and USANS
studies performed by Loizou et al\textsuperscript{13} on these PEO-Laponite gels can be used to deduce the structure on length scales ranging from 1 to 20,000nm approximately. The low q range obtained from the USANS data\textsuperscript{13} confirms the presence of large scale structures and indicates the presence of open self similar structure. Data obtained from a Fourier transformation of the real space SEM image shown in Figure 3.2 are self consistent with the USANS scattering data.

3.4 Conclusion

Large scale structures of polymer-clay nanocomposite hydrogels are characterized using a combination of microscopic techniques. These structures correlate on various length scales from a micrometer to nanometer length scale. By combining these techniques, the picture that begins to emerge for these strong gels from which meter long fibers can be drawn is one in which clay platelets covered by a 1.5 nm thick polymer coating are tethered together in fibrous bundles that form a very open fractal like aggregate up into the micron régime. Confirmation of this picture, understanding the role of the excess polymer, and understanding to what extent the unique macroscopic properties are related to the above structure, are part of our much larger ongoing effort requiring contrast matching techniques and studying how these characteristics change as a function of the various gelation parameters of concentration, ionic strength, polymer molecular weight, pH, and temperature.

3.5 References


Chapter 4
Unusual Multilayered Structures in PEO/Laponite Nanocomposite Films

4.1 Introduction

Highly ordered polymer nanocomposites are complex materials that display a rich morphological behavior due to variations in composition, structure, and properties on a nanometer length scale.\(^1\),\(^2\) When combining materials over length scales ranging from 1-10 nm, the interface of the components becomes substantially important to the materials performance.\(^3\) Organizing clay platelets of high aspect ratios at the nanometer length scale is thus a challenging and rewarding research area in materials science.\(^4\)

Several solution and melt fabrication techniques leading to materials with intercalated to exfoliated structures have been used for the preparation of poly-ethylene-oxide (PEO)-clay nanocomposites. Since both the untreated clay and PEO are hydrophilic, no clay surface modification is necessary for complete exfoliation in aqueous solution. Moreover, PEO has been found to penetrate into both Laponite and Montmorillonite clay and promote the exfoliation process in aqueous solutions. However the strong interactions between the two components often lead to aggregation that is difficult to avoid.\(^5\) It has been observed that after air drying of solutions, the clay particles remain trapped in the gel-like polymer film reminiscent of the exfoliated polymer clay gel in the “wet state”.\(^2\)

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The film quality can be improved by slow solvent evaporation where the clay platelets have sufficient time to assemble under gravitational and osmotic forces before the viscosity of the system influences particle realignment.\(^6\)

An industrially promising method is the melt intercalation of polymer into clay where the polymer chains have been shown to be more effectively intercalated than in solution.\(^7\) New methods are being developed for the fabrication of molecularly ordered composite films via self-assembly that may replace the Langmuir-Blodgett techniques.\(^8,9\) Multilayered films have been prepared by sequential adsorption of polymer and clay.\(^10\) Atomic force microscopy (AFM) on some of these multilayered films revealed that polymer-Laponite clay films exhibit significantly higher surface coverage than Montmorillonite clays.\(^8\)

We are interested in the fabrication of highly oriented PEO-Laponite nanocomposite films from the corresponding aqueous gels. Previous work relevant to this contribution described rheological\(^11\) and small-angle neutron scattering (SANS)\(^12\) studies on PEO-clay network-like solutions and gels. In solution the polymer and clay interact in a dynamic adsorption/desorption equilibrium to form a three-dimensional network.\(^13\) The network mesh size and the orientation of the clay platelets in solution are important to the structures of the dried films. We also examined the orientation of platelets in multilayered polymer-Laponite and polymer–Montmorillonite films\(^14\) by small- and wide-angle scattering.\(^15\)

The objectives of the present contribution are to prepare nanocomposite films with a defined orientation of the Laponite clay platelets from network-like polymer-clay gels. We will examine the film structural features on multiple length scales using various scattering and microscopy techniques. Only completely dried films were investigated. On a nanometer length scale, SAXS, WAXS, and AFM complementary study the structure and shear-induced
orientation of polymer and platelets. SEM and optical microscopy investigate the morphology of the films on a micron length scale. We also compare our results to previously reported PEO/Montmorillonite multilayered films.  

4.2 Experimental

Laponite (LRD) is synthetic hectorite type clay consisting of relatively monodisperse and well-defined platelets with a diameter of 25-30 nm and a thickness of ca. 1 nm (Southern Clay Products). Poly(ethylene-oxide) (PEO) with an $M_w = 10^6$ g/mol and a molecular mass distribution ca: 1.5 was purchased from Polysciences Inc. Multilayered films were prepared via gel/solution exfoliation while optimal solutions were obtained for a particular polymer clay ratio, pH and ionic strength as described before by Schmidt et al$^{11,12,13}$ and Malwitz et al.$^{14}$ Here multilayered films will be discussed that have been prepared from an aqueous gel containing mass fractions of 3 % LRD clay and 2 % PEO at ambient temperature. The solution pH and ionic strength were controlled by the addition of NaOH (pH = 10) and NaCl (1 mM), respectively. Gels were spread onto glass slides layer-by-layer and dried at 25 °C in desiccators and under vacuum. Multilayered films containing ca. 60 % of Laponite clay and 40 % of PEO polymer (by mass fraction) were obtained. More detailed film preparation is described elsewhere.$^{15}$ Time-resolved small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering or diffraction (WAXS) measurements were performed at the Advanced Polymers Beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Optical microscopy was performed using an Olympus BX51TF microscope with crossed polarizers. SEM experiments were performed using a Cambridge 260 Stereoscan Electron Microscope. Fractures in all three planes were investigated and only representative images are presented. Sample preparation for the AFM measurements included cryo-ultracut slicing (Leica ultracut with FC4 from
Reichert-Jung). Samples were cut at -120 °C, below the PEO glass transition temperature ($T_g = -55$ °C). The images were recorded with a Nanoscope IIIa (Veeco Instruments).\cite{16} Duplicate measurements on all instruments show excellent reproducibility with a relative uncertainty of less than 5%.

4.3 Results and Discussion

The structure and properties of the PEO-Laponite nanocomposite films strongly depend on their morphology, polymer-clay interactions, and shear-orientation. Our previous work on PEO-Laponite solutions and gels demonstrated that in the wet state, the polymer chains are entangled with the clay particles forming a transient network.\cite{11,12,13} Similar results were observed for PEO-Montmorillonite gels.\cite{17} The solution structure and processing conditions strongly influence the morphology of the dried film. Rheological experiments on PEO-Laponite gels for those used in the films preparation have shown that the Laponite clay platelets align at low shear rates, and after cessation of shear relax from alignment rapidly.\cite{17} The collapse of network structure as the solution dries, likely leads to highly oriented layers in the dried film.

4.3.1 X-ray Scattering and Atomic Force Microscopy

The physical picture of the clay platelet orientation as concluded by the WAXS is illustrated in Figure 4.1a. The isotropic patterns in the x-z plane and the anisotropy observed in the x-y plane suggest that the predominant orientation of platelets is with the surface normal perpendicular to the film plane (x-z plane) (Figure 4.2). From the 2D SAXS and WAXS patterns, the intensity as function of $q$ can be calculated in x, y and z directions. The SAXS intensity in the x and y direction of the 2D SAXS pattern (Figure 4.2) is shown in Figure 4.3a. A maximum at $q_{\text{max}} \approx 0.01 \text{ Å}^{-1}$ corresponds to a d-spacing, $d_{\text{SAXS}} = 2\pi/q_{\text{max}}$, on the order of ca. 63 nm. This value is ca. two times the clay diameter (30 nm) and may be related to a distance between
polymer covered clay-rich domains containing several platelets. Comparable SANS experiments on these films also show $d_{\text{SANS}} \approx 63$ nm but with less resolution due to smearing from the form factor.\textsuperscript{15} It is interesting to note that a PEO-Montmorillonite film containing 40% of clay (different clay type and clay size) will show a very similar d-spacing and similar layer size but the layer nanostructure is very different when observed with AFM.\textsuperscript{14}

**Figure 4.1** a) With the clay platelets aligned in the spread direction of the film (x-z plane) we observe an anisotropic WAXS pattern with the X-ray beam oriented in z-configuration and an isotropic WAXS pattern with the beam oriented in y-configuration.

Figure 4.3b displays the relative intensity versus 2 theta, as obtained from WAXS shown in Figure 4.2. Intensities were calculated in the x-, y-, and z-direction. The scattering profile obtained in the y-direction is significantly different from those obtained in the x- and z-direction indicating that this sample is highly oriented. The typical crystalline structure of pure PEO is a well-known monoclinic lattice with the WAXS normally showing several orders of diffraction. However, here we do not observe any peaks originating from PEO crystals. The peaks observed
in the WAXS y-direction mainly correspond to distances between the clay platelets within the clay rich domains or clay stacks. The PEO adsorbed to the clay is thus mostly amorphous.

Figure 4.2 SAXS and WAXS measured parallel and perpendicular to the spread direction of the films. Top row: SAXS in x-z plane (left) and x-y plane (right). Bottom row: WAXS in x-z plane (left) and x-y plane (right).

The d spacing obtained from present SAXS and previous SANS\(^{15}\) (d ≈ 63 nm) can be correlated with the spacing of the striped texture as measured from AFM d\(_{\text{AFM}}\) ≈ 66 nm (average over many measured spacings, Figures 4.4). The domain distance is marked by arrows on the micrograph (Figure 4.4). These domains consist of intercalated stacks of platelets, however from AFM alone it is not possible to determine how many clay platelets are inside one domain. Planned transmission electron microscopy may visualize the content of one single domain. The anisotropic SAXS pattern (Figure 4.2) can be correlated with the fast Fourier transform AFM data (Figure 4.4), which shows a broad anisotropic streak perpendicular to the striped texture.
AFM data show two kinds of layers: nm size layers and micron thick layers (Figure 4.4). Micron thick layers may be compared to SEM data shown in Figure 4.5a.

On similar length scales, AFM and SAXS are complementary methods. SAXS yields reciprocal space information and an average degree of orientation, while AFM visualizes real space structures within discrete sections of the sample. This explains the slight differences in $d_{\text{AFM}}$ and $d_{\text{SAXS}}$ spacings. However, the existence of the ordered and layered structure observed with AFM is unusual. The orientation of clay platelets with a diameter of ca. 30 nm and a thickness of 1 nm does not explain the presence of ordered layers with an average thickness of ca. 63 nm (Figures 4.4). We presume that the 63 nm layers correspond to clay domains or clay stack layers mentioned above. The x-direction correlation length observed in the AFM image (Figure 4.4) is ca. 25-30 nm and corresponds to the clay diameter. The clay particles can only adsorb 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 network like polymer-clay phases and polymer-rich phases. During the drying and spreading process, these two phases lead to the layered structure observed with AFM and SAXS. This interpretation is consistent with similar behavior of bulk nanocomposites observed in literature. It should be noted that the films need to be kept in desiccators since both the clay and polymer are hygroscopic and reversible absorption/desorption of water may lead to swelling or shrinking of the polymer, and thus to increasing or decreasing of layer spacing. This is a property that makes the material applicable as potential humidity sensor.

Crystallinity, as determined by DSC, changed from near 0% to 3% within 1 year. WAXS data shown in Figure 4.3b and described before confirm the adsorbed PEO is mostly amorphous. From our preliminary microscopy and scattering results and from literature on
Figure 4.3 a) SAXS intensity for x and y directions. A maximum in SAXS gives a characteristic dimension of $d_{SAXS} = 2\pi / q_{\text{max}} = 63$ nm. b) WAXD pattern measured in the x, y, and z directions.
polymer clay solutions we know that the PEO polymer chains strongly absorb to the clay particles. The absorbed polymer layer was calculated to be ca. 1.5 nm on each side, increasing the average thickness of a wrapped clay platelet from a total of 1 nm (= thickness of clay platelet) to ca. 4 nm (polymer wrapped clay platelet). If the domains visualized by AFM contain only stacked and wrapped platelets, one ca. 63 nm thick domain would contain a maximum of ca. 15 platelets (4nm x 15 = 60nm). The minimum distance between these wrapped platelets would be ca. 3nm (adsorbed polymer layer on each side = 1.5nm X 2). However defects and excess polymer that is not absorbed to the clay particles may reduce the number of platelets inside one domain. WAXS data in y direction do not show “perfect” lamellar order of 1:2:3:4 in q (momentum transfer) thus complicating the structural information. Further experiments and data evaluation is necessary to quantify these results.

4.3.2 Scanning Electron Microscopy

SEM was used to determine the film morphology on the micron length scale (Figure 4.5a,b). As mentioned previously, the aqueous PEO-Laponite gels can be described as interconnected networks. When the solvent was evaporated, the network collapsed and films were obtained with layered structures that can be observed on several length scales. In the y-x plane of the films (Figure 4.5a), SEM was used to examine whether an interface exists between spread layers. Similar to PEO-Montmorillonite films that we have studied before\textsuperscript{14} no boundaries between spreading layers (each 5-7 μm) could be detected, indicating substantial intermixing of spread layers. Nevertheless a highly ordered and layered structure of the films was observed in the x-y plane, while smooth and flat surfaces were observed in the x-z plane (Figure 4.5b). The few broad layers visible come from an imperfect fracture along the x-z plane. The layered texture of the x-y SEM image is not uniform and was calculated to have an average dimension of $d_{SEM} \approx$
Figure 4.4 Left: AFM images from the x-y plane sections of multilayered film. top) (2 μm x 2 μm) AFM “height” image. bottom) (2 μm x 2 μm) AFM “Phase” image. The vertical grey scale is 50°. Right: top) (700 nm x 500 nm) AFM “Phase” image of the details of multilayered structure. The vertical grey scale is 25°. Arrows indicate the width of the individual layers. Bottom) Cross section of the corresponding “height” image of the above AFM image. The direction of the cross section is indicated in the above AFM image by the dotted white line. The two arrows show thick layers. The dotted black circle shows three individual layers lying perpendicular to the film surface. FFT showing the regularity of the multilayer structure that can be compared with the SAXS data shown in Figure 2 top right.

0.3 ± 0.17 μm per layer. Even though the exact shear rate during the spreading process cannot be controlled, SEM shows high reproducibility in data. According to AFM and SAXS measurements each of the ca. 0.3 μm thick layers consists of smaller layers, which are on average ca. 60 nm thick (Figures 4.4 and 4.5). As a result of processing conditions, that is, drying and layer-by-layer spreading, we also observe clusters of smaller domains, and some larger aggregates. Several AFM images in horizontal and vertical distances must be probed to observe
these structures. The layer structures observed by SEM are considerably smaller than the calculated width of a single layer spread to form the nanocomposite film. Defects and fracture of the film (Figure 4.5) show smooth surfaces between layers as well as some folding of layers. This suggests strong interconnectivity between the polymer and clay produces large flat surfaces. Although we observe structures on the micron length scales all these films were completely transparent in the dry state. Optical transparency of samples with micron size texture is usually possible when refractive index matching of the large scale structures is present.

From the smooth fracture visible in Figure 4.5 (and from other SEM images not shown here), we conclude that the polymer clay interactions parallel to the micron size layers seem not as strong as those perpendicular to the layers. Inspection of several SEM images also suggests that a fractured sample preferentially breaks parallel to the layered structure. This is influenced by the formation of two-phase nanocomposites and suggests that there may be excess polymer between layers. The network like polymer-clay intercalates and the polymer-rich phases in between layers may not need to have strong interconnections since the clay can adsorb only a maximum amount of polymer until all the clay surfaces are covered. Any excess polymer in solution and in the bulk is not directly cross-linked to the clay particles but covers polymer clay aggregates.

We conclude that the strength of the polymer-clay network in solution strongly influences the alignment of polymer and clay during the spreading process. 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 as well as structural changes. While in solution the clay is completely exfoliated, the dried film shows significant change in structure. One example is the presence of domains containing several clay platelets in a stacked order (Figures 4.4). Although the
relaxation in solution is very fast, we assume that it is the shear combined with the slow drying of thin layers within a concentration gradient that leads to the orientation. An ongoing study will try to determine the rate of drying for locking in the orientation vs. the relaxation. Preliminary results show that a thick polymer clay film that has not been sheared but just dried is brittle, porous and cloudy. The spreading and drying procedure influences both the micro- and macrostructure and transparency. Evaporation of the solvent at ambient temperature combined with shear orientation strongly improved the film quality, the mechanical properties (as compared to a non-sheared and non layers thick film) and increased the orientation of clay platelets that are layered between the polymers.

4.3.3 Optical Microscopy

The macrostructure of the transparent films was also characterized by polarized microscopy, which showed differences in birefringence in each plane (Figure 4.5c,d). A small section of a one layer film was removed (by scratching or cutting) to expose the x-y plane. The x-z plane did not show birefringence, which indicates there is little polymer crystallinity in the x-z plane. Any existing PEO crystallites, that are not detectable by WAXS and DSC, are also not large enough to be detected by optical microscopy. With increasing temperatures ranging from 25 °C to 200 °C, the birefringence of the x-y plane gradually fades due to melting of oriented polymer chains. Observation of the exposed edge of the film, the x-y plane, shows some birefringent pattern even after annealing for one hour at 200 °C. The total birefringence of the film is dominated by the orientation of the clay platelets and possibly stretched polymer chains within the sample. Stretched polymer chains in confinement do not necessarily need to be crystalline. Since the polymer is almost amorphous (according to WAXS and DSC) birefringence may be somewhat influenced by shear effects during the scratching or cutting of
Figure 4.5 SEM images of freeze fractured surfaces: a) SEM view on top of the x-y plane, b) SEM view on top of the x-z plane. Planes are described in Figure 1. c,d) Optical micrograph of a transparent 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 20 were used. e) Transparent nanocomposite film of 1nm thickness.

At high temperatures, we believe that birefringence comes from the clay alone while at low temperatures both polymer and clay contribute to total birefringence in the x-y plane.

4.4 Conclusion

Previous work on bulk PEO-nanocomposites have shown that it is difficult to increase the clay intergallery spacing beyond a certain distance by adding more polymer to the system and that excess polymer will phase separate upon the removal of water. Our recent work on PEO-Montmorillonite multilayered films (clay content: 40%), has shown excess polymer to phase separate within highly ordered nm size layers. Present study on PEO-Laponite films (clay content: 60%), show additional periodicity within nm size layers (Figure 4.4). As the water
evaporates during the film preparation, the electrolyte concentration increases causing phase separation of PEO at higher concentrations. The presence of salt is in part responsible for the development of the unusual layered structures. Differential scanning calorimetry suggests that the high concentration of Laponite clay (60%) is sufficient to suppress the PEO crystallization. Films with high clay contents may be used as precursors for ceramic materials or microelectronics. The crystallinity of various bulk PEO nanocomposites at much lower clay concentrations has been studied in the past extensively.\textsuperscript{6,21} The suppression or induction of crystallinity in confinement is very important in controlling the structure in our multilayered films, issues that will be addressed in future research.

4.5 References


Chapter 5
Layered Structures of Shear-Oriented and Multilayered PEO/Montmorillonite Nanocomposite Films

5.1 Introduction

Polymer clay nanocomposites are hybrid materials that exhibit a change in composition, structure and properties over the scale of nanometers. Ordering layered silicates with high aspect ratio at the nanometer length scale is a challenging and active research area in materials science and engineering. Approaches developed so far range from manipulation of individual particles to exploitation of self assembly in colloids. The large aspect ratio of platelets promotes a supramolecular organization similar to other mesoscopic systems such as liquid crystalline polymers, surfactants or block copolymers.

The effect of shear on the orientation of polymer nanocomposites has been examined by a number of groups and in some cases the three dimensional orientation of the polymer and clay has been determined. Small and wide angle scattering and microscopy are powerful techniques used to characterize structure and orientation. For example Poly(ethylene oxides) PEO-clay blends have been investigated and accelerated crystallization and clay induced orientation of PEO crystallites has been observed. Earlier work has found that intercalation of PEO within galleries of clay resulted in hybrid structures that can accommodate a maximum ratio of polymer to clay and any excess polymer leads to the formation of two phases such as 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 the 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 structure 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. 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. 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. 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. 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. The reason was that water is a good solvent for PEO and the polymer water interactions impede complete intercalation.

There has been new technology of adsorption from solution 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. For example Atomic Force Microscopy on multilayered clay films revealed that polymer Laponite films are characterized by significantly higher surface coverage than natural
clays such as Montmorillonite. These films as well as those studied by Kleinfeld et al\textsuperscript{37} were prepared by sequential adsorption of polymer and clay.

Previous work relevant to this paper described a rheological and small angle neutron scattering study (SANS) on network like solutions of clay and poly (ethylene-oxide)\textsuperscript{38-41}. The polymer and the clay interact in a dynamic adsorption/desorption equilibrium to form a 3D network\textsuperscript{41}. 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{42}

The objective of the present contribution is to use network-like polymer-montmorillonite solutions\textsuperscript{38} 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 solvent is evaporated. Only completely dry films will be 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 the sample preparation conditions. On a nanometer length scale, SANS and AFM are complementary used to study the structure and shear-induced orientation of polymer and platelets after a film is spread and dried from a network-like polymer clay solution. SEM and microscopy investigate the morphology and porosity of the films on a micron length scale. Hybrid films such as the ones described in this paper offer a range of challenges and opportunities.

5.2 Experimental

Natural clay montmorillonite (Cloisite NA+, CNA) (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 and a clay polydispersity of ca. 30 % according to the supplier. Poly (ethylene-oxide) \( (M_w = 10^6 \text{ g/mol, molecular weight distribution ca: } 1.5) \) was purchased from Polysciences Inc. Films were prepared via solution exfoliation. Optimal solutions are obtained for a particular polymer clay ratio, pH and ionic strength as described by Malwitz et al\textsuperscript{38}. 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 (no peaks 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 of oriented polymer covered clay particles are present. Both the pH and the ionic strength of the solution were controlled by the addition of NaOH \((\text{pH} = 10)\) and NaCl \((3 \text{ mM})\), respectively. Under these conditions, flocculation and degradation of the clay particles are avoided. Sample preparation can be reduced to 3 weeks when samples are mixed/sheared and centrifuged daily. Simply dissolving the polymer and the clay in water is not sufficient to completely exfoliate the samples. Instead 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% of clay and 67% of PEO polymer were obtained. Preliminary annealing studies and thermogravimetric analysis indicate that water is dried out of the films \(< < 0.5\%\). More detailed film preparation is described under references\textsuperscript{42} and notes\textsuperscript{43}. Multilayered films with an average layer thickness of ca 5-7 μm were obtained by manually spreading the filled polymer gel on a glass substrate with a blade. Films with the same
spread direction were dried layer by layer onto each other until a total multilayer film of ca. 1-2 mm was obtained. The simple preparative method used by us offers a powerful strategy to building ordered films by shear orientation from solution. One reason why we chose the spreading and drying procedure is the high modulus of the 33 % clay polymer nanocomposites, which made shear orientation in the bulk with conventional rheological instrumentation difficult. Spincasting or dipping of the gum-like hydrogel was problematic due to high viscosity and elasticity as well as impurities, which were hard to remove.

Optical microscopy was performed with an Olympus BX51TF microscope under crossed polarizers. A small section of a one layer film was removed (by scratching) to expose both the x-z and the x-y plane and to compare results with those obtained from the 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 coated with gold/palladium in an Edwards S-150 sputter coater. Fractures in all 3D planes have been investigated and only representative images are presented.

Sample preparation for AFM included cryo-fracture and cryo-ultramicrotom slicing. Samples from both methods showed same morphology and structure when investigated. Here representative AFM results from the dried and cryo-fractured samples are presented. All the AFM experiments have been carried out in air at room temperature using a Nanoscope III Multimode Microscope from Digital Instruments operating in the tapping mode to minimize the sample distortion due to mechanical interactions between the AFM tip and the surface. Integrated silicon tips with a radius of curvature of about 10 nm and cantilevers with a nominal spring constant of 30 Nm$^{-1}$ have been 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. “Height” images are obtained by using the feedback loop which keeps the amplitude at a constant value $A_{sp}$ by translating vertically the sample with the piezoelectric scanner. The feedback loop is controlled by the set–point amplitude ratio $r_{sp} = A_{sp}/A_0$ 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, that is, 512 x 512 data points. Duplicate measurements on all instruments show excellent reproducibility. AFM experiments were performed by Dr. Vincent Ferreiro.

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 a nanometer length scale. In 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 any more. 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 these nanocomposites makes them extremely tunable through small changes in the chemistry and structure of the polymers.\textsuperscript{38} The polymer molecular weight strongly influences the density and 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 the films) have shown that the CNA clay platelets already align at shear rates below 5 s\textsuperscript{-1} and after cessation of shear relax from that alignment very slow (within many hours).\textsuperscript{48} 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.

5.3.1 Atomic Force Microscopy

The collapsed network structure from solution lead to highly oriented layers in the dried film. A striped texture with a d spacing of 56nm is obtained from AFM images. The d spacing obtained from SANS\textsuperscript{47} (d\textsubscript{SANS}≈63 nm) is more or less consistent with the spacing of the striped texture measured from AFM d\textsubscript{AFM}≈ 56 nm (average over many measured spacings, see Figure 5.1). In making these measurements, 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, and thus to increasing/decreasing of layer spacing. This is a property that makes the material applicable as potential humidity sensor.\textsuperscript{49}
The anisotropic SANS pattern as obtained by Malwitz et al\textsuperscript{47} can be well correlated with the Fast Fourier transform AFM data (Figure 5.1b) showing that a broad anisotropic streak in diagonal (Figure 5.1b) is perpendicular to the striped texture (Figure 5.1a). On similar length scales, both methods complement each other. While SANS\textsuperscript{47} 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 $d_{\text{AFM}}$ and $d_{\text{SANS}}$ spacing are to be expected. The existence of the highly ordered and layered structures observed with AFM is unusual and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5.1}
\caption{Representative AFM data from the x-z plane sections of multilayered films. a). (952 x 952 nm) AFM "height" image of the x-z plane sections of multilayered films. The AFM experimental conditions were: $A_0 = 54 \text{ nm}$; $f_0 = 179 \, 788 \text{ Hz}$; $A_{\text{sp}} = 52 \text{ nm}$ with $f_{\text{sp}} = 179 \, 572 \text{ Hz}$; $z$-range = 90 nm, b). FFT spectrum of figure 3a. c). Cross section of figure 3a.}
\end{figure}
unexpected. The orientation and size of the clay platelets which are ca. 100 nm in diameter and 1 nm thick, does not explain the highly ordered layers and their thickness of ca. 56 nm (Figure 5.1). We note however that the clay can adsorb only a maximum amount of polymer till 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.\textsuperscript{26, 27} We assume that during the drying process, these two phases lead to the layered structure observed with AFM and SANS. Also of note is that this interpretation is consistent with similar behavior reported by Vaia et al,\textsuperscript{26, 27} Wu et al\textsuperscript{26, 27} and Schmidt et al.\textsuperscript{39}

5.3.2 Scanning Electron Microscopy

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 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 micron size observed by SEM). In the y-z plane (Figure 5.2a) 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 5.2b) 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 ± 280 nm in length and approximately 170 ± 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 e.g. the “shear rate” during the spreading process and the drying procedure. Fracture of the film (Figure 5.2c) 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 clay platelets are shear-oriented preferentially in the spread direction. We conclude that the strength of the polymer clay 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.\textsuperscript{38} 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.

5.3.3 Optical Microscopy

Polarizing microscopy showed differences in birefringence in each plane, x-z and x-y (Figure 5.3). 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\textdegreeC the birefringence gradually disappears due to 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\textdegreeC. 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 birefringence comes from the clay alone while at low temperatures both polymer and clay contribute to 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 that excess polymer will phase separate upon removal of water.\textsuperscript{25} With our polymer nanocomposites, both the pH and the ionic strength of the solutions were controlled by the addition of NaOH and NaCl, respectively.
Figure 5.3 Optical micrograph of a spread nanocomposite film with scratched surface. A small section of a one layer film was removed (by scratching) to expose the x-y plane. Crossed polarizers and a magnification: 20X were used.

As the water evaporates during the film preparation, the electrolyte concentration increases causing phase 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 some PEO crystals that may have 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 anymore. The crystallinity of various PEO nanocomposites has been studied in the past.\(^{24, 25, 50}\) 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.

5.4 Conclusion

Nanocomposite multilayered films were studied with a combination of scattering and microscopic techniques. 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 clay platelets oriented inside the network with the clay surface normal perpendicular to the spread direction. On a nanometer scale the clay can adsorb only a maximum amount of polymer till 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 determining the thickness and density of the polymer-clay interfacial regions, 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 determining 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.

5.5 References


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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 hour's one film was spread and dried, which gives ca. 7 to 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.
Chapter 6
Supramolecular Structures in PEO/Montmorillonite Nanocomposite Multilayered Films†††

6.1 Introduction

Novel physical properties of soft and bulk polymer nanocomposite materials are strongly dependent on the structures at the nanometer length scale and the supramolecular organization of these nanostructures. The presence of the nanoparticle and the interaction of the polymer with the particle as well as the particle orientation in an aqueous precursor phase may lead to a variety of ordered composite materials in the bulk or film. Anisotropic clay particles promote supramolecular organization similar to other systems such as liquid crystalline polymers, surfactants, block copolymers and peptides. Supramolecular structures are held together by intermolecular forces rather than covalent bonds. The interactions between the molecules are mainly non-covalent in nature such as hydrogen bonding, Van der Waals and electrostatic interactions. Depending on the concentration of polymer and clay, the polymer type and molecular weight, the clay size, shape and surface chemistry, one may generate a variety of dispersions, solutions, smart gels, shake gels, glues and gum-like gels all of which may be excellent precursors for hierarchically structured bulk materials. Some of these soft and hard nanocomposite materials are sensitive to external stimuli including: light, temperature, pH, salt concentration, shear, pressure and electric fields, leading to novel properties that attract much scientific and technological interest.

To examine the polymer-clay interactions, a combination of methods is advisable. Among them, microscopy and scattering are techniques for studying structure and providing a measure of size, shape and interfacial polymer conformation. Recent advances in ultra small angle scattering techniques offer advantages and complementary information.\textsuperscript{25} Rheology and mechanical testing may nicely distinguish between properties of chemically\textsuperscript{21} versus physically cross-linked polymer-clay materials.\textsuperscript{17,18} Since shear can influence both the macroscopic texture and the orientation of the anisotropic particle on the nanometer length scale, it is helpful to combine the above mentioned techniques and correlate changes in the mechanical properties with changes in structure on different length scales.

In this work we are interested in the fabrication of hierarchically ordered model poly (ethylene) oxide (PEO) nanocomposites. The exfoliation, intercalation and aggregation of clays in PEO nanocomposites has been extensively studied in the past.\textsuperscript{26-32} The dispersion of clay platelets in polymer nanocomposite films can be achieved using both solution and melt fabrication techniques.\textsuperscript{28,29,33} Polymers such as PEO are able to intercalate and exfoliate clays directly from the polymer melt as well as promote the exfoliation process in aqueous solution. If the clay and polymer are hydrophilic, no clay surface modification is necessary for complete exfoliation of clay in aqueous solution. The products obtained from simple melt and solution intercalation of PEO into clays are less ordered but may have identical structures.

Hydrophilic polymers such as PEO strongly adsorb to natural Montmorillonite as well as synthetic Laponite clay. The amount of polymer adsorbed to the clay is controlled by the layer charge density on the clay.\textsuperscript{31} In PEO-Montmorillonite nanocomposites studied in literature the heterogeneous nucleation of PEO competes with the PEO coordination to sodium ions, which inhibits PEO crystallinity.\textsuperscript{34-36} The addition of salt and clay to polymer electrolytes such as PEO
leads to a class of materials that offer great potential in electrochemical applications. By inducing anisotropy over large length scales and via supramolecular ordered structures, new ways are found for fabricating scientifically and technologically novel materials with enhanced mechanical, optical properties and conductivity.

The supramolecular organization of clay platelets in polymer nanocomposite films can be achieved using solution fabrication techniques such as self-assembly, a variety of layer-by-layer approaches as well as the Langmuir-Blodgett method. We are interested in the fabrication of highly oriented PEO-Montmorillonite and PEO-Laponite multilayered films from the corresponding high viscous aqueous gels and solutions. Our previous rheological and small-angle neutron scattering (SANS) studies on these PEO-clay solutions and gels have investigated the shear orientation and structure in solution. In solution the polymer and clay form three-dimensional networks. The adsorbed PEO polymer is strongly attached to the clay and the excess polymer that is not adsorbed is stabilizing the polymer clay network. The excess polymer in solution usually leads to formation of polymer-rich phases that penetrate the network-like polymer-clay phases. For “non-oriented” bulk materials these disordered phases have been observed before in literature. For multilayered films made from the corresponding gels and solutions we are the first to explore the spontaneous multilayer formation and the supramolecular organization of clay platelets into unusual and highly ordered structures.

6.2 Experimental

We have prepared viscoelastic solutions of the natural smectite type clay, Montmorillonite, Cloisite NA+ (CNA), (Southern Clay Products), and poly(ethylene-oxide) (PEO), purchased from Polysciences Inc., (M_w = 1 x 10^6 g/mol, M_w/M_n ca: 1.5, R_g ≈ 100 nm in H_2O). The CNA clay produces an opaque suspension of predominantly “exfoliated” platelets
(no peaks at high q in SANS)\textsuperscript{44} that range on average in size from ca. 70 to 150 nm across and are ca. 1 nm thick (Atomic Force Microscopy). Several $<$10 nm and ca. $>$1-2 micron large platelets can also be observed thus the reported polydispersity of 30\% for the platelet diameter\textsuperscript{42} may not be accurate for every type of natural clay, but dependent on the batch and the source. Polydispersity also depends on the treatment and purification of CNA clay, especially if the purification process removes the smaller platelets or the largest ones. Discrepancies between measured sizes for natural clays from the same supplier are known.\textsuperscript{44,45}

\textbf{Figure 6.1} A physical picture of general clay platelet orientation in a multilayered polymer nanocomposite film is shown as well as the definition of planes.

Multilayered films were prepared from solution via gel/solution exfoliation while exfoliated and stable solutions were obtained for a particular polymer clay ratio, pH and ionic strength as described before.\textsuperscript{16-18,46} Here multilayered films are discussed that have been prepared from an aqueous solution containing mass fractions of 3 \% clay and 2 \% PEO at ambient temperature. The solution pH and ionic strength were controlled by the addition of NaOH (pH = 9-10) and NaCl (1 mM), respectively. Using a pH $>>$10 or pH $<<$9 in solution leads to chemical breakdown of the clay over time.\textsuperscript{47} Gels were spread onto glass slides layer-by-layer
and dried at 25 °C in desiccators and under vacuum. While one spread and dried film (ca 3-7 microns thick) already produces multilayers as examined by SEM, the film thickness of one spread film is too small to be cut and thoroughly investigated by scattering and microscopic techniques used by us. Therefore we use a layer by layer spreading and drying technique to obtain thicker films for better investigation. SEM was repeatedly used to examine the interface between the spread layers but no interface could be detected indicating intermixing of spread layers.

**Figure 6.2** SANS intensity as averaged in 10 degree sectors for all three directions in space. 2D SANS spectra from a ca 1mm thick multilayered film obtained in the x-z plane and in the x-y plane. SANS by Elena Loizou

Reproducible results were obtained when using and comparing two preparation techniques: i) a simple spreading device can be used that guarantees the same thickness of each
spread layer and ii) the films are spread manually with a blade. Multilayered films containing ca. 60 % of CNA clay and 40 % of PEO polymer (by mass fraction) were obtained (CNA60%-PEO40%). More detailed film preparation is described elsewhere.\textsuperscript{48} The shear-orientation combined with the drying procedure as well as control of the film thickness is absolutely necessary to obtain the highly ordered multilayers; simply drying the film is not sufficient. The film structure of the CNA60%-PEO40% films has been found to be independent from the spreading direction.

SANS measurements were preformed on the 30 m SANS NG7 instrument at the Center for Neutron Research (NCNR), National Institute of Standards and Technology (NIST).\textsuperscript{49} In a standard y-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 configuration, the incident beam is parallel to the spread direction of a 0.5 mm thick PEO-clay film (see Figures6.1&6.2). The neutron beam in z-beam configuration provided SANS intensities in the x-y plane. The primary contrast in the SANS experiment is between the silicate and PEO. This allows SANS experiments to detect the overall orientation of the clay platelets in a polymer matrix (Figure 6.2).

Sample preparation for the AFM measurements included cryo-ultramicrotom slicing (Leica ultracut with FC4 from Reichert-Jung) and freeze fracture. Samples were cut at -120 °C, below the PEO glass transition temperature (\(T_g = -55 \, ^\circ C\)). The images were recorded with a Nanoscope IIIa Dimension 3100 (Veeco Instruments).\textsuperscript{51} As reported in a previous paper\textsuperscript{51}, AFM “phase imaging” can be used to distinguish clay particles from the PEO matrix due to their difference in mechanical properties. SEM experiments were performed using a Cambridge 260
Stereoscan Electron Microscope. Many fractures in all three planes were investigated and only representative images are presented.

6.3 Results and Discussion

The solution structure and fabrication conditions strongly influence the morphology of the multilayered dried films. In solution the adsorbed PEO polymer is strongly attached to the clay and the excess polymer that is not adsorbed is stabilizing the polymer-clay network. The predominant orientation of CNA platelets in solution is with the flow and with the surface normal along the velocity direction. The orientation of CNA platelets in the dried film is expected to be in the film plane (Figure 6.1). A simple physical picture of clay platelet orientation in the multilayered films as well as the definition of planes is shown in Figure 6.1.

6.3.1 Small Angle Neutron Scattering

The orientation of the clay platelets can be deduced from the SANS results (Figure 6.2). The isotropic SANS pattern in the x-z plane and the anisotropy observed in the x-y plane confirms the orientation of the platelets to be with the surface normal perpendicular to the film plane (x-z plane). From the 2D SANS patterns in x-z and x-y direction, the intensity as a function of q can be calculated in all three directions in space.

Figure 6.3 AFM a) height image and b-c) phase images from the x-y plane sections of CNA60%-PEO40% multilayered films. AFM by Dr. Vincent Ferreiro
Anisotropy is observed over at least 2 orders of magnitude in q which indicates orientation of clay platelets over the whole q range is detected. A change in slope between 0.001-0.01 and 0.01-0.1 reciprocal Angstroms or the hint of a shoulder that is observed around q= 0.01 reciprocal Angstroms (2π/q=60 nm) may be correlated with the ca. 56nm thickness of layers detected by microscopy. Intensities in x and z directions as well as the x directions from both configurations overlap as expected. Since the SANS is averaged over the sample volume, the 2D SANS patterns shown in Figure 6.2 look similar to SANS patterns from other oriented nanocomposites studied in the past.\textsuperscript{23,24} However, results from microscopy show very unusual and unexpected structures. SANS experiments were performed by Elena Loizou\textsuperscript{50}.

6.3.2 Atomic Force Microscopy

The polymer-clay morphoplogy and texture orientation as displayed from representative Atomic Force Microscopy (AFM) is illustrated in Figures 6.3&6.4. Compared to what is usually found in literature on polymer nanocomposite orientation, our results show an unusual and unexpected 3D ordered and layered structure of blob-like chains and layers. The orientation of individual CNA clay platelets with an average diameter of ca. 70-150 nm and a thickness of 1 nm does not easily explain the presence of ordered layers of elongated “blobs” (Figures 6.3&6.4). The average blob thickness is ca. 56 nm and the average blob length is ca. 100 nm (Figures 6.4) while a chain of blobs can be very long. The 56 (±16) nm blob chain thicknesses (y-direction) correspond to polymer wrapped clay stack layers as seen from the side (blob may contain several platelets). X-ray diffraction experiments performed by Stefanescu et al\textsuperscript{50} confirm the presence of stacked clay platelets. Although in solution the clay platelets were found to be exfoliated (no peaks in SANS and SAXS) in the film, the platelets re-intercalate and order supramoleularly. The high polydispersity of natural Montmorillonite CNA clay (average
size 70-150 nm) leads to heterogeneities and more defects in orientation compared to the low
disperse synthetic Laponite LRD clay (30 ± 5 nm diameter platelets). Multilayered films shown
in Figures 6.4a and 6.4b strongly reflect the differences in polydispersity of CNA versus LRD
clay. The average x-direction correlation length observed from several AFM images (such as
Figure 6.3 & 6.4) is ca. 100 (±20) nm per blob for CNA60%-PEO40%. This blob length
corresponds to an average clay diameter for CNA platelets which is around 100nm (Figure 6.4).
For LRD60%-PEO40% shown in Figure 6.4b the correlation length of the blobs observed is
much smaller, more uniform and on the order of 30-60nm.

![AFM images from the x-y plane sections of multilayered films for CNA60%-PEO40% and LRD60%-PEO40%, both phase images.](image)

**Figure 6.4** a) AFM images from the x-y plane sections of multilayered films for CNA60%-PEO40% and b) LRD60%-PEO40%, both phase images. For a) and b) the clay concentration is high enough as to distinguish individual or bundles of clay particles. AFM by Dr. Vincent Ferreiro

If we assume that ca. 100nm is the correct average CNA clay platelet diameter then we
may wonder what happened with the few large platelets that are >1 microns in size? AFM from
pure and diluted CNA solutions suggests the presence of few large platelets >1 microns. It is
possible that many of the large platelets are broken down during the sample preparation process and those few remaining form large defects that are not shown with AFM but may be visualized by optical microscopy. An alternate interpretation suggests that it is possible that the larger polymer covered platelets are arranged between the blob-like chains and layers since the length of some of these layers is on the order of several 1000 nm. This interpretation is supported by the nm size layered structures we have observed for films at higher salt concentration studied by us in the past. Here large amounts of excess PEO may cover up any blob like chains and lead to a different type of layered structure. Due to higher polymer concentrations neither height nor phase imaging can distinguish between individual platelets at CNA40%-PEO60% concentrations studied in the past. Although the 2D SANS data for both, the CNA40%-PEO60% films studied in the past and the CNA60%-PEO40% films presented here look qualitatively very similar, the local morphology such as the interconnected blobs versus layers, is very different.

To better understand the film structure formation we need to know the polymer clay interactions in solution. In solution the clay particles can only adsorb a maximum amount of polymer until all the clay surfaces are covered. The polymer and the clay build a network-like structure that is interpenetrated by a sub-network of interconnecting pores containing excess polymer and water. Since the polymer adsorbed clay is completely exfoliated in solution (no peaks in diffraction patterns from solution) this solution-structure must collapse, reorder and re-intercalate into blob-like chains during the film formation process. The more or less uniform blob size observed in the film is highly reproducible and must be related in some way to the network like structure in solution. For synthetic Laponite clay the absorbed polymer layer has been measured before to be ca. 1.5 nm on each face. In the film the excess polymer is wrapped around the stacked Laponite clay platelets forming 30-60 nm blobs (Figure 6.4b).
Montmorillonite (CNA) clay does the same just that the blobs observed are more polydisperse and elongated due to larger aspect ratio (ca 100nm long and 56nm thick blobs) (Figures 6.4a). Our preliminary results from solutions also showed that the platelets within a polymer-clay

![Figure 6.5](image)

**Figure 6.5** A representative AFM image is shown from the x-z plane section of a multilayered film for CNA60%-PEO40%. Cursor profile and height histogram are also shown. No layered structure is visible. AFM by Dr. Jayne Garmo

network are interconnected over the edge more than over the face. We hypothesize that when the network is stretched, and the solvent evaporates simultaneously, the network collapses, the clay platelets re-intercalate and the edge to edge connection in solution may favor the formation of blob-like chains and sheets in the film. The sliding of already existing blob chains and sheets of a sheared but not completely dried film may also influence the observed layered structures which are very similar to shear oriented liquid crystalline lamellar phases. As for the surface structure of the layers, AFM from representative samples in the x-z plane is shown in Figure 6.5. Cursor profile and height histogram are also shown. No layered structure is observed.
6.3.3 Scanning Electron Microscopy

SEM is used to determine the film morphology on the micron length scale (Figure 6.6). As mentioned previously, the aqueous CNA-PEO solutions can be described as interconnected networks. When the sample is shear-oriented and the solvent evaporates simultaneously, the network collapses which leads to layered film structures that can be observed on several length scales. In the x-y plane of the films (Figure 6.6), SEM was used to examine whether an interface exists between individual spread layers. Similar to other polymer-clay multilayered films that we have studied before, no boundaries between spreading layers (each 3-8 μm) could be detected, indicating substantial intermixing of spread layers. Nevertheless a highly ordered and layered structure of the films is observed in the x-y plane, while no layers are observed in the x-z plane. The layered texture observed in the x-y direction is not uniform and is calculated to have an average dimension of \(d_{\text{SEM}} \approx 60-70\) nm per layer (Figure 6.6c). Even though the exact shear rate during the spreading process cannot be controlled, SEM shows high reproducibility in data. The film structure has also been found to be independent from the spreading direction.

According to AFM measurements each of the ca. 60-70 nm thick layers observed by SEM corresponds to the blob like chains and layers that are on average 56 nm thick (Figures 6.3&6.4). Reference PEO films made from pure PEO solutions with the same salt concentration as the CNA60%-PEO40% films showed no layered structures suggesting that the addition of salt to pure PEO solutions does not lead to any layer formation. On a micrometer to centimeter length scale, the CNA60%-PEO40% films presented here look different from the CNA40%-PEO60% films studied in the past. The lower polymer concentration used here leads to a more open structure with less interconnected layers in the x-y plane (Figure 6.6) and no layers in the top surfaces (x-z plane, see figure 6.5). The CNA60%-PEO40% films presented
here also look very different from the LRD60%-PEO40% films studied in the past. At the same polymer, clay and salt concentrations, the larger CNA platelets (ca 100nm) lead to less oriented micrometer size layers compared to the smaller LRD platelets (ca. 30nm). This is counterintuitive since we expect large CNA particles to align more preferentially than the smaller ones at a similar concentration. The origin of these effects is unclear but must be related to the shear alignment and relaxation of clay platelets in solution. Future work will investigate these effects in more detail. Inspection of several SEM images suggests that the fractured CNA nanocomposite film does not break parallel to the layers while the LRD nanocomposite film does. SEM images shown in figure 6.7 represent the X-Z and X-Y planes of the multilayered film and illustrate the differences in morphology of the two surfaces. The multilayered films do not show any layers in the x-z (top surface) plane of the film. LRD60-PEO40 multilayered films also do not show any layered type of structures in the x-z plane of

Figure 6.6 SEM images of freeze fractured x-y plane surfaces of CNA60%-PEO40% multilayered films at different magnifications. A distinct layered structure is visible.
the film. Layered type of structure is seen in the x-y (fractured) plane of LRD60-PEO40\textsuperscript{24} and CNA60-PEO40 multilayered films, but the layered structure is different.

![SEM images of x-z and x-y plane surfaces of CNA60%-PEO40% multilayered film.](image)

**Figure 6.7** SEM images of x-z and x-y plane surfaces of CNA60%-PEO40% multilayered film.

### 6.3.4 Optical Microscopy

The microscopic structure of the multilayered films was characterized by polarized optical microscopy, which showed differences in birefringence in each plane (Figure 6.7). From our experience with other nanocomposite films such as LRD60%-PEO40% at the same salt concentration \textsuperscript{24} we would expect to see no birefringence in the x-z plane and strong birefringence in the x-y plane which is predominantly coming from clay platelets that are hierarchical ordered on all length scales. For CNA-PEO films at higher polymer concentration and different salt concentration we would expect and observe birefringence in both planes resulting from both the polymer and the clay.\textsuperscript{46} When comparing films ideally one would like to limit the number of parameters being altered in the films made from solutions.
Figure 6.8 Representative optical microscopy image from a nanocomposite film with a cut surface. Crossed polarizers are used. A small section of a one layered film was removed to expose the x-y plane. The film is shown at room temperature after being heated and cooled. Birefringent speckles and birefringence of the x-y plane do not disappear at high temperatures. This film has been heated and cooled to remove any birefringence coming from additional shear effects during the scratching or cutting of the film.

However, this is often impossible due in large part to the very complicated phase diagrams of these complex systems in aqueous solutions that may require change of parameters (such as salt, excess polymer) to prevent the solution/dispersion from phase separation.53

The x-z plane (see Figure 6.1 for plane, Figure 6.7 for optical microscopy) for CNA60%-PEO40% films shows only few speckles which are due to the birefringence observed from predominantly single large clay platelets and clusters. With increasing temperatures in a range from 25 to 200°C the overall birefringence is only somewhat reduced probably due to melting of any oriented polymer. To the eye no significant differences in birefringence are visible. 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. For CNA60%-PEO40% studied here the polymer contribution to the total birefringence is either small or “not visible” to
the eye, suggesting that optical microscopy is not the best method for detecting PEO crystallites that may be confined between the layers. The birefringence of the scratched film in x-y plane changes as the film is rotated on a polarizing stage. The birefringence increases gradually and there is maximum birefringence at ca 45 degrees of rotation.

6.3.5 Differential Scanning Calorimetry

The polymer and clay composition of our multilayered CNA60%-PEO40% films is confirmed by DSC experiments performed by Stefanescu et al. While the crystallinity of various bulk PEO nanocomposites at low clay concentrations has been studied in the past extensively, here we focus on supramolecularly oriented and anisotropic materials at high clay concentrations. DSC studies by Stefanescu et al. show that 52% of the total polymer content is crystalline and 48% is amorphous. These results suggest that the high clay concentration is sufficient to suppress 48% of the PEO crystallization in the film. We expected that the CNA clay adsorbed polymer could be amorphous since it is confined to the clay surface and cannot move easily. The excess polymer would then form most of the crystalline phase. However qualitatively none of the PEO crystallites are visible with optical microscopy thus PEO crystallites must be either too small as to be detected by optical microscopy or there is polymer crystallinity confined within the clay layers. Differences in crystallinity of the CNA60%-PEO40% films presented here (52%) compared to the same composition LRD60%-PEO40% films studied in the past (near 0%) show that clay size dependence leads to unexpected but reproducible phenomenology at the nanoscale.

6.3.6 X – Ray Diffraction

X-ray diffraction studies on CNA60%-PEO40% multilayered films by Stefanescu et al. indicate the presence of stacked layers. Although the polymer-clay solutions from which the
nanocomposite films are made of, are completely exfoliated (no peaks visible) XRD confirms the
dried multilayered films are highly structured. Similar to the SANS data shown in Figure 6.2, the
XRD averages over the sample volume, thus both SANS and XRD do not show the hierarchical
arrangements as microscopy does.

6.4 Conclusion

Supramolecular order and hierarchical structuring is observed in the nanocomposite
multilayered films on various length scales. On the nanometer length scale a high degree of order
is reflected in the XRD pattern but AFM is necessary to visualize the supramolecular structure.
Compared to work done in the past our nanocomposite films have highly anisotropic structure
from the nanometer, via micrometer to the cm length scale while many previously reported
nanocomposites have only local ordered structures. Overall our results suggest the re-
intercalation of clay platelets in films made from exfoliated polymer-clay solutions as well as the
possibility to supramolecular order and hierarchical structure on the nanometer, via micrometer
to the centimeter length scale. The structure and properties of our multilayered nanocomposite
films may provide a useful route in the preparation of novel materials such as anisotropic solid
state electrolytes with enhanced ionic conductivity in only one direction.

6.5 References


(2) Schmidt, G.; Malwitz, M. M. Current Opinion in Colloid & Interface Science, 2003, 8,
103-108.


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(41) Decher, G.; Schlendorff, J. *Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials*; VCH Verlagsgesellschaft, **2003**.

(42) Polydispersity is estimated to be ca. 30% by the supplier.


Chapter 7
Summary and Future Directions

7.1 Summary

Poly(ethylene oxide)-clay nanocomposite solutions and films are studied on various length scales using a combination of imaging techniques such as optical microscopy, scanning electron microscopy, environmental scanning electron microscopy and atomic force microscopy and are complemented with scattering and diffraction studies.

On a micrometer length scale, multilayered films prepared from PEO-LRD and PEO-CNA solutions show highly ordered and layered structures. On a nanometer length scale, layers are seen in the form of interconnected blobs which consist of a bundle of polymer intercalated clay platelets. Clay can adsorb only a certain amount of polymer, and excess polymer stabilizes the polymer-clay network in solution. Evaporation of the solvent in the dried films leads to phase separation of excess polymer. The formation of polymer-clay intercalates and pure polymer phases leads to layered types of structures. Hierarchical ordering of the polymer intercalated clay platelets leads to the formation of anisotropic and supramolecular structures on various length scales. Small angle neutron scattering results indicate that the shear-orientation of polymer-clay solutions leads to a collapse of the network-like structure, and the clay platelets in the multilayered films are oriented in the spread direction. Birefringence seen in PEO-clay single layered films indicates anisotropy and orientation caused by polymer and clay on a micron length scale.

Poly(ethylene oxide) crystallinity can be suppressed or reduced by high concentrations of clay in the nanocomposite films. As an outlook for future directions, preliminary studies on nanocomposite films using differential scanning calorimetry (DSC) and Fourier transform
infrared spectroscopy (FTIR) are presented. Fibers prepared from PEO-CNA and PEO-LRD solutions and gels are also presented.

7.2 Preliminary Studies Using Differential Scanning Calorimetry (DSC)

7.2.1 Experimental

Differential scanning calorimetry was performed on multilayered films of PEO40-LRD60, PEO63-LRD37, PEO85-LRD15 and pure PEO using a TA 2920 Modulated DSC instrument. The weight of the sample used was determined using a high resolution modulated TA 2950 instrument. The aluminium caps were tared using a TGA instrument. A small amount of the sample was placed in the bottom cap and sealed with another cap. The weighed sample was placed in the specimen chamber of the DSC instrument along with the reference pan.

The samples were heated at a rate of 5°C/min up to 250°C with an equilibrating temperature of 10°C. A ramp of 5°C/min up to 85°C was chosen. Details of the composition of various multilayered films are given in the following table.

**Table 7.1** Designation of the polymer clay samples in PEO-LRD multilayered films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>% wt of Polymer</th>
<th>% wt of Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO40-LRD60</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>PEO63-LRD37</td>
<td>62.5</td>
<td>37.5</td>
</tr>
<tr>
<td>PEO85-LRD15</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>PEO67-CNA33</td>
<td>67</td>
<td>33</td>
</tr>
</tbody>
</table>

7.2.2 Results and Discussion

The melting temperatures and the total heat of enthalpy for each sample were obtained from the plot of ΔH vs. temperature curve of DSC. The percentage crystallinity of the sample is calculated using the following formula:
The results obtained from DSC are tabulated in the following table:

**Table 7.2** DSC results showing the percent crystallinity of PEO-LRD samples.

<table>
<thead>
<tr>
<th>Multilayered Film</th>
<th>Tm</th>
<th>ΔH enthalpy</th>
<th>Percent crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO40- LRD60</td>
<td>61.81°C</td>
<td>20.03 J/g</td>
<td>11.3</td>
</tr>
<tr>
<td>PEO63-LRD37</td>
<td>66.28°C</td>
<td>79.85 J/g</td>
<td>45</td>
</tr>
<tr>
<td>PEO85-LRD15</td>
<td>68.17°C</td>
<td>128 J/g</td>
<td>72.23</td>
</tr>
<tr>
<td>PEO</td>
<td>71.03°C</td>
<td>177.2 J/g</td>
<td>100</td>
</tr>
</tbody>
</table>

The thermal properties of PEO-LRD nanocomposite multilayered films are studied using Differential Scanning Calorimetry and are dependent on the concentration of the polymer, clay and trace amounts of water present in the multilayered films. In a fully exfoliated polymer-clay solution, the clay platelets act as multifunctional cross linking points and interact with the polymer forming a network-like structure.\(^1\) Clay can adsorb only a certain amount of polymer and excess polymer in solution stabilizes the polymer-clay network. Studies performed by Loizou et al showed that a network-like structure is present on a micrometer and nanometer length scale\(^2\) in PEO-LRD gels. Spreading of the polymer-clay solution and simultaneous evaporation of the solvent leads to a collapse of the network-like structure, and the polymer covered clay platelets are shear-oriented along the spread direction.\(^3\) Evaporation of the solvent causes phase separation of excess polymer, and leads to the formation of PEO crystallites in multilayered films.

In solution, PEO is in the dissolved form and does not phase separate. Poly (ethylene oxide) of higher molar mass such as 1000kg/mol consists of longer chains which interact with...
the clay platelets at many points along the chain. Polymer chains which are not adsorbed to the clay platelets phase separate during drying and crystallize. As the amount of polymer is increased in the nanocomposite films, such as PEO63-LRD37 and PEO85-LRD15 multilayered films, there is excess polymer which phase separates. Hence the percent weight of crystalline PEO increases with an increase in the PEO content in the nanocomposite films. During the process of drying, an increase in salt concentration in the multilayered films may also lead to phase separation and crystallization of excess polymer.

From the DSC results, it may be assumed that PEO chains which are adsorbed to the clay platelets remain in the amorphous form while PEO chains which are tethered to the clay platelets are in the crystalline form. High concentrations of clay in PEO40-LRD60 films can suppress PEO crystallinity in 89.7% of PEO (see table 7.2). The amorphous nature of PEO is also inferred by the absence of PEO spherulites in the single layered films of PEO40-LRD60 sample when viewed with crossed polarizers in x-z plane. 4

In calculating the percent crystallinity of PEO-laponite nanocomposites, 100% crystallinity of pure PEO sample is assumed. The glass transition temperature of pure PEO 11 is -55°C and PEO-laponite nanocomposites 12 show an increase in Tg. The melting temperature of pure PEO 12 is 66°C. The decreased mobility of the polymer chain in between the silicate layers is mainly responsible for an increase in the glass transition temperature reported in literature. 12 Presence of clay in the nanocomposite films leads to a decrease in PEO crystallinity. This results in less perfect crystals resulting in lower melting temperatures for PEO-laponite nanocomposites. The crystallization of PEO is also hindered by high concentrations of clay.

Multilayered films are prepared by a manual layer-by-layer approach. The films are spread manually on a glass slide by sequential adsorption of a thick layer of nanocomposite
Figure 7.1 DSC curves. (a) PEO40-LRD60 and (b) PEO63-LRD37 multilayered films.
Figure 7.2 DSC curves. (a) PEO85-LRD15 multilayered film and (b) Pure PEO
hydrogel or solution. Each spread layer is air dried at room temperature and the prepared multilayered films are placed in dessicators. The formation of well-dispersed and oriented multilayered films is not possible with conventional methods like dipping or spin casting because of high viscosity of the solutions and gels. Reproducible results were obtained with the manual spread technique. For this work we have chosen only those solutions and gels for film preparation, where the shear rate and exact film thickness are not critical to the final film structure and where the multilayer size and order can be reproduced easily.

The nanocomposite films are hygroscopic and show reversible adsorption/desorption of water. Since the samples which are ca. 6 months old were used to perform preliminary DSC studies, some amount of moisture may be absorbed which may lead to decreased amounts of crystalline PEO in the nanocomposite films. The amorphous nature of the polymer provides more surface area in the nanocomposite films and hence more amount of water can be adsorbed.

The enthalpy of melting of the nanocomposite films increases with an increase in polymer concentration. This can be attributed to the large differences in the amount of crystalline PEO present in the nanocomposite films. The melting temperature of PEO in the nanocomposite films containing high concentrations of clay is lower than the films containing high concentrations of polymer. This can be attributed to the relative proportions of crystalline and amorphous PEO present in the films. In PEO40-LRD60 films, most of the polymer is in amorphous form and hence melts at 61.8°C. PEO63-LRD37 and PEO85-LRD15 films melt at 66.28°C and 68.17°C (see table 7.2) respectively. This can be attributed to high amounts of crystalline polymer present in these samples. From DSC studies, it can be inferred that the amount of crystalline polymer present in the nanocomposite films depends on the amount of clay. Higher concentrations of laponite clay (60wt %) can suppress crystallization of PEO in the
nanocomposite multilayered films. Polymer crystallinity can be tuned by the concentration of clay in the nanocomposite films.

7.3 Concentration Dependence of Structure in PEO-Laponite Multilayered Films

The composition dependent structure of the nanocomposite multilayered films is investigated on a micron length scale using SEM. Images in the x-y plane (side surface fracture) of the film show that the occurrence of micron size layers is strongly dependent on clay content. The definition of planes is also shown in Figure 7.3d, for better comparison.

Although all samples were made from exfoliated polymer-clay solutions, PEO63-LRD37 and PEO85-LRD15 (see figure 7.3) films exhibited fewer or no layers, suggesting that clay...
concentration is critical in layer production. The micro- and nano-structures of selected PEO40-LRD60 nanocomposite films studied in the past have shown that the solution structure and processing conditions strongly influence the overall morphology of the dried films. The collapse of a polymer-clay network structure as the solution dries leads to a highly oriented thick layers in the dried film on a micrometer length scale (see figure 7.3a). The number of multilayers can only be estimated since one single spread produces multiple layers on large length scales. Only representative SEM images of multilayered films in the x-y planes (side surfaces) are shown in Figure 7.3. Among many other parameters, the sample preparation and the resulting structure strongly influence the crystallinity. For example, not completely exfoliated nanocomposite solutions containing pure clay aggregates will lead to films which have more excess PEO. This excess PEO is not bound to the clay and will crystallize. In our study, sample preparation and composition are kept constant to minimize defects while investigating the structure and thermal properties of selected multilayered nanocomposite films.

Formation of polymer-clay fibers is seen in the multilayered films containing high concentrations of polymer such as PEO63-LRD37 and PEO85-LRD15 films in the x-y plane. Polymer-clay fibers were previously observed in PEO67-CNA33 multilayered films which contain high concentrations of polymer. Formation of such fibers is not detected with either pure PEO or clay solutions. The clay platelets act as cross-linking points in the polymer-clay network connecting various polymer chains. A bundle of polymer intercalated clay platelets covered by excess polymer may be involved in the formation of fibers which are seen along the fractured surface of the multilayered films.

Studies performed by Lal et al. showed that the thickness of an adsorbed polymer layer is ca. 1.5 nm on each side of the clay platelet. Polymer-clay fibers are not observed in PEO40-
LRD60 multilayered films which contain high concentrations of clay. PEO63-LRD37 and PEO85-LRD15 films have excess polymer in addition to the polymer intercalated between the clay galleries and may facilitate the formation of polymer-clay fibers.

Figure 7.4 Polymer-clay fibers seen in the x-y plane of the multilayered films. (a) PEO63-LRD37 film and (b) PEO85-LRD15 film.

7.4 Preliminary Studies Using Fourier Transform Infrared Spectroscopy (FTIR)

7.4.1 Experimental

FT-IR spectroscopy was performed on the multilayered films of PEO40-LRD60, PEO63-LRD37, PEO85-LRD15, CNA40 (see table 7.3), pure PEO and LRD clay. Infra-red grade potassium bromide which was dried in a vacuum oven was used for preparing KBr pellets. A small amount of the sample was mixed with KBr and finely ground in a pestle with a mortar. The ratio between the sample and KBr was approximately 3:100. The spectra were acquired using a Thermo Nicolet FTIR spectroscopy instrument.

7.4.2 Results and Discussion

The amorphous or crystalline nature of the polymer in the nanocomposite films can be inferred from FTIR studies. Absorption peaks at 1361, 1343, 1280, 1242, 1149, 1060, 963 and 947 cm\(^{-1}\) are attributed to the vibrational modes of PEO in the crystalline phase. Temperature
dependent studies on high molecular weight PEO and PEO-LiCF$_3$SO$_3$ performed by Dissanayake et al.\textsuperscript{10} show that these bands in the FTIR spectrum disappear above the melting temperature of PEO (above 60°C) and are attributed to modes in the crystalline phase of PEO. The absorption peaks\textsuperscript{9} at 1241 cm$^{-1}$ are only observed in the PEO40-LRD60 film indicating that most of the polymer is in an amorphous state. The absorption peaks at 1342, 1280 and 1241 cm$^{-1}$ in PEO63-LRD37 and PEO85-LRD15 films indicate that most of the polymer is in crystalline state.\textsuperscript{9}

A broad absorption peak between 3450-3400 cm$^{-1}$ is found in all the multilayered films of LRD, CNA, pure polymer and pure clay. This peak can be attributed to an O-H stretching vibration. A corresponding C-O stretching vibration is found between 1650-1600 cm$^{-1}$ for all the films, pure polymer and pure clay. Pure PEO exhibits a symmetric CH$_2$ stretch at 2887 cm$^{-1}$ (broad band) and at 2740 cm$^{-1}$ (narrow band). The broad band at 2887 cm$^{-1}$ shifts to 2917 cm$^{-1}$ in the LRD60 with 60% weight of the clay. Shifting of the band towards higher frequencies may indicate a more polar environment and strong interactions between the polymer and clay in the PEO40-LRD60 multilayered film.\textsuperscript{9} No shift of this broad band is observed for PEO85-LRD15, PEO63-LRD37 and PEO67-CNA33 films. The intensity of the peak is also diminished.

A band of low peak intensity which is found in the pure PEO at 1967 cm$^{-1}$ is also present in PEO63-LRD37 and PEO85-LRD15 films. This peak is absent in PEO40-LRD60 film. A broad peak of high intensity which is due to asymmetric CH$_2$ bending vibration at 1467 cm$^{-1}$ in the pure polymer is shifted to 1457 cm$^{-1}$ as a small peak of low intensity in PEO40-LRD60 film. A change in the structure and morphology of the nanocomposites may be inferred as the proportion of the clay changes in these multilayered films. A shift in the asymmetric CH$_2$ wagging vibration from 1342 cm$^{-1}$ to 1353 cm$^{-1}$ in PEO40-LRD60 film also indicates increased
polymer-clay interactions.\(^9\) The asymmetric CH\(_2\) twisting vibration at 1281 cm\(^{-1}\) is not seen in PEO40-LRD60 film and the peak at 1241 cm\(^{-1}\) is of low intensity.

![Figure 7.5 FTIR spectra for (a) Pure PEO (1M), (b) PEO40-LRD60 film, (c) PEO63-LRD37 film, (d) PEO85-LRD15 film and (e) Pure LRD clay.](image)

The broad asymmetric C-O-C stretch is shifted from 1099 cm\(^{-1}\) to 1071 cm\(^{-1}\) in PEO40-LRD60 as a peak of medium intensity. A medium band\(^8\) between 1010 cm\(^{-1}\) and 1000 cm\(^{-1}\) appears in the nanocomposites of LRD series. This band is broad and of high intensity in PEO40-LRD60. This is due to Si-O stretch.\(^8\) A band at 652 cm\(^{-1}\) due to O-H bending is in the Spectra of LRD clay, PEO63-LRD37 and PEO40-LRD60. Significantly, this band is absent in PEO85-LRD15 which has 85% wt of the polymer. The out of plane vibration\(^8\) due to MgO at 536 cm\(^{-1}\) in the pure LRD clay is shifted to 451 cm\(^{-1}\), 456 cm\(^{-1}\) and 446 cm\(^{-1}\) in PEO85-LRD15,
PEO63-LRD37 and PEO40-LRD60 films respectively. This indicates a change in the interactions in the interlayer of the nanocomposites. The stretch due to Si-O in PEO67-CNA33 is at 1045 cm\(^{-1}\) and a shift is observed in the Mg-O stretch from 420 cm\(^{-1}\) to 466 cm\(^{-1}\).

![FTIR spectra for (a) Pure PEO and (b) PEO67-CNA33 film.](image)

**Figure 7.6** FTIR spectra for (a) Pure PEO and (b) PEO67-CNA33 film.

The symmetric CH\(_2\) rocking vibration which is more pronounced in the pure PEO gradually diminishes as the percentage of clay is increased in the nanocomposites. The peak due to asymmetric CH\(_2\) rocking vibration at 961 cm\(^{-1}\) is in pure PEO and PEO85-LRD15. As the percentage composition of the polymer decreases, this peak diminishes which may indicate a decrease in the amount of crystalline polymer in the nanocomposite films.\(^9\)
Table 7.3 FTIR peak positions (cm\(^{-1}\)) and assignments for PEO, LRD clay, LRD15, LRD40, LRD60, and CNA40. The mode assignments given are: St (stretching); B (bending); W (wagging); T (twisting); R (rocking). The asymmetric and symmetric modes are denoted as subscripts. (CH\(_2\))

<table>
<thead>
<tr>
<th>PEO</th>
<th>LRD clay</th>
<th>LRD15</th>
<th>LRD40</th>
<th>LRD60</th>
<th>CNA40</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td></td>
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<td>St (CH(_2))(_s)</td>
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7.5 PEO-Clay Nanocomposite Fibers

Fibers prepared from PEO-LRD and PEO-CNA solutions and gels are studied using polarized optical microscopy (POM) and scanning electron microscopy (SEM). Fibers were manually drawn from the polymer clay solutions and gels. Thinner fibers which are produced by further stretching are highly birefringent under crossed polarizers. Birefringence in the polymer-clay fibers may be attributed to the orientation of polymer and clay upon stretching.

7.5.1 PEO-Laponite Fibers

![Optical Microscopy: Fibers prepared from PEO-LRD sample. (a) Birefringent coiled fiber and (b) Birefringent twisted fiber.](image)

**Figure 7.7a** Optical Microscopy: Fibers prepared from PEO-LRD sample. (a) Birefringent coiled fiber and (b) Birefringent twisted fiber.

In the present study, manually drawn fibers from the polymer – clay solutions and gels are studied. The objective of this study is to characterize the fibers that contain different types of clays. PEO-LRD and PEO-CNA fibers contain high percent weight of the polymer and clay. Fibers of various diameters were drawn and observed using an optical microscope with crossed polarizers. The average thickness of the fibers is approximately 3 – 6 µm. Thinner fibers (ca 3 - 5µm) prepared from PEO-LRD sample (see figure 7.7a) are birefringent and visible under crossed polarizers. Twisted and coiled fibers could be produced by stretching and releasing the
Figure 7.7b SEM images of PEO40-LRD60 fibers.

Figure 7.8 Surface structures of (a) PEO40-LRD60 and (b) PEO67-CNA33 fibers observed using SEM.

PEO-LRD gel onto a glass slide. The thicker fibers of PEO-LRD sample prepared on the glass slide are not visible under crossed polarizers. Speckles formed due to the PEO crystallites are also absent. Fibers are visible under crossed polarizers only after the fibers are drawn thinner (approximately 8μm). The thinner fibers of PEO-LRD sample are highly birefringent indicating the orientation of polymer and clay upon elongation of fibers. Scanning electron microscopy of PEO-LRD fibers (see figure 7.8a) showed smooth surface texture with less striation. The surface of PEO-LRD fibers is textured with an average diameter of 1.44 ±0.02 μm.
7.5.2 PEO – Montmorillonite Fibers

Poly(ethylene-oxide)-montmorillonite fibers showed birefringent speckles caused due to PEO crystallites. Birefringence may also be caused due to anisotropic clay clusters present in the polymer-clay sample. The surface of PEO-CNA fiber (see figure 7.8b) is rough with a wavy pattern (2.56±0.07µm in diameter). Fibers of PEO-CNA and PEO-LRD viewed using SEM show structural differences. PEO-LRD fibers have a smooth surface whereas; the surface of PEO-CNA is ridge-like and wrinkled. The morphology changed to wrinkle-like and ridge-like patterns with Montmorillonite clay. These differences can be attributed to the composition and the type of clay present in both the fibers. The size, type and the interactions of the clay with the polymer may play an important role in forming these types of structures.
7.6 References


(8) Olphen, H. V.; Fripiat, J. J. *Data handbook for clay materials and other non-metallic minerals*, Pergamon press **1979**, 41,42,313,33


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