SELF-ASSEMBLED AND FLOW INDUCED NANO-STRUCTURES IN POLYMER NANOCOMPOSITES

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SELF-ASSEMBLED AND FLOW INDUCED NANO-STRUCTURES IN POLYMER NANOCOMPOSITES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Dilru R. Ratnaweera
May 2012

Accepted by:
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Dr. Steven J. Stuart
Dr. Jason McNeill
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Dr. David A. Zumbrunnen
ABSTRACT

Distribution of nanoparticles (NPs) in polymers and role of NPs in modifying the structure of the polymeric matrices were studied using X-ray diffraction, neutron scattering, neutron reflectivity and atomic force microscopy techniques. Dispersion of NPs in polymers is challenging due to the aggregation tendency of NPs and inherent mixing challenges of polymer. Several strategies were used to control the NP distribution in polymers, including “smart blending” and tailoring the interactions of the polymers.

In smart blending chaotic flow fields were used to disperse and orient montmorillonite NPs in homopolymer melt of polyamide 6 (PA6). The roles of duration of chaotic advection on the melt (N) and NP concentration on polymer chain orientation and crystalline morphology were investigated. The major crystalline form of PA6 changed from a stable α form to a meta-stable, which is defined as a state with local stability to small perturbations in the system, γ form upon addition of NPs. This crystalline transformation is enhanced with increasing N for lower NP concentrations. At higher NP concentrations, polymer chain packing is mainly controlled by the surface forces of NPs. In these nanocomposites the polymer chains orient perpendicular to the NP surface as well as to the extrusion direction. Upon annealing and stretching, the fraction of the stable crystalline form increases and the polymer chains orientate parallel to the NP surface. Using small angle neutron scattering we were able to show that in blended films amorphous and crystalline domains form stacks where water uptake of amorphous domains is significantly higher than the crystalline ones.
A second approach included tailoring interaction of polymer and NPs. For this purpose we used block copolymers. Block copolymer can be used as a template to disperse NPs into specific domains of the matrix polymer. Using fluorinated segments affects many of the polymer properties. The first stage of this study investigates the effects of fluorine on a model diblock copolymer, polytrifluoro propyl methylsiloxane-\textit{b}-polystyrene, in solution. We found that this polymer forms assemblies with different shapes ranging from spherical to elliptical micelles in solutions. These micelles exhibit unique temperature stability and associated into micelles at small volume fractions of the fluorinated block compared to the diblock copolymer micelles in lower segregation limit. As the temperature increases the micelles dissociate into free chains to form unimolecular micelles.

In the second phase of the study, copolymer templates were used to control the dispersion of NPs in thin polymer films. A semi-fluorinated random copolymer, biphenyl perfluorocyclobutyl, was used as a matrix polymer. Fluorinated blocks segregated toward the lower surface energy air/polymer interface while the hydrogen rich blocks moved to the substrate/polymer interface due to differences in surface energies of the fluorinated and protonated blocks. This segregation results in multi layer thin films with alternative fluorine rich and hydrogen rich layers. The dimensions of the NPs and the combine size of the fluorinated and protonated blocks were about the same. NPs migrate to internal surface induced interfaces in contrast to block copolymer in the lower segregation limit where NPs were segregated to the external interfaces due to translational and conformational entropic contributions. Modifying the NPs with a single matrix polymer
chain further reduced the tendency of the NPs to migrate to the external interfaces and induced layering at the center of the film. The different distributions of NPs in the polymer affected the distribution of water molecules, which are absorbed from saturated vapor, in polymer films. We found that the amount of solvent penetration in thin films is governed by the density of NPs at the air/polymer interface.
DEDICATION

This dissertation is dedicated to my parents who gave me courage and support during all these years, to my wife Thashi, for her support, love, understanding and being with me to share all my ups and downs and to my one year old daughter who gave me courage and love that kept me going through hard times.
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I would like to extend my gratitude to Dr. Jaroslaw Majewski, Dr. Manish Dubey and Mr. Michael Jablin for their help and technical support on neutron reflectivity experiments at Los Alamos National Laboratory. I want to thank Dr. Rex Hjelm and Dr. Monika Hartl at Los Alamos National Laboratory and Dr. Ken Littrell at Oak Ridge National Laboratory for their technical expertise on small angle neutron scattering experiments. Also I would like to thank Dr. Don VanDerveer at Clemson University for his help on X-ray diffraction measurements.

Last but not the least, I would like to thank all the colleagues in my research group, especially Umesh M. Shrestha, Thusitha Etampawala and Naresh C. Osti for their help with scattering experiments and for their valuable discussions.

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CHAPTER 1

Introduction

This dissertation aims to understand the factors that control the distribution of nanoparticles (NPs) in polymers and the role of NPs in modifying the structure and properties of the polymeric matrices by following the structures of different NP-polymer systems.

NPs are defined as “organic or inorganic particles with at least one characteristic length scale is in the range of 1-100 nm”. Due to their small size, they inherit higher number density and surface area to volume ratio compared to micron size particles. Therefore, dispersed NPs in polymer increase the number of polymer chains resides near the NP surfaces. This reduces the conformational freedom of polymer chains compared to the chains in the pure polymer, which alters the properties of the polymer such as mechanical and thermal stability. Presence of NPs alters the distribution of end-to-end distances of polymer chains and changes the orientation of chains, which modifies the crystalline and amorphous fractions of the polymer.

In addition to the role of NPs in modifying the polymer properties, characteristics of NPs can themselves introduce novel properties to the nanocomposites. For example, by dispersing small amounts of NPs with impenetrable barrier for small molecules such as water and oxygen, improve the barrier resistance of polymers. Incorporation of optically active NPs into polymers can modify the optical properties such as absorption and emission wavelengths of nanocomposites by controlling the size, shape and interparticle distance of NPs.
While incorporation of NPs into polymer enhances above qualities, the dispersion of NPs in polymeric matrices remains a challenge. NPs often form aggregates or phase separate from the matrix polymer due to the incompatibilities between NPs and the matrix. In addition, local structure of the polymer and the method used to make nanocomposites affect the way that NPs distributed within the polymer matrices.

**Dispersion of NPs in Polymers**

The technological significance of nanocomposites leads to many experimental efforts to incorporate NPs into polymers.\(^{15-19}\) However, there is very limited theoretical guidance to understand the critical parameters that control the dispersion of NPs in nanocomposites. The equilibrium state of a given mixture is determined by the free energy change upon mixing.\(^{20}\) Entropy always favors mixing and enthalpic contribution may facilitate or prevent mixing.\(^{20}\) In order to understand these contributions, thermodynamics of basics of mixing will be introduced herein.

One of the simplest models that accounts for enthalpy and entropy of mixtures or blends of polymers is the Flory-Huggins mean field theory.\(^{20}\) Let us consider the mixing of two species, A and B. According to this theory, entropy of mixing per lattice site \((\Delta S_{Mix})\) for a binary mixture is given by \(^{20}\),

\[
\Delta S_{Mix} = -k_B \left[ \frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) \right]
\]  

(1.1)
where \( \phi \) and \( 1 - \phi \) are the volume fraction of species A and B respectively. \( N_A \) is the number of lattice sites occupied by molecule A, \( N_B \) is the number of sites occupied by molecule B and \( k_B \) is the Boltzmann constant. Therefore, entropy of mixing depends on the volume fractions and number of monomers of both molecules. For regular solvents \( N_A = N_B = 1 \) and have the highest entropy. For polymer solutions \( N_A = N \) and \( N_B = 1 \). Having large number of monomers in a molecule significantly reduces the entropy of the system.

However, \( \Delta S_{Mix} \) always favors mixing.\(^{20} \)

The Flory interaction parameter (\( \chi \)) measures the differences in the pair interaction energies between species in the mixture and species in their pure forms.\(^{20} \) The (\( \chi \)) is given by;

\[
\chi = \frac{z}{2} \left( \frac{2u_{AB} - u_{AA} - u_{BB}}{k_B T} \right)
\]

Where \( u_{ij} \) is the pair interaction between species \( i \) and \( j \) (\( i, j = \text{A, B} \)) and \( z \) is the coordination number of the lattice. The energy of mixing per lattice site (\( \Delta U_{Mix} \)) is given as,

\[
\Delta U_{Mix} = \chi \phi (1 - \phi) k_B T
\]

Overall Helmholtz free energy change of mixing per lattice site due to entropic and enthalpic contributions is given in equation 1.4, which is also known as the Flory-Huggins relationship.\(^{20} \) The first two terms explain the entropic contribution and the last term describes the energetic contribution.
\[
\Delta F_{\text{Mix}} = \Delta U_{\text{Mix}} - T \Delta S_{\text{Mix}}
\]

\[
= k_B T \left[ \frac{\phi}{N_A} \ln \phi + \frac{(1 - \phi)}{N_B} \ln(1 - \phi) + \chi \phi(1 - \phi) \right] \quad (1.4)
\]

Several groups have extended the Flory-Huggins approach to incorporate NPs in polymers. One of the challenges is to overcome clustering of NPs themselves. Douglas and coworkers have explored the origin of nanoparticle aggregation for NPs with short range interactions in polymer melt and how aggregation affect on rheology using molecular dynamics simulations.\(^{21}\) They found that the transition between clustered and dispersed state is a thermo-reversible process as shown in Figure 1.1.\(^{21}\) Also they have found that shear viscosity of nanocomposites with dispersed NPs is larger than the viscosity of the aggregated nanocomposites.

![Schematic representation of clustered and dispersed NPs in polymer matrix](image)

Figure 1.1 Schematic representation of clustered and dispersed NPs in polymer matrix

The same group has investigated the effects of the shapes of the NPs on the viscosity and tensile strength (breaking stress) by molecular dynamics simulations.\(^{22}\) The highest viscosity was observed with rod-like NPs due to higher number of bridged
polymer chains between NPs compared to sheet like particles. Also they have observed the sheet-like NPs in clusters while rod-like NPs exist in a dispersed state. However, the highest tensile strength is observed for the nanocomposite with sheet like NPs.\textsuperscript{22}

Sanat Kumar and coworkers investigated the effects of short polymer grafts on the surface of NPs on the dispersion of NPs in polymeric matrices by mean field approximation.\textsuperscript{23} They have shown that the miscibility of NPs can be described by a $\chi$ parameter, which is the interaction between the polymer and grafted chains. According to their study, dispersion of brush-coated NPs in polymer matrix is enhanced by lowering the size, which increases the surface curvature and the spacing between grafted chains, of the particle and increasing the length of the grafted polymer chains, which increases the interaction between the polymer and the grafts. Also interpenetration of matrix polymer into the grafted layer is essential for large NPs to make a better dispersion by increasing the interaction.\textsuperscript{23}

Forming a nanocomposite requires overcoming mixing barriers, which are inherent to polymers due to incompatibilities among domains, and aggregation tendency which is characteristic of NPs. Several strategies have been developed experimentally to overcome aggregation tendency of NPs in polymers.\textsuperscript{24-25} Chemical modifications are often done by attaching small molecule organic ligands to NPs or by functionalizing particle surface with grafted layer of polymer to tune the polymer/NP interfacial energy, which enhance the $\Delta U_{Mix}$ by favoring the $\chi$.\textsuperscript{26} Green et al. have studied the dispersion of NP in homo-polymers, where NPs were modified with grafted chains, which are chemically similar to the matrix polymer.\textsuperscript{27-28} They have shown that the miscibility of
NPs in polymers increases when the ratio of the degree of polymerization of the graft and matrix polymer is around 1 or higher.\textsuperscript{27-28} As the length of the grafted chains increases, energetic contribution dominates over the entropic effects and facilitates the mixing. Chen and coworkers have observed that high grafted chain density results in poor dispersion of NPs in polymer matrix due to inaccessibility of polymer chains to interact with the brushes.\textsuperscript{29} Also they have shown the effects of the size of the NPs on dispersion in polymers, where dispersion of NPs were observed only when the sizes of the NPs are smaller than the radius of gyration ($R_g$) of the polymer, which results in higher translational entropy of NPs and large conformational freedom for polymer chains. In addition to chemical modifications of NPs, mechanical flows were used to disperse NPs in polymer melts.\textsuperscript{30-31}

The structure of the polymer itself plays an important role in determining the NP distribution in nanocomposites. When NPs are dispersed in homo-polymers, each individual particle has equal average energetic contribution from its surrounding. But this does not happen in polymers having different blocks and different interaction energies. For example, in block copolymers, different molecular assemblies are possible depending upon the volume fraction of individual blocks, architecture of the blocks, degree of polymerization ($N$), $\chi$ parameter between blocks and temperature of the system.\textsuperscript{32-33} Presence of incompatible blocks in the polymer results in different $\chi$ parameters for NPs and blocks. Therefore, uneven distribution of NPs will occur within copolymer matrices.\textsuperscript{34} One can form a nanocomposite with NPs only in specific domains of the block copolymer by tailoring the interactions between NPs and blocks.\textsuperscript{34} Therefore,
knowledge of the matrix polymer structure is important in understanding the distribution of NPs in polymers.

**Overview of the Study**

This work includes several approaches to incorporate NPs into polymers. The first section will introduce blending of NPs into polymers. The second section explores polymeric micelles as a vehicle to assemble NPs. The last section will introduce interfacial effects on the dispersion of NPs in thin films.

*a) Dispersion of NPs in Homopolymers Using Chaotic Blending*

This section focused on dispersion of sheet like montmorillonite clay NPs in a nylon 6 (Polyamide-6, PA6) homopolymer matrix using a chaotic advection blender.\(^{35-38}\)

![Chemical structure of nylon 6](image)

**Figure 1.2** Chemical structure of the a) \(\alpha\) and b) \(\gamma\) crystalline forms of nylon 6.
PA6 is a semi-crystalline polymer with two major crystalline forms as indicated in Figure 1.2. \(^{39-40}\) One of the crystalline forms is called the alpha (\(\alpha\)), which is thermodynamically stable and has hydrogen bonds in between fully extended anti-parallel polymer chains. \(^{39-40}\) The other crystalline form has hydrogen bonds in between parallel pleated chains and is known as the \(\gamma\) form, which is in a meta-stable state. In the \(\gamma\) form, the plane of the amide group is roughly perpendicular to the plane of the \((\text{CH}_2)_5\) group and in \(\alpha\) form those planes are parallel. \(^{39-40}\)

The NP used in this study is montmorillonite clay sheets (disks) modified with quaternary ammonium salt. \(^{41}\) Diameter of a NP is ca. 100nm and the thickness is ca. 1nm. These NPs are preferred to make sheet stacks due to the intermolecular hydrogen bonds occur in between grafted layers. \(^1\)

\[\text{Figure 1.3 Schematic representation of a) surface modified NP and b) NP stack}\]

In this study multilayered nanocomposite films consisting of PA6-rich and NP-rich layers were obtained from the blender and orientation and distribution of NPs were controlled by selecting the duration of chaotic advection on the melt, which is given by the process parameter \(N\). At first, the films made from the blender were studied to understand the effects of \(N\) and NP concentration on the crystalline morphology of PA6
and orientation of polymer chains and NPs with respect to the extrusion direction. According to our studies, PA6 chains were mainly associated in a meta-stable \( \gamma \) crystalline form. Therefore, samples were annealed at higher temperatures to drive the meta-stable state into stable crystalline phase and the corresponding structural changes were studied. PA6/silicates nanocomposites are mostly used as packaging materials because of their enhanced barrier resistant to water/humidity. In the third phase of the study, structural changes occurred in these films were studied after exposed to water.

b.) Diblock Copolymers Assemblies

Incompatibility, which is proportional to \( \chi N \),\textsuperscript{20} between blocks drives diblock copolymers into specific structures. Formation of such structures affects the distribution of NPs in the nanocomposites. In most studies enhanced segregation is obtained by increasing \( N \).\textsuperscript{42} In the current study, fluorine was introduced into one of the blocks to increase the \( \chi \) between the fluorinated and protonated blocks. The semi-fluorinated diblock copolymer used in this study is polytrifluoro propyl methylsiloxane-\( b \)-polystyrene (SiF-PS), which is shown in Figure 1.4.

Incorporation of fluorine into polymers enhances chemical and thermal stability of the materials and provides controlled surface energy, control dielectric constant and controlled reflective index.\textsuperscript{43-46} However, fluorine increases the rigidity of the polymer, which reduce conformational freedom of the chains, and affects the segregation. In order
to remove this effect, a siloxane group was introduced to the SiF block, which allows us to separate the effects of rigidity form those results from incompatibility between blocks.

Figure 1.4 The chemical structure of polytrifluoro propyl methylsiloxane-\textit{b}-polystyrene (SiF-PS) diblock copolymer.

In this study, self-assemblies of SiF-PS with different SiF volume fractions were studied in toluene. Toluene is a good solvent for the PS block and a poor solvent for the SiF. Therefore, in solution SiF-PS assemble into micelles with SiF block in the core and PS in the corona. Understanding the structure and properties of such nano structures will allow us to embed and disperse NPs in semi-fluorinated block copolymers.

In this part of the study we only followed the assembly of semi-fluorinated diblock copolymer in solution and did not proceed to incorporate NPs into polymer micelles due to limitation of materials and neutron beam time.
c.) Dispersion of NPs in Semi-Fluorinated Copolymer Thin Films

The concept of forming specific phase segregated microstructures in semi-fluorinated polymers was used to control the distribution of NPs in polymer thin films. The surface structure of a multicomponent system with different surface energies is not the same as its bulk structure. Lower surface energy components such as fluorinated segment segregate towards the air/polymer interface to minimize the interfacial energy while relatively high surface energy components associate away from that interface. Segregation of blocks with different surface energies and inherent ordering of the copolymer due to incompatibilities of the blocks results in multi layered structure in thin film as shown in Figure 1.5.

![Figure 1.5](null) Schematic representation of multi layered diblock copolymer thin film.

In this phase of the dissertation, dispersion of polyhedral oligomeric silsesquioxanes (POSS) NPs in a semi-fluorinated copolymer of biphenyl perfluorocyclobutyl (BPh-PFCB) was studied. Degree of polymerization of BPh-PFCB is ca. 20. POSS consists of an octahedral Si-O-Si cage modified with 8 grafted chains.
Incorporation of POSS into polymeric matrices enhances thermal and oxidative resistance, enhances mechanical properties and reduces dielectric constant of the materials.\textsuperscript{47-49} In order to control the dispersion, POSS cages modified with either protonated or fluorinated grafted chains were introduced to the polymer. In some POSS cages, one silicon corner was modified with a single matrix polymer chain to enhance the compatibility (lower the $\chi$) between NP and polymer. The chemical structures of the matrix polymer and different POSS cages used in this study are illustrated in Figure 1.6.

![Chemical structures](image)

**Figure 1.6** The chemical structures of **a)** random copolymer of Biphenyl Perfluorocyclobutyl (BPh-PFCB), **b)** POSS cages modified with R groups and **c)** POSS modified with BPh-PFCB (t-POSS).

These nanocomposites are famous for their superior hydrophobicity on the surface. The next part of the study focused to understand the correlation between solvent penetration and NP distribution in nanocomposite thin films, where distribution of water molecules was followed for nanocomposites with different NP distributions.
References


CHAPTER 2
Experimental Methods

Several experimental techniques were used in the study including X-ray scattering, small angle neutron scattering (SANS) and neutron reflectometry (NR). All these techniques are well established.\textsuperscript{5-6, 9-14} In this section the basic concepts of these techniques are outlined. Additional complimentary techniques such as Atomic Force Microscopy (AFM) were used as needed.

**X-ray and Neutron Scattering**

X-ray and neutron scattering techniques are widely used for investigating the structure of materials.\textsuperscript{1-4} Both techniques follow the same basic principles of scattering except the way the radiation interacts with matter, where X-rays interact with the electrons and neutrons are scattered by the nuclei.

When X-rays/neutrons hit the material, part of radiation is absorbed, another part is transmitted and the rest is scattered.\textsuperscript{5} When atoms are located in well defined lattice the diffraction is described by Bragg’s law given in equation 2.1, where $\lambda$ is the wavelength, $d$ is the distance between lattice planes and $n$ is the order of the diffraction.\textsuperscript{5} This relationship is obtained by calculating the path difference of the scattered beams from two lattice points as indicated in Figure 2.1.
Figure 2.1 Schematic representation of Bragg’s diffraction by lattice sites in two parallel layers. $\theta$ is the incident angle and $d$ is the distance between lattice planes.

\[ n\lambda = 2d \sin \theta \]  

The spatial relation of the diffraction lines and their relative intensities identify the arrangement of atoms in a lattice. In amorphous materials, pure liquids and solutions one measures $g_{\rho}(r)$, which is the correlation between densities of scattering centers, or $P(q)$ the scattering of a single scattering object/aggregate. The $g_{\rho}(r)$ calculates how the densities $\rho(u)$ and $\rho(u+r)$ separated by distance $r$ are correlated to each other as shown in equation 2.2. Besides in complex fluids one often studies objects such as micelles or collapsed polymers in solution.

\[ g_{\rho}(r) = \int \rho(u)\rho(u+r)du \]
Figure 2.2 Schematic representation of momentum transfer vector and energy transfer during scattering. $\vec{k}_i$ and $\vec{k}_s$ are momentum transfer vectors of incident and scattered waves and $E_i$ and $E_s$ are the energy of the incident and scattered beams.

\[ \vec{q} = \vec{k}_s - \vec{k}_i \]  
\[ E = E_s - E_i \]

Scattering from a single particle is schematically shown in Figure 2.2. In elastic scattering, where kinetic energy of the incident particle is preserved after scattering, momentum transfer ($\vec{q}$) is given by equation 2.3, where $\vec{k}_i$ and $\vec{k}_s$ are the momenta of the incident and scattered waves respectively. The magnitude of the $\vec{k}$ is given by $2\pi/\lambda$. The energy transfer ($E$) is also given as the difference between the energy of the scattered beam ($E_s$) and the energy of the incident beam ($E_i$) as shown in equation 2.4. In elastic scattering $E=0$ and inelastic scattering has $E\neq0$. The magnitude of the $\vec{q}$ in terms of incident angle ($\theta$) and $\lambda$ is obtained by solving equation 2.3 and it is given by:

\[ \vec{q} = \frac{4\pi \sin \theta}{\lambda} \]
As indicated above, $\vec{q}$ depends on both $\theta$ and $\lambda$. Therefore, in scattering experiment, $\vec{q}$ is obtained either by varying $\theta$ or $\lambda$. The relationship between $\vec{q}$ and $d$ is obtained by combining the equation 2.1 and 2.5.

\[
\vec{q} = \frac{n2\pi}{d}
\]  

(2.6)

Therefore, small angles provide information of larger structures and large angles provide information of small structures.

**Small Angle Neutron Scattering**

Neutrons are chargeless particles with mass of 1.0087 atomic mass units and spin of $\frac{1}{2}$. Neutrons scattered by nuclei in sample or from magnetic moment created by unpaired spins. Interaction of neutrons with matter is short range, which results in weak interactions with matter and therefore, high penetration ability. Neutrons are made in either spallation sources or reactors. Unlike x-rays, penetration of neutrons does not generate significant heat and cause less damage to the material that interacts with neutrons. Wavelength of neutron scattering is in the range of 0.1 Å – 30 Å depending on the source and temperature of the neutrons. Therefore, neutron scattering probes the dimensions range from atomic scale to macromolecular scale. Since the neutron interacts
with nuclei, isotopic labeling becomes a useful tool, where hydrocarbon chains label with deuterium interact very different in comparison with their protonated analogs.\textsuperscript{7-8}

Mathematical formulas will be provided later in the chapter.

In a basic scattering experiment incident beam is a plane wave and upon scattered by the object wave is expressed in terms of spherical wave as illustrated in Figure 2.3.\textsuperscript{6}

![Figure 2.3 Basic geometry of scattering.](image)

In scattering techniques, the flux of the scattered rays ($J$) is measured with respect to that of the incident rays ($J_0$) as a function of $q$. $J/J_0$ is the normalized intensity ($I(q)$), which is also given by the square of the amplitude ($A$) of the scattering wave as shown in equation 2.7.\textsuperscript{5-6} The relationship between the $A$ and the scattering length density distribution ($p(r)$) is given below, where $n_\alpha(r)$ is the density distribution of species $\alpha$ at position $r$ and $b_\alpha$ is the scattering length, which provides the efficiency of scattering by a particle, of species $\alpha$. 

20
In order to quantify the flux of the scattered beam, one has to calculate the amount of energy transmitted per second through a unit solid angle (Ω) as indicated in Figure 2.3.6

The ratio \( \frac{J}{J_0} \) is known as the differential scattering cross section \( (d\sigma/d\Omega) \), where \( \sigma \) is the cross section. \( d\sigma/d\Omega \) is defined as “the probability that a photon or neutron impinging on the sample is scattered into a unit solid angle in the given direction”.6 This ratio equals to the square of the scattering length as given in equation 2.8.6

\[
\frac{d\sigma}{d\Omega} = \frac{J}{J_0} = I(q) = b^2 \quad (2.8)
\]

Integrating the \( d\sigma/d\Omega \) over all the solid angles provides the total scattering cross section \( (\sigma_{tot}) \).6 These cross sections are obtained for scattering from a single particle. However in scattering measurement, scattering occur from ensemble of particles. Therefore, differential scattering cross section should include the contributions from all the nuclei in the sample as indicated in equation 2.9.6
N is the number of scattering particles. The first term corresponds to coherent scattering and the second term has the incoherent contribution to the differential scattering cross section. The coherent scattering is comprised of both inter and intra molecular scattering interferences as indicated in equation 2.10. \( v \) is the volume of the particle and \((\Delta b_v)^2\) is the scattering contrast, which is the difference of scattering length densities (SLD) \((b/v)\) between the scattering object and the medium (equation 2.11). \( P(q) \) is the form factor of the scattering object, which is the Fourier transform of the density of the scattering objects and the \( S(q) \) is the structure factor, which contains the information about the correlation among scattering objects.\(^5\)-\(^6\)

\[
\frac{d\sigma}{d\Omega} = b^2 \sum_{j,k} \exp(-iq(r_j - r_k)) + N\left(b^2 - \langle b \rangle^2\right)
\]  \hspace{1cm} (2.9)

\[
I(q) = \frac{d\sigma}{d\Omega} = Nv^2(\Delta b_v)^2 P(q)S(q)
\]  \hspace{1cm} (2.10)

\[
\Delta b_v = \left| \left( \frac{b_1}{v} \right) - \left( \frac{b_2}{v} \right) \right|
\]  \hspace{1cm} (2.11)

When the concentration of the particles is sufficiently low, particles are located far apart and there are no correlations among them. Therefore, scattering has contributions only from the form factor of the scattering objects. The relationship of scattering amplitude to the shape of the object is obtained by Fourier transforming the
amplitude in equation 2.7 with respect to the coordinates of the object.\textsuperscript{5-6, 9} For example, the Fourier transform of equation 2.7 using spherical coordinates gives the amplitude of a spherical scattering object as indicated in equation 2.12,\textsuperscript{6} where \( R \) is the radius of the sphere. One can get the \( I(q) \) by taking the square of the amplitude and it is related to the form factor as indicated in equation 2.13.\textsuperscript{6}

\[
A(q) = \rho v \frac{3(\sin qR - qR \cos qR)}{(qR)^3}
\]

\[
I(q) = \rho^2 v^2 \frac{9(\sin qR - qR \cos qR)^2}{(qR)^6} = \rho^2 v^2 F(q)
\]  

(2.12)

(2.13)

Scattering form factors for some common shapes are introduced in table 2.1.\textsuperscript{5-6, 10-11}

**Table 2.1** Examples of form factors of common shapes

<table>
<thead>
<tr>
<th>Shape</th>
<th>Form factor ((F(q)))</th>
</tr>
</thead>
</table>
| Gaussian polymer chain | \[
P(q) = \frac{2}{\lambda^2} [x - 1 + \exp(-x)] \\
x = qR_g^2
\]                                                                |
| Thin rod               | \[
\frac{2}{qL} \int_0^\infty \frac{\sin x}{x} dx - \frac{\sin^2 (qL/2)}{(qL/2)^2}
\]                                                                 |
| Thin flat disk         | \[
P(q) = \frac{2}{q^2 R^2} \left[ 1 - \frac{1}{qR} J_1(2qR) \right]
\]                                                                 |

\( R_g \) is the radius of gyration of the scattering object, \( L \) is the length of the rod, \( R \) is the radius of the disk and \( J_1 \) is the first order Bessel function.
For any internal correlation $I(q)$ is given by,

$$I(q) = \int g_x(r) \exp(-iqr)dr$$

(2.14)

Several approximations had been derived to obtain initial analysis of scattering data for an unknown form factor. One of the important approximations used in this study is the Guinier approximation, which estimates the overall radius of gyration ($R_g$) of the scattering object with an unknown form factor. The Guinier approximation is valid when $qR_g < 1.5 - 6, 9$

$$I(q) \approx I(0) \exp \left( -\frac{q^2 R_g^2}{3} \right)$$

(2.15)

Where $I(0)$ term in equation 2.15 is the intensity at $q=0$.

Dimensions of the scattering object are retrieved from the $R_g$ for different shapes as indicated in table 2.2. 10-11
Table 2.2 Examples of radius of gyration \((R_g)\) of different shapes

<table>
<thead>
<tr>
<th>Shape</th>
<th>(R_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere of radius (R)</td>
<td>(R_g^2 = \frac{3}{5} R^2)</td>
</tr>
<tr>
<td>Cylinder (Rod or Disk) of diameter (D) and</td>
<td>(R_g^2 = \frac{L^2}{12} + \frac{d^2}{8})</td>
</tr>
<tr>
<td>length (L)</td>
<td></td>
</tr>
<tr>
<td>Ellipsoid of semi axes (a), (b) and (c)</td>
<td>(R_g^2 = \frac{1}{5}(a^2 + b^2 + c^2))</td>
</tr>
</tbody>
</table>

The slope of the data at high \(q\) in \(I(q)\) vs \(q\) plot provides information about the fractal dimension \((D)\) of the scattering object. At higher \(q\) the \(I(q)\) is proportional to \(q^{-D}\). Some fractal dimensions for specific surface fractals are given in table 2.3. \(^5\)

Table 2.3 Fractal dimensions of specific shapes

<table>
<thead>
<tr>
<th>Shape</th>
<th>Fractal dimension ((D))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid rod/cylinder</td>
<td>1</td>
</tr>
<tr>
<td>Polymer chains with excluded volume</td>
<td>3/5</td>
</tr>
<tr>
<td>Two dimensional object with smooth surface</td>
<td>2</td>
</tr>
<tr>
<td>(lamelle, disk)</td>
<td></td>
</tr>
<tr>
<td>Three dimensional object with smooth surface</td>
<td>4</td>
</tr>
<tr>
<td>(sphere, lamella phase)</td>
<td></td>
</tr>
</tbody>
</table>


**Specular Neutron Reflectometry**

Reflectivity techniques are used to obtain information on the surfaces and interfaces of materials.\textsuperscript{12-14} This information includes the surface structure, interfacial roughness and distribution of components along and normal to the surfaces of the material. The scattering geometry of reflectivity is given in Figure 2.4, where $\theta_0$, $\theta$, $\theta_1$ are the incident, reflected and refracted angles respectively. The $k_0$, $k$ and $k_1$ are the wave vectors of incident, reflected and refracted beams. When incident and reflected beams are in the same plane (YZ) and $\theta_0 = \theta$, the reflectivity technique known as the specular reflectivity. In specular reflectivity, the wave vector $q_z$, which is given by $k-k_0$, is observed perpendicular to the sample surface as indicated in Figure 2.4.\textsuperscript{6} The relationship of $q_z$ to wave vectors, wavelength ($\lambda$) and $\theta_0$ is given in equation 2.16,\textsuperscript{6} which contains information along the z direction. In neutron reflectivity (NR) depth resolution is about 1-10 Å and neutrons penetrate hundreds of nanometer through the samples without harming the material.\textsuperscript{15} The scattering occur on the XY plane is known as the off-specular scattering. In the current study we use only the specular neutron reflectivity and more details of this technique will be discussed herein. Theory of this technique was discussed in several references.\textsuperscript{5-6, 15}
Regardless of the type of radiation, scattering from surface can be explained from principles of optics. The reflective index ($n$) of a material is given by \(^6\);

\[
n = 1 - \delta + i\beta
\]

(2.17)

\[
\delta = \frac{2\rho}{2\pi}
\]

\[
\beta = \frac{2\rho_{abs}}{4\pi}
\]
The \( \delta \) gives the information about the transmission and reflections, where \( \rho \) is the scattering length density (SLD) of the material and \( \lambda \) is the wavelength. The imaginary part arises from the absorption of neutrons by material, where \( \rho_{\text{abs}} \) is the absorption cross-section of the material. For non magnetic materials, \( \rho_{\text{abs}} \) is negligible for most of the elements compare to \( \rho \). In vacuum \( n \) is equals to 1 and in most of the materials it is less than 1.

Snell’s law describes the relationship of the incident and refracted angles to the refractive indices of the medium 0 and 1 as follows.\(^6\)

\[
n_0 \cos \theta_0 = n_1 \cos \theta_1 \quad (2.18)
\]

When the incident angle is smaller than the critical angle (\( \theta_c \)), the incoming waves are totally reflected. The value of the critical angle \( \theta_c \) depends on the ratio of \( n_1/n_0 \).

\[
\cos \theta_c = \frac{n_1}{n_0} \quad (2.19)
\]

The \( z \) component of the refracted wave vector is given in equation 2.20, which is derived from 2.18 and 2.19 equations. The wave vector \( k_{z1} \) equals to \((2m_i/\lambda)\sin \theta \cdot k_{z0} \) and \( k_{z1} \) are the \( z \) components of the incident and refracted waves and \( k_{z0} \) is the \( k_{z0} \) at \( \theta_0=\theta_c \).\(^6\)

\[
k_{z1} = (k_{z0}^2 - k_{zc}^2)^{1/2} \quad (2.20)
\]
At a smooth interface, the wave amplitude is continuous varies from medium 0 and 1. Therefore, the amplitude of the reflected beam \( r_{0,1} \) is obtained by matching the amplitudes of the beams in both sides of the 0-1 interface, which results in

\[
r_{0,1} = \frac{k_{z0} - k_{z1}}{k_{z0} + k_{z1}}
\]  

(2.21)

By taking the absolute square of the amplitude \( r \) one can get the reflectivity as follows, which is known as the Fresnel’s law.\(^6\)

\[
R = \left| \frac{k_{z0} - k_{z1}}{k_{z0} + k_{z1}} \right|^2
\]  

(2.22)

Equation 2.22 can be further expanded by combining equation 2.20 as follows. When \( \theta_0 \gg \theta_c \), tail of the reflectivity curve falls as \( q^{-d} \).

\[
R = \left| \frac{k_{z0} - \sqrt{k_{z0}^2 - k_{zc}^2}}{k_{z0} + \sqrt{k_{z0}^2 - k_{zc}^2}} \right|^2 = \left| \frac{1 - [1 - (k_{zc} / k_{z0})^2]^{1/2}}{1 + [1 - (k_{zc} / k_{z0})^2]^{1/2}} \right|^2
\]  

(2.23)

Up to now the reflectivity from an interface between two media was considered. When the material is coated on to a substrate, infinite numbers of reflections are possible within the medium 1 due to reflections that occur from the interfaces as shown in Figure

29
2.5. The sum of the amplitudes of the all the beams comes from the medium 1 to medium 0 provides the total amplitude, which is given by equation 2.24.

\[ r = \frac{r_{01} + r_{12} \exp(-i2\phi)}{1 + r_{01}r_{12} \exp(-i2\phi)} \]  \hspace{1cm} (2.24)

\( r_{01} \) and \( r_{12} \) are the amplitudes of the reflected beams from the 0-1 and 1-2 interfaces respectively. \( \phi \) is the phase shift owing to the differences in path lengths of reflected beams, which is given by

\[ \phi = \frac{2\pi}{\lambda} n_i \sin \theta_i t = k_{z1}t \]  \hspace{1cm} (2.25)

where \( t \) is the thickness of the layer and \( k_{z1} \) is the z component of the wave vector of the reflected beam from 0-1 interface. By taking the absolute square of 2.24 gives the reflectivity (\( R \)) for the system showed in Figure 2.5. This method can be extended to a system with any number of layers to calculate the contribution to the total reflection from the reflections occur from individual layers.

\[ R = \left| \frac{r_{01} + r_{12} \exp(-i2\phi)}{1 + r_{01}r_{12} \exp(-i2\phi)} \right|^2 \]  \hspace{1cm} (2.26)
Another definition of the intensity is the absolute square of the Fourier transform \((F)\) of the SLD distribution \((\rho)\) in the system. Therefore, \(R\) can express in terms of SLD distribution normal to the sample surface as follows.

\[
R = \frac{16\pi^2}{q^4} \left| F \left\{ \frac{d\rho(z)}{dz} \right\} \right|^2
\]  

(2.27)

Interfaces of the materials are not fully smooth as assumed in the Fresnel reflectivity. In the presence of rough interface, reflectivity curve decays more rapidly than \(q^4\). Therefore, effects of the diffuse interface have to be taken into account. The diffuseness is introduced as a smearing function \((g(z))\), which characterizes the nature of the interface. Equation 2.28 gives the \(g(z)\) by assuming the diffuse interface is described by a Gaussian function. The \(\sigma\) represents the roughness of the interface.

\[
g(z) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{z^2}{2\sigma^2}\right)
\]  

(2.28)
Therefore, SLD distribution $\rho(z)$ for diffuse interface is given by

$$\rho(z) = \rho H(-z) g(z)$$  \hspace{1cm} (2.29)

where $H$ is the Heaviside unit step function, which is 1 for $z>0$ and zero elsewhere. Then, $\rho(z)$ is substituted into equation 2.27 to incorporate the roughness of the interfaces to the reflectivity.

Figure 2.6 shows a neutron reflectivity pattern of a polymer film of 500Å coated on a silicon substrate. The reflectivity is given as the ratio of $I/I_0$ and equals to one below the critical angle. The $q$ corresponds to $\theta_c$. $q_c$ relates to the SLD at the surface layer of the film as indicate in equation 2.30. SLD obtained from this relationship provides an insight to the chemical composition of the surface layer.

$$q_c = 4\sqrt{SLD \times \pi}$$  \hspace{1cm} (2.30)
Figure 2.6 Theoretical neutron reflectivity profile for a polymer film with 500Å thickness on a silicon substrate.

Fringes, which are also known as Kiessig fringes, observed at higher \( q \) values \((q > q_c)\) are due to the constructive and destructive interferences occur from waves reflected from interfaces with different SLDs. The distance between two consecutive minima \((\Delta q)\) provides the estimated total film thickness \((t)\) as follows.\(^6\)

\[
t = \frac{2\pi}{\Delta q}
\]  

(2.31)

Analysis of the reflectometry data is done by fitting a model reflectivity to the experimental one. The model can be an outcome of a theoretical prediction for given system or an optical approach where the sample is viewed as successive layers of different scattering length densities. In both approaches the model curves incorporates the ideal Fresnel reflectivity and accommodates roughness.
References


11. Hammouda, B. *Probing Nanoscale Structures- The SANS Toolbox*, 2008, National Institute of Standards and Technology, Gaithersburg, MD.


CHAPTER 3

Structure Studies of Hierarchical Multilayered Nanocomposites Formed by Chaotic Advection: Competition of Shear and Interfacial Effects

Abstract

The effects of chaotic advection on a hierarchal nanocomposite of Nylon 6 (PA6), a polyamide with disk shape nanoparticles (NPs), were studied at different concentration of NPs. These hierarchal nanocomposites consist of alternating pure PA6 and PA6/NP layers. They were formed by a novel blending process, where melts of pristine PA6 and PA6 with embedded NPs were segregated into discrete layers by chaotic advection and extruded into film form in a continuous process. Previous studies have shown that on the micron length scale, the NPs are localized within multiple layers of pristine polymer and layers of dispersed NPs. Here we investigate the effects of processing parameter N, on the polymer structure and the distribution of the NPs on the nano-meter length scale. Our X-ray studies show that blending results in increased γ crystalline phase and decreased α crystalline form. The effects of the processing varied with the concentration of the NPs. For nanocomposites with lower NP concentrations the amount of the γ crystalline form increased with N. However, at higher NP concentrations interfacial effects of NP play a significant role in determining the structure. The NPs oriented along the melt flow direction and the polymer chains oriented perpendicular to the NP surfaces.
Introduction

Structured layers of polymers that contain different types of nano-particles (NPs) offer a means to tailor multifunctional materials. Properties and response can be controlled on multiple levels. NPs play an important role in modifying the properties of polymers.\textsuperscript{1-2} Incorporation of small amounts of NPs significantly changes physical characteristics of polymers.\textsuperscript{3-4} For example, a fivefold increase in tensile strength was observed when mica NPs were added to PA6.\textsuperscript{5} NPs affects optical properties such as enhancing optical transparency\textsuperscript{6} and nonlinearity of the optical response.\textsuperscript{7} Additional effects such as controlled permeability,\textsuperscript{8} higher thermal stability\textsuperscript{9} and controlled electrical conductivity\textsuperscript{10} were also observed. The dispersion and orientation of the NPs affect the actual properties.\textsuperscript{11} While dispersion and orientation of NPs and polymer chains potentially enhance variety of physical properties of nanocomposites, dispersion of NPs in a polymeric matrix remains a challenge due to the tendency of NPs to aggregate coupled with general blending challenges of polymers.\textsuperscript{12-13}

Current and potential technological benefits of polymer nanocomposite lead to numerous efforts including blending techniques\textsuperscript{14-16} and chemical modifications of the NPs and matrix polymers to enhance compatibility.\textsuperscript{2,17} The interaction energies between NPs and polymers, the sizes of NPs and their relative dimensions with respect to the polymer rigid segment as well as the shape of the NP affect the dispersion of the particles and the properties of the nano composite.\textsuperscript{18-21} Producing a structured multilayer composite with different types of NPs poses additional challenges of tailoring effectively
the interface between the layers, forming a mechanically stable interface and confining the NPs to specific layers.

Zumbrunnen and co-workers have recently demonstrated \(^{22-26}\) that polymer multi-layers can be formed using a blending technique often referred to as “smart blending”, where chaotic advection is introduced into the melts of two polymers, resulting in localization of the polymers into layers. In a subsequent study \(^{27}\) we have shown that using Smart Blending, where one of the melts contains NPs, a hierarchal nanocomposites that consist of alternating layers of a polymer and polymer-NP can be made. An example of the morphology of a blended PA6/montmorillonite nanocomposite, as observed by TEM is shown in Figure 3.1.\(^{27}\) The thicknesses of the NP-containing layers and the intervening pristine polymer layers as well as the extent of NP orientation are affected through specification of the duration of chaotic advection.\(^{27}\) In this process, initially thick layers become thinner layers by recursive stretching and folding that characterizes chaotic advection.\(^{22-27}\) The thicknesses of these layers depends on the relative amounts of polymer containing NPs and the pristine polymer melt in the mix and the processing conditions. The chaotic advection takes place in a continuous flow to allow continuous extrusion of the films.

The macroscopic properties of such a hierarchal composite depend on the micron length scale structure couples with that of periodicities arising from the polymer structure and the dispersion of the NPs. The current study explores the effects of chaotic advection on the structure of the nanocomposite on a 0.1-2.5nm length scale, where the packing of the polymer molecules is detected. PA6/ montmorillonite NPs, a well-studied
nanocomposite, is used as a model system. PA6 is a semi-crystalline polymer that has two major crystalline forms: $\alpha$ and $\gamma$. The $\alpha$ form consists of hydrogen bonds in between the fully extended anti parallel PA6 chains and the $\gamma$ form has hydrogen bonds in between parallel pleated chains.\textsuperscript{28-30} In the $\gamma$ form, the plane of the amide group is roughly perpendicular to the plane of (CH$_2$)$_5$ group where in the $\alpha$ form those planes are parallel. The $\alpha$ form has a monoclinic unit cell and the $\gamma$ form closely resembles a hexagonal structure.\textsuperscript{31} The $\alpha$ form is thermodynamically stable and the $\gamma$ form is meta-stable. Previous studies have shown that adding NPs to PA6 enhance the formation of $\gamma$ form regardless of the blending technique.\textsuperscript{2, 32} Other factors that affect type of crystalline phase formed include cooling rates,\textsuperscript{33} where enhancement of the $\gamma$ crystalline form was observed when quenching by liquid N$_2$.\textsuperscript{34}

**Figure 3.1** TEM image of a 2 vol % PA6/montmorillonite nanocomposite formed by chaotic advection at N=16 and extruded as 150 micron thick films. Dark regions correspond to the NP rich areas and light regions correspond to the matrix polymer.\textsuperscript{27}
The current study investigated for the first time the effects of chaotic advection on the structure of hierarchal nanocomposites following the structure of the polymer. The X-ray patterns measured are averaged over both pure polymer and the polymer nanocomposite. The results are compared with those of the extruded pure polymer under similar conditions. The study has shown that chaotic advection changes the ratio between the crystalline forms of the polymer depending on the concentration of the NPs, where at higher concentrations of NPs, surface effects become significant.

**Experimental Section**

Master batches, a mixture of the polymer with NPs, of different NP percentages were prepared from PA6 (Capron B135QP, BASF Corporation, Mount Olive, New Jersey) and NP (Closite 30B, Southern Clay Products, Gonzales, Texas) using a twin-screw extruder. Corresponding glass transition ($T_g$) and melting temperatures ($T_m$) of the master batches were measured using differential scanning calorimeter (DSC) and the corresponding values are given in table 3.1. DSC measurements were performed on a Mettler Toledo 910e at flow rates of 10°C/minute. Samples were sealed in aluminum pans to avoid contact with air during the measurements. Nanocomposite films with NP volume fractions (vol %) of 2.0%, 2.8%, 3.5%, and 5.6% were obtained by introducing the matrix PA6 polymer and master batches in equal proportions to the smart blender to obtain extruded films of about 150 micron thickness. Films were produced with differing
extents of chaotic advection controlled through specification of N; a parameter that specifies the motion of rods that blend the polymers.\textsuperscript{22} A list of samples measured and their volume fractions are given in table 3.2.

An X-ray powder Sintag diffractometer with Cu K\textsubscript{\alpha} radiation, with wavelength of $\lambda = 1.54\text{Å}$ was used to obtain powder X-ray patterns. All the samples were cut to a 1cm$^2$ films. The scattering intensities were normalized to a unit thickness. Further studies were carried out on a Rigaku single crystal instrument with Mo K\textsubscript{\alpha} radiation $\lambda = 0.71$ Å, equipped with a two-dimensional detector. The patterns were recorded along three different directions with respect to extrusion direction as shown in Figure 3.2. Degrees of crystallinity and $\alpha/\gamma$ ratios were calculated from X-ray data with PeakFit 4.2 program from Seasolve software inc., which de-convolutes overlapped peaks and integrates the peak areas. Two-dimensional X-ray images were analyzed using Fit 2D program\textsuperscript{36} to obtain radial distributions and intensity profiles along different directions.

![Figure 3.2](image)

**Figure 3.2** Directions of incident X-ray beams with respect to the extrusion direction.
Table 3.1 Glass transition ($T_g$) and melting temperatures ($T_m$) of master batches with different NP volume fractions (vol %).

<table>
<thead>
<tr>
<th>vol %</th>
<th>$T_g$(°C) (±0.2)</th>
<th>$T_m$(°C) (±0.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45.2</td>
<td>220.1</td>
</tr>
<tr>
<td>5</td>
<td>43.4</td>
<td>218.8</td>
</tr>
<tr>
<td>10</td>
<td>46.8</td>
<td>220.7</td>
</tr>
</tbody>
</table>

Table 3.2 Films studied.

<table>
<thead>
<tr>
<th>N, (vol % = 0.0)</th>
<th>N, (vol % = 2.0)</th>
<th>N, (vol % = 2.8)</th>
<th>N, (vol % = 3.5)</th>
<th>N, (vol % = 5.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6</td>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>12</td>
<td>10</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>14</td>
<td>12</td>
<td>12</td>
<td>10</td>
<td>9</td>
</tr>
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<td>20</td>
<td>20</td>
<td>12</td>
<td>20</td>
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</tr>
<tr>
<td>30</td>
<td>25</td>
<td>16</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22</td>
</tr>
</tbody>
</table>

Results and Discussion

X-ray patterns of a granular PA6 of the master batch and a film which was chaotically extruded are shown in Figure 3.3. The pattern of the pristine polymer (Figure 3.3-a) consists of two broad peaks superimposed by a smaller peak in the center. Based on the literature, the peaks at 4.39 Å and 3.75 Å correspond to the α crystalline form and the center at 4.16 Å corresponds to the γ crystalline form. The α form dominates the crystalline structure of granular PA6 and exhibit two diffraction lines: 4.39 Å refers to as
\( \alpha 1 \) and originates from \((200)\) diffraction plane and \(3.75 \text{ Å (\( \alpha 2 \))}\) from that corresponds to the \((002)\) plane.\(^{37-38}\) The peak of the \(\gamma\) form corresponds to the \((001)\) diffraction plane. These diffraction lines correspond to the chain-chain correlations in crystalline domains. These values for the positions of the \(\alpha\) and \(\gamma\) peaks were used to determine peak assignments. The patterns were deconvoluted assuming a Gaussian line shape,\(^{33}\) to resolve the relative amounts of \(\alpha\) and \(\gamma\) as well as to determine the ratios of crystalline to amorphous fractions. The results are shown as solid lines in Figure 3.3.

The X-ray pattern of the chaotically blended PA6, shown in Figure 3.3-b, consists predominantly of a peak that corresponds to the \(\gamma\) form, accompanied by two less intense \(\alpha\) peaks. The ratios of \(\alpha\) to \(\gamma\) changes from 27.4 to 0.8 and crystalline/amorphous change from 0.7 to 0.6 upon extruding the PA6 granules to make films at N=30.

All the chaotically blended samples, with and without NPs have shown predominantly the \(\gamma\) crystalline form of the PA6. We attribute the formation of the meta-stable form to shear effects that affected the alignment of the polymer chains.\(^{15}\) Extruded films of the chaotic blender consist of alternate layers with NP rich and NP free PA6 domains as indicated in TEM image in Figure 3.1. Therefore, X-ray data consist of average of scattering contributions from both pure polymer and the nanocomposite. These layers are sufficiently thick to neglect interfacial effects arising from the PA6 – PA6/NP boundaries. The differences between extruded PA6 and the layered nanocomposite are attributed to effects of the NPs.
Figure 3.3 X-ray patterns and analysis of PA6 films a) pristine and b) chaotically blended at N=30.

When NPs are embedded in the polymer, the crystallinity of the γ form is enhanced as observed in Figure 3.4 where the X-ray patterns for extruded PA6 with and without NPs at N=0, are shown. The peak in the pure PA6 is significantly broader than that of the films with NPs. The X-ray line width is inversely proportional to the size of the coherently scattering domains and ordering in the system. The peak widths at full width at half maxima δ (FWHM) are given in table 3.3. Increasing NP concentration from 0 to 5.6 vol% decrease the line widths from 0.29 Å⁻¹ to 0.07 Å⁻¹ at N=0. These values correspond to π/δ, the size of the coherently scattering domains, of ~20 Å to ~90Å. With increasing NP concentrations the interfacial area between the NPs and the polymers increases, enhancing the correlation between the chains. In contrast to the significant effects of N shown on the micron length scale, N which was varied from 0 to 30 hardly affected the domain sizes over which the polymer chains scatter coherently.
The fractions of the $\alpha$ and $\gamma$ crystalline are presented in Figure 3.5 as the ratio of the two crystalline forms ($\alpha/\gamma$) as a function of N for different NP concentrations. At low NP concentrations, 2.0 and 2.8 vol %, $\alpha/\gamma$ ratio decrease with N, where at higher concentrations this ratio remains constant. In low particles concentrations, blending at higher N values results in enhancing the $\gamma$ crystalline form. This trend at low NP concentration is similar to that observed in pure PA6 films where $\alpha/\gamma$ ratio decreases from 1.8 to 0.8 as N goes from 0 to 30. Enhancing the NP concentration increases the surface area between the polymer and the NP. A large surface area results in increase cohesiveness of the polymer and NP affecting the polymer orientation.
Table 3.3 X-ray peak widths for nanocomposite films as a function of N and NP concentrations.

<table>
<thead>
<tr>
<th>NP vol %</th>
<th>N</th>
<th>FWHM (δ) (Å⁻¹) (±0.001)</th>
<th>NP vol %</th>
<th>N</th>
<th>FWHM (δ) (Å⁻¹) (±0.001)</th>
<th>NP vol %</th>
<th>N</th>
<th>FWHM (δ) (Å⁻¹) (±0.001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0</td>
<td>0.29</td>
<td>2.0</td>
<td>12</td>
<td>0.07</td>
<td>5.6</td>
<td>7</td>
<td>0.06</td>
</tr>
<tr>
<td>4.0</td>
<td>0</td>
<td>0.14</td>
<td>2.0</td>
<td>14</td>
<td>0.06</td>
<td>5.6</td>
<td>9</td>
<td>0.09</td>
</tr>
<tr>
<td>5.6</td>
<td>0</td>
<td>0.07</td>
<td>2.0</td>
<td>20</td>
<td>0.07</td>
<td>5.6</td>
<td>20</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

While increasing the NP content affects the melting temperature the polymer and the overall viscosity of the mixtures, the blending temperatures are sufficiently above $T_m$ that the chaotic flows at the NPs are rather similar for all samples. While chaotic advection dominates at low NP concentrations and surface interactions control the system at higher NP concentrations.

Figure 3.5 $\alpha/\gamma$ crystalline ratios variation with N for samples at the indicated NP compositions. The solid lines are drawn as a guide line to the eye.

The overall degree of crystallinity is affected by the N and the concentration of the NPs. Total crystalline fraction present in the nanocomposite blends as extracted from
the peak deconvolution is shown in Figure 3.6. This fraction has contributions from both $\alpha$ and $\gamma$ crystalline forms. Nanocomposites with 2 vol % and 2.8 vol % NPs have comparably low crystallinity compared to higher NP concentrations. Increasing particle concentration increases the crystallinity. This is attributed to enhanced fraction of confined polymer chains within NPs, which facilitates the formation of more crystalline domains. However no significant effects are observed as a function of N.

![Figure 3.6 Total crystalline/amorphous ratio variation with respect to N for samples at the indicated NP compositions. Lines are drawn as a guide to the eye.](image)

Additional experiments were carried out using a two-dimensional detector to follow effects of N and the NP concentrations on the orientation of the components. The X-ray patterns were measured in three directions with respect to the film plane and the direction of extrusion. The patterns corresponding to PA6 at N=0 and N=30 are shown in Figure 3.7. The intensity of the lines is affected by the amount of material in the X-ray beam. The first intense diffraction line from the center corresponds to the $\gamma$ (001) diffraction of PA6, which is observed in all three directions. Two less intense arcs are observed corresponding to $\gamma$ (001) diffraction in edge and end patterns along the equator.
Figure 3.7 a) Two-dimensional X-ray pattern of PA6 films at N=0 and N=30 from edge, through and end directions. The white regions in the middle of the images correspond to the shadow of the beam stopper. b) The intensity along the \( \gamma \) crystalline ring marked in \( \gamma \) for the different directions. c) The cross sections of the N=30 along the X and Y directions.
In PA6 extruded different ways, no orientation is observed, and the intensity of this line is increased with N. We attribute the alignment observed to the effects of the chaotic advection, where the chains lie in the direction of the flow and the (001) plane lies perpendicular to the long axis of the polymer chain. The intensity of the \( \gamma \) (001) diffraction was integrated along the diffraction ring to obtain the radial distribution of the \( \gamma \) form. The results are shown in Figure 3.7b, where we observed the two peaks correspond to the intense arcs in the equatorial direction. The cross sections of N=30 patterns in the X and Y directions further confirms the slight intensity different of \( \gamma \) (001) along equatorial and meridial directions as indicated in Figure 3.7c. For pure PA6 there is no specific orientation as observed in injected molded samples.39 Therefore, orientation of \( \gamma \) form observed in pure PA6 is due to the alignment of polymer chains in chaotic flow fields.

When NPs are added the packing and orientation of the polymer chains become significantly more defined. The 2-D patterns for 5.6 vol % NP nanocomposites are presented in Figure 3.8a. The most center diffraction, at \( \sim 18\text{Å} \), corresponds to the inter-platelet distance between NPs. This diffraction spot is clearly observed in the edge and end views and not in the through direction. As indicated in Figure 3.8c, the diffraction of intercalated NPs occurs only along the equator for edge and end directions and not from the meridial direction. Therefore the long axis of the particles orient along the extrusion direction as was previously shown by TEM. N hardly affects the platelets orientation. These results are consistent with previously reported studies PA6/NP nanocomposites that were prepared by injection molding.2
Figure 3.8 a) Two dimensional X-ray patterns of PA6 with 5.6 vol % NP nanocomposite films at N=0 and N=20 from edge, through and end directions. b) The intensity along the $\gamma$ crystalline ring marked in $\gamma$ for the different directions. c) The cross sections of the N=0 along X and Y directions.
In the *through* direction the $\gamma$ form diffraction line of PA6 is isotropic. However, in the *edge* and *end* directions, a six-fold symmetry in (001) is observed. As shown in Figure 3.8c, the intensities of the arcs along the equator are higher than the ones closer to the meridian. The radial distributions of $\gamma$ form of PA6 for 5.6 vol % NP at N=0 and N=20 presented in Figure 3.8b, show the six-fold symmetry and relative intensities of arcs. The data are consistent with both hexagonal and monoclinic structures. The monoclinic unit cell of $\gamma$ form was observed when PA6 is treated with iodine to induce the $\gamma$ crystalline form. The melt spun PA6 have pseudo-hexagonal symmetry whereas injection molded PA6 nanocomposites exhibit a six-fold symmetry due to the presence of pseudo-orthorhombic lattice. In the current study we have observed limited number of diffractions, which do not allow us to distinguish crystalline packing that corresponds to the six-fold symmetry.

The $\gamma$ (001) diffraction is in a plane perpendicular to the polymer chain axis. Since orientation of PA6 can only be observed in the *edge* and *end* configurations, polymer chain axis lies on average perpendicular to *edge* and *end* scanning directions. Therefore, these polymer chains are oriented perpendicular to the flow direction as well as to the surface of NPs as shown in Figure 3.9. Generally, polymer chains arrange parallel to the surfaces of the internal layers containing them. Such layers were themselves formed by shear acting predominantly in the smart blender in the direction perpendicular to the extrusion direction. This effect is consistent with studies by Kumar and co-workers that observed interpenetration of the polymer matrix into the grafted layer on the NP.
Figure 3.9 A schematic representation of the relative orientations of NPs and PA6 chains in nanocomposites.

The (020) diffraction is observed at 8.14Å along the meridian of the edge and end patterns, which further confirms the perpendicular orientation of polymer chains with respect to NP surface. The diffraction spot for the (020) plane is observed in samples with lower N values. With increasing N, the (020) diffraction is no longer visible.

Conclusions

The structure of a hierarchical PA6/montmorillonite NP composite was investigated at different NP concentrations as the extent of the chaotic advection were varied. The ratio of the α/γ crystalline forms was affected by both parameters. Competition between effects of chaotic strength and interfacial effects of the NPs were observed. At low loading of NPs, the α crystalline form transform into the γ, where at
higher loadings no changes were observed. In nanocomposites, polymer chains align perpendicular to interface of the NPs. This study has observed the effects of competition between interfacial interactions and advection flow dominates the resulting structure within the nanocomposite NP rich layer.

References

4. Weon, J. I.; Sue, H. J. Polymer 2005, 46, 6325-6334. (Mec)


CHAPTER 4

Effects of Annealing and Stretching on the Structure of Chaotically Blended Nylon-6/Clay Nanocomposites

Abstract

Polyamide 6 (PA6)/clay nanocomposites were made using a blender with chaotic flow where the duration of chaotic advection on the melt, which is given by the processing parameter of the blender N, and NP concentration were found to be affected on the overall crystalline morphology. In as-prepared films the meta-stable γ crystalline form, which has hydrogen bonds between parallel chains, dominates over the stable α form, which has hydrogen bonds in between anti-parallel chains. PA6 chains orient perpendicular to the surface of the NP as well as to the extrusion direction. In the current study the crystalline morphologies of nanocomposites with different Ns were studied upon annealing and stretching, using one and two dimensional X-ray diffraction techniques. Annealing and stretching of chaotically blended films changed the major crystalline form into α form. The α/γ and crystalline/amorphous ratios were increased significantly with degree of stretching. Both annealing and stretching caused the long axis of the polymer chains to align parallel to the NP surface.
**Introduction**

Polyamide 6 (PA6)/montmorillonite clay nanocomposites have been widely studied because of their enhanced properties such as improved mechanical\(^1\)\(^-\)\(^4\) and barrier properties\(^5\) compared to the virgin polymer. These superior properties of nanocomposites are determined by the way the nanoparticles (NPs) interact with polymer and how they dispersed within the matrix. However, the dispersion of NPs in polymers is challenging due to the aggregation tendency of NPs and phase separation owing to the incompatibilities between polymer and NPs. Melt blending techniques are widely used to overcome these challenges and to achieve better dispersion of NPs in polymers, where the final structure has been significant affected by the thermal history as well as the stretching and folding mechanism of the blender.\(^7\)\(^,\)\(^8\)

PA6 is a semi-crystalline polymer consists with two major crystalline forms, which are the \(\alpha\) and the \(\gamma\). The \(\alpha\) form is thermodynamically more stable than the other, where polymer chains are arranged in extended anti-parallel fashion.\(^16\)\(^-\)\(^18\) The \(\gamma\) form, which is in meta-stable state, comprised of twisted parallel chains.\(^19\) Few hydrogen bonding sheets were formed in the \(\gamma\) phase compared to the \(\alpha\). The \(\alpha\) form is dominated in pure PA6. Upon addition of NPs, the major crystalline form changed into \(\gamma\).\(^16\) These different molecular arrangements results in different thermal and mechanical properties. For example, the \(\alpha\) phase has higher elastic modulus below the glass transition temperature \((T_g)\) of the polymer compared to the \(\gamma\) form. However, above the \(T_g\), \(\alpha\) crystallites show rapid decrease in modulus.\(^20\) Therefore, one can alter the heat distortion
temperature of the materials by changing crystallinity from \( \alpha \) to \( \gamma \) by adding NPs to the matrix polymer. In addition to the elastic modulus, other physical properties such as hardness and conductivity also alter around \( T_g \) and can be tuned by controlling the \( \alpha \) and \( \gamma \) crystalline fractions.

In this paper, we will discuss the PA6/montmorillonite NP nanocomposites made from melt blending technique coupled with chaotic flow.\(^9\)\(^{,}\)\(^10\) A specific rod rotation sequence was utilized within the processing equipment known as “smart blender (continuous chaotic blender – CCB)” to generate chaotic flow.\(^11\)-\(^13\) These rod rotations cause the material around each rod to move in separate speeds and cause stretching, folding and reorienting of melt domains. Eventually, it makes a multilayer structure of two polymer melts introduced to the blender.\(^13\),\(^14\) On micron length scale NPs were localized within multiple layers, where the layer thicknesses, orientation of NPs and their distribution were controlled by selecting the duration of chaotic advection given by the process parameter of the blender (N). CCB provides better means for nanocomposites in terms of both exfoliation and orientation of NPs.\(^11\)-\(^15\)

In PA6/NP blends, PA6 was trapped in a meta-stable crystalline state \(^{21}\)-\(^{24}\) and it can revert to the \( \alpha \) form by annealing at higher temperatures, where increased polymer chain mobility allows them to rearrange into stable crystalline form.\(^{25}\)-\(^{27}\) Also stretching the nanocomposite films enhances the \( \alpha \) form and increases the overall crystallinity of PA6.\(^{28}\) In the current study, we focused on the effects of annealing and stretching on the structure of PA6/NP nanocomposite films made by CCB with different Ns and NP concentrations. X-ray diffraction was used to probe the dimensions from 0.1-2.5nm,
which predominantly captures the packing of the polymer chains as well as the closely packed NPs. This study has shown that both annealing and stretching significantly enhance the α crystalline fraction of PA6. Also the orientation of the polymer chains was changed with respect to the orientation of NP upon annealing and stretching.

**Experimental Section**

A master-batches of different volume fractions (vol %) of NPs were prepared from PA6 (Capron B135QP, BASF Corporation, Mount Olive, New Jersey) and NP (Closite 30B, Southern Clay Products, Gonzales, Texas) using a twin-screw extruder. Nanocomposite films with overall NP vol % of 2.0, 2.8, 3.5 and 5.6 were obtained by supplying the PA6 (matrix polymer) and master-batches in equal proportions to the CCB to obtain films with different Ns as showed in table 4.1.

Samples were annealed at different temperatures in between room temperature and above the melting temperature, which is 210°C for PA6, for 12 hours. Then samples were cooled down slowly to room temperature.

**Table 4.1 Films studied**

<table>
<thead>
<tr>
<th>N, (vol %=0)</th>
<th>N, (vol %=2.0)</th>
<th>N, (vol %=2.8)</th>
<th>N, (vol %=3.5)</th>
<th>N, (vol %=5.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3</td>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>12</td>
<td>10</td>
<td>8</td>
<td>7</td>
</tr>
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<td>20</td>
<td>12</td>
<td>12</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>16</td>
<td>20</td>
<td></td>
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<tr>
<td>25</td>
<td>20</td>
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Selected nanocomposites films were stretched simultaneously from both edge and end directions at 200°C. Degree of stretching is given as the ratio of the sizes of the stretched films over unstretched films along each direction. Three different stretching limits were studied. Those are 1.5×1.5, 2.0×2.0 and 2.5×2.5.

Powder X-ray (Powder Sintag) with Cu Kα radiation (λ = 1.54Å) was used to obtain one dimensional X-ray profiles. All the samples were cut to 1cm² in size and the intensities obtained from the instrument were averaged to a unit thickness. Further studies were carried out on a Rigaku single crystal instrument with Mo Kα radiation (λ = 0.71 Å) equipped with a two-dimensional detector. Films were investigated along three different directions with respect to extrusion direction as illustrated in Figure 4.1. Degrees of crystallinity and α/γ ratios were calculated from X-ray data with PeakFit 4.2 from Seasolve software inc., which de-convolutes overlapped peaks and integrates the peak areas. Two-dimensional X-ray images were analyzed using Fit 2D program, which gives radial distributions and intensity profiles along different directions.

**Figure 4.1** Directions of incident X-ray beam with respect to the extrusion direction.
Results and Discussion

I. Annealing Study

Figure 4.2a represents the X-ray patterns for PA6 rich with α crystalline form, which consists of two intense α crystalline peaks superimposed with a small γ peak at the center and a broad amorphous peak. The α crystalline peaks are corresponded to the (002) and (200) diffractions at 3.75Å (α2) and 4.39Å (α1) respectively. The diffraction from γ form occurred at 4.16Å from (001) crystalline plane. These dimensions are corresponding to the chain-chain correlation of PA6 explained in the introduction.

![Graph of X-ray patterns](image)

**Figure 4.2** X-ray patterns and analysis of PA6 in the a) pristine form and b) chaotically blended films at N=30.

The X-ray pattern for the chaotically blended PA6 is shown in Figure 4.2b, which has major contribution from the γ form and less contribution from the α crystalline form. Chaotically blended samples with and without NPs show similar X-ray patterns as in
Figure 4.2b and the annealed samples show similar patterns as in Figure 4.2a. These peak positions were used in the peak deconvolution routine to extract the $\alpha/\gamma$ and crystalline/amorphous fractions assuming Gaussian line shape.

Figure 4.3 represents the X-ray patterns for PA6 nanocomposites with 3.5 vol % NPs at N=20 as a function of annealing temperature. These data were shifted in both horizontal and vertical directions for clarity. At room temperature, one broad peak was appeared around 4.16Å, which mainly corresponds to the $\gamma$ crystalline form of PA6 as introduced in Figure 4.2b. As temperature increases to 130 °C, peaks start to separate and the intensity of the center peak ($\gamma$) decreases. These changes confirm the conversion of the $\gamma$ crystalline form to the $\alpha$. It is important to mention that the change in crystalline forms starts around 130 °C, which is way below the melting point of the polymer, which is ca. 210 °C for PA6. Up to 210 °C, the $\alpha$1 has higher crystalline fraction than the $\alpha$2. Upon annealing little above the melting temperature, the $\alpha$2 starts to dominate over the $\alpha$1, indicating different degrees of ordering in crystalline planes. By looking at these changes, three different annealing temperatures, which are 25 °C, 210 °C and 240 °C, were selected for the rest of the study. At higher temperatures polymer chains get more mobile and arrange into thermodynamically stable, anti-parallel configuration. This means that confinement of polymer chains within NP interfaces does not prevent the reorientation of polymer chains. Unlike the blending process, cooling process of the films after annealing was taken place slowly and it allows matrix polymer to return to the stable anti-parallel configuration.
De-convolutions of X-ray peaks were carried out as introduced in the Figure 4.2 and the extracted $\alpha/\gamma$ ratios at different temperatures are given in Figure 4.4. At room temperature, the $\gamma$ form increases with N for lower NP vol % as illustrated in Figure 4.4a. This trend at low NP concentration is similar to that observed in pure PA6 films where $\alpha/\gamma$ ratio decreases from 1.8 to 0.8 as N goes from 0 to 30. This trend of decreasing $\alpha/\gamma$ ratio with N did not follow for samples with higher NP concentrations where the $\alpha/\gamma$ ratios were hardly changed with N. As the NP concentration increases, surface area of NPs increases. Therefore, instead of blending effects surface forces of NP determined the arrangement of polymer chains. Samples annealed at 210 °C are shown in Figure 4.4b and they have significantly higher $\alpha/\gamma$ ratios compared to unannealed nanocomposites. Any specific trend of $\alpha/\gamma$ ratios was not observed with N or NP concentration.

**Figure 4.3** X-ray patterns of nanocomposites films with 3.5 vol % NPs at N=20 as a function of annealing temperature.
Figure 4.4 α/γ crystalline ratio as a function of N for different NP vol % of a) unannealed and b) annealed samples at 210°C. Lines were drawn as a guide to eye.

Extracted crystalline/amorphous ratios were given in the Figure 4.5. Crystalline fraction of unannealed samples has increased with increasing concentration of NPs in the polymer and hardly shows any dependence with N. Upon annealing, the crystalline to amorphous fraction increased in virgin PA6 as well as in nanocomposites with all NP concentrations. Therefore, one can predict two processes that occur in nanocomposite upon annealing. Those are the conversion of the γ form to the α form and conversion of amorphous domains to crystalline domains. In annealed samples polymer chains are more mobile and they are in a shear-free medium, which allows polymer chains to make interactions with neighbors to form more stable crystalline domains.
Figure 4.5 Crystalline/amorphous ratios in nanocomposite films as a function of N for a) unannealed and b) annealed at 210°C conditions. Lines were drawn as a guide to eye.

Further studies were carried out to understand the effects of annealing on polymer chain orientation using X-ray diffractometer with 2D detector. Details of the orientation of NP and PA6 chains in chaotically blended system were introduced in our previous study.  Those findings were briefly summarized herein. All nanocomposite films were studied from three different directions with respect to the extrusion direction as introduced in Figure 4.1. X-ray images for the unannealed nanocomposites with 5.6 vol% of NPs are shown in Figure 4.6a. The most center diffraction, at ~ 18Å, corresponds to the inter-particle distance between NPs. This diffraction is observed from the X-ray data from edge and end directions along the equator of the images, which is clearly shown in radial distributions in Figure 4.6b and cross sections in Figure 4.6c. This confirms the orientation of long axes of NPs is along the extrusion direction. This was further
confirmed from TEM images of the films. N hardly shows any effect on the platelet orientation.

**Figure 4.6** a) Two dimensional X-ray patterns of PA6 nanocomposite with 5.6 vol % NPs at N=20 from edge, through and end directions. b) The intensity along the gamma crystalline ring marked in $\gamma$. c) The cross sections of the images along the X and Y directions.

PA6 has six-fold symmetry only in edge and end directions due to the diffraction from $\gamma$ (001) crystalline plane. However, intensities of these arcs are not similar as indicated in radial distribution profiles in Figure 4.6b. The intensities along the equator
(X) are higher than the intensity along the meridian (Y) as illustrated in cross sections along X and Y directions in Figure 4.6c. The $\gamma$ (001) crystalline plane is perpendicular to the polymer chains axis. Since orientation of PA6 only can be seen in edge and end views, polymer chain axis should on average perpendicular to the edge and end scanning directions. Therefore, these polymer chains are oriented perpendicular to the flow direction as well as to the NP surface.

Similar type of orientation study was followed for annealed nanocomposite using 2D X-ray measurements. As shown in X-ray patterns in Figure 4.3, total separation of $\alpha$ peaks occur after 210 °C, which is the melting temperature of the PA6. In order to show the differences between nanocomposites before and after annealing, annealing data above 210°C were introduced along with un-annealed data in Figure 4.7a. These images and their corresponding radial distribution profiles and cross sections in Figure 4.7b and c show the dramatically change in orientation of PA6 crystalline planes.

For all annealing conditions diffraction from NP was observed along the equator. Therefore, long axes of NPs have not changed upon annealing. As mentioned earlier, as prepared nanocomposites predominantly have the $\gamma$ crystalline form, which is shown in the 2D diffraction pattern in Figure 4.7a. When annealing temperature increases to 210°C, the meta-stable $\gamma$ form convert into the $\alpha$ form, which is indicated by two intense circles due to the diffraction from $\alpha1$ and $\alpha2$ crystalline planes. The six-fold symmetry still remains in the $\alpha1$ and $\alpha2$ diffraction circles. This can be further seen from the radial distribution at 210°C. Therefore, samples at both 25°C and 210°C temperatures retain the same polymer chain orientation with respect to the extrusion direction as well as to NPs.
Figure 4.7 a) X-ray patterns of nanocomposites with 5.6 vol % NP for N=20 at 25 °C, 210 °C, 230 °C and 240 °C from edge view. b) Corresponding radial distributions of the major crystalline forms. c) Cross sections of the images along X and Y directions.

When temperature increases to 230°C, orientation was changed as indicated in Figure 4.7a. Six-fold orientation of α1 changes into four-fold symmetry, where it has major orientations along both equator and meridian. Increasing temperature further
moves the α1 diffraction to meridian and α2 retains mainly in the equator. The six-fold symmetry changes into biaxial monoclinic orientation. This specific orientation was observed for all Ns upon annealing. In addition, (020) diffraction appears along the equator at 8.14Å, which is originally observed along the meridian for as prepared nanocomposites.

According to the X-ray data, before annealing, long axes of polymer chains are oriented perpendicular to the NP surface. However, during annealing polymer chain starts to relax back to stable configuration and make hydrogen bonds between parallel chains. These modifications in the polymer chain packing results in PA6 chains to orient parallel to the NP surface. This transformation is schematically represented in Figure 4.8.

**Figure 4.8** Schematic representation of PA6 chain axis orientation with respect to the orientation of NPs in pristine and annealed nanocomposites.
II. Stretching Study

Stretching of the films was carried out at 200°C, which is a little lower than the melting point of PA6. According to the X-ray data of the annealed samples, films at 200°C are rich with the α crystalline form and the overall crystallinity of the films increase compared to the unannealed samples. Figure 4.9 represents the X-ray diffraction patterns for stretched nanocomposites with 2.8 vol % NP at N = 12. The α2 diffraction is more intense than the α1 and γ diffractions. As the degree of stretching increases, the α1 and γ fractions decrease and α2 increases.

Figure 4.9 X-ray patterns of PA6 nanocomposites with 2.8 vol % NPs at N=12 as a function of degree of stretching.

Peak deconvolution was carried out to extract the α/γ and crystalline/amorphous ratios in stretched films. Figure 4.10a shows the α/γ ratio as a function of amount stretched for different Ns of 2.8 vol % nanocomposites. For films at given N, the α/γ ratio increases with degree of stretching. As illustrated in Figure 4.10b, total crystalline portion in the nanocomposites also increases with degree of stretching. The highest contribution to the crystalline portion comes from the α2 diffraction. As the degree of stretching
increases polymer chains start to align along the stretching directions and this enhances the crystalline fraction in stretched samples.

![Graphs showing α/γ crystalline and crystalline/amorphous ratios as a function of degree of stretching for nanocomposites with 2.8 vol % NPs at different Ns. Lines were drawn as a guide to eye.]

Figure 4.10 a) α/γ crystalline and b) crystalline/amorphous ratios as a function of degree of stretching for nanocomposites with 2.8 vol % NPs at different Ns. Lines were drawn as a guide to eye.

Two dimensional X-ray studies were carried out to clarify the effects of stretching on the orientation of NP and polymer chains. Figure 4.11a represents the 2D X-ray patterns for the stretched (2×2) nanocomposites with 2.8 vol % of NPs at N=12. The edge and end images look similar. The α2(002) diffraction is observed along the equator and α1(200) is observed along the meridian. Therefore, polymer chain orientation in stretched PA6 films is similar to that of the annealed nanocomposites at 240 °C. The radial distribution profiles and cross sections of the X-ray images along equator and meridian are shown in Figure 4.11b and c respectively.
Figure 4.11 a) Two dimensional X-ray patterns of 2×2 stretched nanocomposite films with 2.8 vol% NPs at N=12 from edge, through and end directions. b) The intensity along α1 and α2 crystalline rings of 2D X-ray images. c) The cross sections along the X and Y directions.
As shown in Figure 4.11b and c, the α2 diffraction arcs are much intense compared to the α1 indicating presence of more ordered 002 crystalline planes in the stretched nanocomposites. The through image shows a weak diffraction ring of α1. However, α2 was not observed in through direction. The 002 crystalline plane corresponds to the hydrogen bonded sheets in PA6. Therefore, more ordering occurs among the hydrogen bonded sheets of PA6 upon stretching in edge and end directions.

Similar orientations of crystalline planes were observed in annealed samples at 240°C as indicated in Figure 4.7a, which is due to the monoclinic symmetry. The diffraction spot from the NP is still observed along the equator, which indicates that the long axes of the NPs are already fall in the stretching direction. Therefore, during the stretching process only the orientation of the PA6 chains were disturbed and they started to arrange parallel to the NP surface as well as the stretching directions.

**Conclusion**

Effects of annealing and stretching on the structure of PA6/montmorillonite clay nanocomposites made by chaotic blender were studied using X-ray diffraction. Nanocomposite films at room temperature were rich with γ crystalline form of PA6 and have six-fold symmetry. Initially polymer chains orient perpendicular to the NP surface. Upon annealing the γ crystalline form changed into α form. And the total crystalline fraction of the nanocomposite slightly increased upon annealing. Annealing above 210°C
converted the crystalline packing into monoclinic symmetry and it changed the orientation of the long axes of the polymer chains parallel to the NP surface.

The α crystalline fraction in stretched samples increased significantly and the α/γ ratio increased with degree of stretching. Stretching increases the crystalline portion of the nanocomposite films regardless of the N. Biaxial stretching enhances the ordering of the α(002) crystalline plane more compared to the α(200) due to the ordering of hydrogen bonded PA6 sheets. Similar to the annealed nanocomposites, orientation of the polymer chains was changed, where the long axis of the polymer chain was aligned parallel to the NP surface and along the stretching directions.

References

4. Weo, J. I.; Sue, H. J. Polymer 2005, 46, 6325-6334


CHAPTER 5

Structural Changes in Chaotically Blended Nylon-6/Clay Nanocomposites
upon Exposed to Water

Abstract

Structural changes occur in water saturated polyamide 6 (PA6)/montmorillonite clay nanocomposite films were studied using X-ray and neutron scattering techniques. These nanocomposites were made with different nanoparticle (NP) concentrations using chaotic advection blender, where the duration of chaotic advection on melt, which is given by the processing parameter N, changed systematically. As chaotically blended nanocomposite films are exposed to water, the major crystalline form of the PA6 changes from the γ to the α form. This transformation was more significant in nanocomposites made at higher Ns. However the total crystallinity and the relative orientations of the polymer chains and the NPs remained the same. D₂O absorption made enough contrast between crystalline and amorphous domains to distinguish their arrangements using small angle neutron scattering, where they associated into stacked sheets. In nanocomposites, 3 or 4 alternative layers of crystalline and amorphous sheets were associated in a single stack while in pure polymer these stacks were made from a single layer of crystalline and amorphous sheets.
Introduction

Incorporation of nanoparticles (NPs) into polymeric matrices often introduces superior properties such as enhanced barrier resistance, higher mechanical and thermal stability compared to the pure polymers.\textsuperscript{1-7} These properties are strongly influenced by the amount of moisture/water absorbed by the hygroscopic matrix polymers. Water molecules interact with matrix polymer and/or with NPs and alter the intermolecular interactions between polymer and NPs, which affects the packing of polymer chains and NPs in nanocomposites. Association of water in polymers alter material properties such as modulus, glass transition temperature ($T_g$) and yield stress.\textsuperscript{8,9}

Nylon6 (PA6)/montmorillonite NP is one of the widely studied nanocomposite systems, where both matrix polymer and NPs absorb water.\textsuperscript{10} It has been reported that PA6 can absorb ca. 10 wt.% of water and hydrogen bond formation occurs between water molecules and the amide groups of PA6.\textsuperscript{11} Replacement of inter-chain hydrogen bonds with water molecules enhances the polymer chain mobility.\textsuperscript{12} Polymers such as PA6 have both crystalline and amorphous domains. Crystalline domains are more resistant to absorption of water compared to the amorphous regions.\textsuperscript{13} This results in uneven distribution of water in polymers. Plesi et al. reported that concentration of water is higher at the center of the amorphous domains and it decreases as goes toward the crystalline/amorphous interface.\textsuperscript{14} In addition, they observed that there is no change in volume or density in the crystalline domains. This further confirmed by Murthy et al. and observed the decrease in water absorption with increase in crystallinity.\textsuperscript{15} Water absorption to amorphous domains does not alter the distance between chains linked by
the hydrogen bonds, but the distance between H-bonded sheets.\textsuperscript{13} PA6 takes longer time to get saturated with water and hardly shows any structural changes upon swelling at room temperature compared to higher temperatures.\textsuperscript{11}

There are two major crystalline forms in PA6.\textsuperscript{16-18} Those are the thermodynamically stable $\alpha$ crystalline form, which has hydrogen bonds in between anti-parallel PA6 chains, and the meta-stable $\gamma$ form with hydrogen bonds occur in between parallel pleated chains.\textsuperscript{16-18} Water saturated PA6 favors the $\alpha$ crystalline form over the $\gamma$.\textsuperscript{19}

Incorporation of montmorillonite NPs into PA6 enhances the barrier resistance of the polymer.\textsuperscript{20-22} Resistant to water is optimal when NPs are fully exfoliated.\textsuperscript{23} In addition, NPs compensate for the reduced mechanical properties due to the presence of water. These nanocomposites absorb water at slower rate compared to the pure PA6.\textsuperscript{11} However, both nanocomposite and the pure PA6 become saturated to the same level as the solvent (water) exposure time goes by.\textsuperscript{11}

In the current work, we studied the effects of water absorption on the structure of PA6/montmorillonite nanocomposite made using a chaotic advection blender, which also known as the smart blender.\textsuperscript{24-28} Nanocomposites with different NP concentrations were made using a novel in situ structuring process, where melt components were assembled into numerous discrete layers by chaotic advection and extruded into film form in a continuous process.\textsuperscript{24-28} On the micron length scale, NPs were localized within multiple layers, where individual thicknesses of internal layers and the orientation and the distribution of the NPs were controlled by selecting the duration of chaotic advection
given by a process parameter N. In our previous studies we have shown that the N has affected on the crystalline structure especially for the lower NP concentrations, where at higher Ns the fraction of meta-stable γ crystalline form increases and the stable α form decreases. Also N affects the dispersion of NPs. Initially NPs were oriented along the extrusion direction and polymer chains were oriented normal to the NP surface. As N increases, NPs were further separated from each other while maintaining the orientation of NPs and polymer chains. Further details of this system can be found in elsewhere.

One- and two-dimensional X-ray diffraction techniques were used to study the structural changes take place in nanocomposite films and small angle neutron scattering (SANS) technique was used to study the distribution of D2O as well as crystalline and amorphous domains in nanocomposites films.

**Experimental Section**

Master-batches of different NP concentrations were prepared from PA6 (Capron B135QP, BASF Corporation, Mount Olive, New Jersey) and montmorillonite NP (Closite 30B, Southern Clay Products, Gonzales, Texas) using a twin-screw extruder. Nanocomposite films with overall NP volume fractions (vol %) of 2.0%, 3.5%, and 5.6% were obtained by introducing the matrix PA6 polymer and master-batches in equal proportions to the smart blender to obtain extruded films of about 150 micron thickness. Films were produced with differing extents of chaotic advection and thereby, differing internal layer refinements through specification of N of the smart blender. The films that were used in the current study are given in table 5.1.
Table 5.1 Films studied.

<table>
<thead>
<tr>
<th>NP vol %</th>
<th>N</th>
<th>NP vol %</th>
<th>N</th>
<th>NP vol %</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0</td>
<td>2.0</td>
<td>6</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>0.0</td>
<td>30</td>
<td>2.0</td>
<td>14</td>
<td>3.5</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>20</td>
<td>3.5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td>30</td>
<td>3.5</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.5</td>
<td>20</td>
</tr>
</tbody>
</table>

First films were studied at dry condition. Then films were soaked in water at 25.0°C for 24 hours (wet at 25°C) and at 100°C for 2 hours (wet at 100°C), until water uptake reached to the maximum level.

An X-ray powder Sintag diffractometer with Cu Kα radiation (wavelength (λ) = 1.54Å) was used to obtain one-dimensional X-ray patterns of nanocomposite films at different wetting conditions. All the samples were cut to 1 cm² in size. Relative orientations of the polymer chains and the NPs were studied using Rigaku single crystal instrument with Mo Kα radiation, which has X-ray wavelength of 0.71 Å, equipped with a two-dimensional detector. Films were investigated along three different directions with respect to the extrusion direction as shown in Figure 5.1. Degree of crystallinity and α/γ crystalline ratios were calculated from X-ray data with the help of a peak fitting program (PeakFit 4.2 from Seasolve software inc.), which de-convolutes overlapped peaks and integrates the peak areas. Two-dimensional X-ray images were analyzed using the Fit 2D program 31 to obtain intensity profiles along different directions.
SANS measurements were carried out to understand the distribution of water in pure polymer and nanocomposite films. SANS experiments were performed at Low Q-Diffractometer (LQD), FP10 beam line in Lujan center in Los Alamos National Laboratory. LQD covers the wavelength range of 1.5 to 15 Å with the $q$ range of 0.003 to 0.5 Å$^{-1}$, where $q$ is the momentum transfer, which is given by $q=4\pi(sin \ \theta)/\lambda$ and $\theta$ is the angle of incident X-ray beam. Instead of H$_2$O, D$_2$O was introduced to the nanocomposites, which can be distinguished from the components of the nanocomposites due to the natural neutron SLD contrast between hydrogenated matrix polymer and the deuterated water. Scattering from empty cell and D$_2$O were measured separately and subtracted from the data. Then the data were normalized to the transmission. SANS data were analyzed using data analysis program developed by Steven Kline in the NIST center for neutron research.\textsuperscript{32}

\textbf{Figure 5.1} Directions of incident X-ray beams used to investigate the films made from CCB with respect to the extrusion direction.
Results and Discussion

X-ray diffraction data for PA6/NP nanocomposites under different wetting conditions are shown in Figure 5.2a. At dry condition, chaotically blended nanocomposites show only one broad peak around 4 Å and it starts to resolve into three peaks upon soaked in water. These peaks arise from two major crystalline forms of PA6, which are α and γ forms as shown in Figure 5.2b and c. The peak at 4.16 Å corresponds to the (001) diffraction of the γ crystalline form. The peaks at 4.39 Å and 3.75 Å correspond to the X-ray diffraction from (200) and (002) crystalline planes of the α form. Peak deconvolutions were carried out to extract the relative amounts of α and γ as well as the crystalline to amorphous fractions in nanocomposite films under different wetting conditions. Literature values of the α and γ peaks positions were used to deconvolute the X-ray patterns assuming a Gaussian line shape. These deconvoluted peaks are shown in Figure 5.2b and c.
In previous studies we have shown that as \( N \) increases the thermodynamically stable \( \alpha \) crystalline form converted into the meta-stable \( \gamma \) form, especially in lower NP concentrations (2 vol %). Also formation of \( \gamma \) crystalline form enhanced upon increasing the volume fractions of the NPs. The blending effect dominates at low NP concentrations and surface forces are prominent at higher NP concentrations. Deconvolution procedure was carried out in the similar manner to extract the \( \alpha/\gamma \) crystalline ratios in

Figure 5.2 a) X-ray data for nanocomposites with 3.5 vol % of NPs at \( N=11 \) for dry and \( \text{H}_2\text{O} \) saturated films at 25°C and 100°C. Deconvolution of X-ray patterns for b) dry and c) wet at 25°C nanocomposite film.
nanocomposite films in wet conditions. Figure 5.3 shows the $\alpha/\gamma$ ratios of nanocomposite films with three different NP volume fractions in dry, wet at 25°C and wet at 100°C conditions.

![Graphs showing $\alpha/\gamma$ ratios](image)

**Figure 5.3** Alpha ($\alpha$) to gamma ($\gamma$) crystalline ratio of nanocomposites at different wetting conditions as a function of N for a) 2.0 vol % b) 3.5 vol % and c) 5.6 vol % NP concentrations. Lines were drawn as a guide to eye.

At all NP volume fractions, the $\alpha/\gamma$ ratio was lowest in the dry films. As chaotically blended films exposed to water, the meta-stable $\gamma$ form decreases and the stable $\alpha$ form increases. The films that were boiled in water have the highest $\alpha/\gamma$ ratio.
The effect of water absorption on changing the crystalline form is pronounced in films made at higher Ns. As more water penetrates, the mobility of polymer chains increased. This might facilitates the rearrangement of polymer chains in anti-parallel fashion to form thermodynamically stable α form.

Figure 5.4 represents the crystalline/amorphous ratios of nanocomposite films as a function of N at dry and wet conditions. The overall crystallinity, which includes the contribution from both α and γ forms, has no significant impact from N. However, the crystalline fractions of nanocomposites were increased with increasing the NP concentration for all nanocomposites.

2D X-ray studies were carried out to understand the effects of water absorption on the orientation of polymer chains as well as the NPs. Films were studied in three different directions as introduced in Figure 5.1. In our previous studies, we observed that the orientation of the long axis of NPs aligned along the extrusion direction. As N increases, NPs were further exfoliated while keeping the same orientation. PA6 arranged into a unit cell with six-fold symmetry and polymer chains were oriented perpendicular to the NP surface as well as to the extrusion direction. As shown in Figure 5.5a, orientation and the packing of the polymer chains and NPs were remaining the same upon exposed to water at both temperatures. However the six fold symmetry is enhanced in the 2D X-ray images of the soaked films compared to that of the dry films. The radial distributions profiles, which include contributions from both α and γ crystalline forms, are shown in Figure 5.5b. The similarities of the orientation patterns of dry and wet nanocomposite films are clearly indicated in these profiles. The appearance of α1 and α2 rings confirms the
transformation of the $\gamma$ crystalline form into the $\alpha$, which is clearly observed in the through view image at 100°C. However, total conversion of $\gamma$ to $\alpha$ was not observed under the experimental conditions.

Figure 5.4 Crystalline to amorphous ratio of nanocomposites at different wetting conditions as a function of N for a) 2.0 vol % b) 3.5 vol % and c) 5.6 vol % NP concentrations.
Figure 5.5 a) 2D-X-ray images for PA6 with 5.6 vol % of NPs at N=9 from edge, through and end directions under dry and wet conditions. b) Radial distribution profiles of α and γ crystalline forms at dry (♦) and wet conditions at 25 °C (■) and 100 °C (▲). These profiles were shifted vertically for clarity.
Diffusion of water into crystalline and amorphous domains is different in PA6, where water penetrates more into the amorphous domains than the crystalline domains due to the differences in polymer chain packing density of domains. Therefore, diffusion of liquids like D$_2$O into semi-crystalline polymers changed the neutron scattering contrast between amorphous and crystalline domains, which allows distinguishing those areas from SANS technique.

Figure 5.6 SANS data as a function of N for a) pure PA6 and b) nanocomposites with 2 vol % of NPs. Symbols represent the data and solid lines correspond to the best fits obtained from unified model. Data were shifted vertically for clarity.

Figure 5.6a shows the SANS data for pure PA6 films in dry condition. At N=0, data hardly show scattering at low q region. The data at N=25 has a less pronounced upturn at low q indicating presence of some scattering domains with much larger
dimensions compared to PA6 at N=0. Scattering at small angles enhanced upon addition of NPs to the polymer as shown in Figure 5.6b.

Data for dry membranes except pure PA6 at N=0 were fitted to the unified form factor which gives the radius of gyration ($R_g$) of the aggregates corresponding to the scattering and power law dependence of the low $q$ region. The size of the aggregates increased with increasing N as shown in Figure 5.7. The dimensions of the aggregates observed in pure polymer are smaller than that of the nanocomposites, where the sizes of the aggregates in pure polymer at N=0 and 25 are around 52Å and 177Å respectively.

![Graph showing $R_g$ vs N]

**Figure 5.7** Radius of gyration ($R_g$) obtained from SANS data for nanocomposite with 2 vol % of NP at dry condition.

As D$_2$O penetrates inside the pure PA6 or nanocomposites, a well defined peak appears ca. 0.07Å$^{-1}$ as show in Figure 5.8. This behavior was reported before for the pure PA6, where the peak dimension corresponds to the distance between D$_2$O saturated regions that are separated by layers of crystalline polymer, which is around 90Å in our
study. The thicknesses of these layers are within the same dimension range regardless of the presence of NPs or the N. However, there is no sharp upturn in low $q$ for the pure polymer compared to that of the nanocomposite films.

Figure 5.8 SANS data for films soaked in water at 100°C for a) pure PA6 and b) PA6 with 2.0 vol % of NPs as a function of N. Symbols represent the data and solid lines are the best fits obtained from stack disk model. Data were shifted vertically for clarity.

SANS data were modeled using a form factor of a stacked disk. This model calculates the distance between disk-like lamellas of D$_2$O rich and poor regions, average number of disks stacked in a single cluster and the dimensions of the disks.

Single stack of disks were observed in the pure PA6 with the radius of ca. 100 nm. N does not show any significant role on the diameter of these sheets. The crystalline layers are ca. 32 Å and the amorphous layers are roughly 26 Å in thickness. In the nanocomposites, similar disk shape lamella were observed and the average stack consists of 3 to 4 sets of D$_2$O rich and poor layers. Therefore, presence of NPs enhances the
lamella structure in the PA6/NP system. These differences in the pure polymer and the nanocomposites were schematically represented in Figure 5.9.

![Diagram showing crystalline and amorphous domains in PA6/NP films]

**Figure 5.9** Schematic representation of the crystalline and amorphous PA6 domains in a) pure PA6 and b) nanocomposite films.

Due to the limitation of the available neutron beam time, we have followed the SANS experiment only for selected samples.

**Conclusions**

Adsorption of water to chaotically blended PA6/montmorillonite nanocomposites changed the major crystalline form of the nanocomposites from $\gamma$ to $\alpha$. This conversion is more significant in nanocomposites made at higher Ns. The overall orientation of the polymer chains in the films does not changed upon absorption of water. Water rich and poor layers formed stacks in nanocomposites indicating presence of alternate layers of amorphous and crystalline domains in the films. SANS studies show the role of NP in
polymer chain stacking to form alternate crystalline and amorphous layers, where 3 to 4 alternative crystalline and amorphous layer stacks were obtained in nanocomposites and single stacks were observed in pure PA6 films.

References

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CHAPTER 6

Self-Assembly of a Semi-Fluorinated Diblock Copolymer in a Selective Solvent

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Abstract

The self-assembly of a highly incompatible siloxane containing, semi-fluorinated diblock copolymer, polytrifluoro propyl methylsiloxane-\textit{b}-polystyrene (SiF-PS), in \textit{toluene} a selective solvent for polystyrene, were studied using Small Angle Neutron Scattering. Incompatibility is often enhanced by inserting fluorine into one of the blocks and as a result not only the interchain interactions are changed but also the rigidity of the blocks. Herein the incorporation of siloxane into the backbone of a semi-fluorinated block maintains its flexibility and allows separation of the effects of direct interactions due to fluorine from those of rigidity. Measurements were carried out in dilute solutions below 1 wt\%, at volume fractions $\phi_{\text{SiF}}$ ranging from 0.0 to 0.5. The high incompatibility of the SiF block drives aggregation at low volume fractions of the SiF block, where spherical core-Gaussian shell aggregates are detected at $\phi_{\text{SiF}} = 0.16$. In the symmetric SiF-PS complex fluid, elongated micelles were observed. The micelles exhibited unique temperature stability in comparison with the aggregates formed by diblock-copolymers in
lower segregation regime. As the temperature increases the micelles dissociate into free chains to form unimolecular micelles.

**Introduction**

Block copolymers dissolved in a selective solvent, which is a good solvent for one block and not for the other, self-assemble into aggregates with different shapes depending on the volume fraction of the blocks and the degree of segregation. Examples include spherical, cylindrical, lamellar and disk like micelles.\(^1\)\(^-\)\(^4\) These self-assemblies consist of a core of the less soluble block surrounded by a highly swollen corona formed by the more soluble blocks. The corona can be described as tethered to the core surface on one end and the other end is immersed in the solution. The structure of the micelles is affected by small variations in chain architecture,\(^5\) the volume fraction of the blocks,\(^6\) temperature,\(^7\) concentration of the block copolymers\(^8\) and the interaction with the solvent.\(^9\) The delicate control over structural changes provides systems that respond upon changes of the surrounding of the polymer\(^6,\)\(^10\) leading to potential applications such as drug delivery,\(^11\) nanolithography\(^12\) and stimuli responsive thin films.\(^13\)

Characteristic dimensions, shapes and stability of block copolymer micelles are governed by the free energy, which consists of three major contributions.\(^6,\)\(^14\) Those are the interfacial free energy between the solvent and the core block, the elastic free energy of the chains in the swollen corona and the stretching free energy of the chains in the core. The basic driving force behind the self-assembly process is to minimize the free energy of the system. Shape transitions of associating block co-polymers in solutions can
be introduced by tuning molecular characteristics which in turn affect the thermodynamic parameters of the system. Among the controllable parameters of block copolymer is the degree of polymerization of each of the blocks. Halperin et al. have shown that when the degree of polymerization of the corona block \( N_{\text{Corona}} \) is larger than that of the core block \( N_{\text{Core}} \), the stretching free energy of the corona block dominates the micellization process and results in a star-like micelle.\(^{14,15}\) However, when \( N_{\text{Corona}} \ll N_{\text{Core}} \), the core stretching term and the interfacial energy dominate the self-assembly, resulting in crew-cut micelles,\(^ {14}\) which were experimentally observed by Likos et al.\(^ {16}\) Additional transformation to cylindrical micelles and to vesicles have been observed as the degree of polymerization of each block is varied.\(^ {3}\) Another way of tuning micelle properties is to control the incompatibility between blocks, \( \chi N \), where \( \chi \) is the Flory interaction parameter and \( N \) is the degree of polymerization. Higher \( \chi \) results in a larger segregation between the blocks in diblock copolymers which alter their phase behavior as well.\(^ {17,18}\) Lodge and coworkers have shown that highly incompatible diblock copolymers such as polybutadiene–poly(hexafluoropropylene oxide) in bis-2-ethylhexyl phthalate, form large elongated and disk like micelles.\(^ {19-21}\) In these highly segregated diblocks, the interfacial tension between core and corona increases and becomes the dominant factor over other free energy contributions. The enhanced segregation results in elongation of the core.

In most studies enhanced segregation is obtained by inserting fluorine into one of the blocks. Besides tuning the interaction energies, introducing fluorine to a polymer backbone enhances chemical and thermal stability, controlled surface energy, control
dielectric constant and controlled reflective index.\textsuperscript{10,22-24} Inserting fluorine however increases the rigidity of the polymer and changes its thermodynamic characteristics. In the current study, we have investigated the shape and transformation of a highly segregating diblock copolymer, polytrifluoro propyl methylsiloxane-\textit{b}-polystyrene (SiF-PS), whose chemical structure is given in Figure 6.1, in toluene. While the fluorine affects interaction and rigidity, the presence of the siloxane group introduces flexibility to the polymer. This chemical composition of the Si-F block, results in a flexible, highly segregated polymer. In solution, the fluorinated segments tend to phase segregate from the protonated chains and from toluene, which is a good solvent for PS but not for the SiF. These segregation drives association into micelles with SiF blocks in the core and PS in the corona, at concentrations above the critical micellization concentration (CMC).

The study varies the volume fractions of the SiF block in the dilute regime as a function of temperature and concentration, and the assembly process is followed by Small Angle Neutron Scattering (SANS). In comparison with characteristics of polymers in the low segregation limit, our results have shown that micellization takes place at significantly lower volume fractions of the SiF block in comparison with diblocks in the low segregation limit and the micellar transformations also take place at lower volume fractions of the Si-F block.


**Experimental Section**

**Materials and sample preparation**

Polytrifluoro propyl methylsiloxane-\(b\)-polystyrene (SiF-PS) diblock copolymer was synthesized using living anionic polymerization described in detail elsewhere.\(^{36,37}\) The polymer characteristics are given in Table 6.1. Dilute solutions of SiF-PS were made in \(d_8\)-toluene purchased from Cambridge isotopes laboratories Inc. Solutions and \(d_8\)-toluene were placed in 1 mm thick neutron quartz cells.

![Figure 6.1](image.png) The chemical structure of polytrifluoro propyl methylsiloxane-\(b\)-polystyrene (SiF-PS) diblock copolymer.

**Table 6.1** Molecular parameters of the SiF-PS polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\phi_{SiF})</th>
<th>Mw of SiF (kg/mol)</th>
<th>Mw of PS (kg/mol)</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiF-PS-1</td>
<td>0.03</td>
<td>1</td>
<td>31</td>
<td>1.08</td>
</tr>
<tr>
<td>SiF-PS-2</td>
<td>0.16</td>
<td>6</td>
<td>30</td>
<td>1.09</td>
</tr>
<tr>
<td>SiF-PS-3</td>
<td>0.50</td>
<td>24</td>
<td>24</td>
<td>1.20</td>
</tr>
</tbody>
</table>
Experiments were carried out on two beam lines as a function of temperature. Most of the experiments were carried out at CG2 at Oak Ridge National Laboratory. Three different configurations were used covering a q range from 0.001 Å\(^{-1}\) to 0.4 Å\(^{-1}\), where q is the momentum transfer, given by \(q = 4\pi \sin(\theta)/\lambda\) and \(\theta\) is the angle of incidence. A q range of 0.001-0.002 Å\(^{-1}\) was obtained using \(\lambda = 18\) Å with a sample to detector distance of 19m; q ranges of 0.006-0.150 Å\(^{-1}\) and 0.04-0.40 Å\(^{-1}\) were obtained using \(\lambda = 6\) Å with sample to detector distances of 6.86m and 1.16m respectively. The instrument is designed to access q ranges as low as 0.001 Å\(^{-1}\). At the time of the measurement, we were able to access down to q~0.008 reliably.

Some of the experiments were carried out at Low Q-Diffractometer (LQD), FP10 beam line in the Lujan center in Los Alamos National Laboratory. LQD covers the wavelength range of 1.5 to 15 Å with the q range of 0.003 to 0.5 Å\(^{-1}\). Background, empty cell and toluene were measured separately and subtracted from the data. The data was then normalized to the transmission of the samples.

SANS data were analyzed using SAS fit program developed by Joachim Kohlbrecher in Paul Scherrer Institute.\(^{38}\) Neutron scattering length densities (SLD) \(\rho = 1.79 \times 10^{-6} \text{ Å}^{-2}\) for SiF, \(1.41 \times 10^{-6} \text{ Å}^{-2}\) for PS and \(5.66 \times 10^{-6} \text{ Å}^{-2}\) for d\(_8\)-toluene were used as starting values in the fitting routine.
Neutron data analysis

The form factors used to analyze the data have been previously derived and are briefly reviewed herein.\textsuperscript{25-32} At low q, the average size of the scattering object is obtained by the Guinier approximation, which is given in equation 6.1 for a spherical particle, where $R_g$ is the radius of gyration, $I(q)$ is the measured intensity, $V$ is the volume of the particle and $q$ is the momentum transfer.

$$I(q) \approx \rho^2 V^2 \exp\left(-\frac{1}{3} q^2 R_g^2 \right)$$

This approximation is valid for dilute and isotropic solutions, where particles in the system scatter independently of each other and are randomly orientated.\textsuperscript{33}

Molecular form factors

The form factor $F(q)$ of an ideal chain is described by a Debye function as given by equation 6.2.\textsuperscript{25,26}

$$F(q) = 2(e^{-x} + x - 1)/x^2$$

$$x = (qR_g)^2$$

Micellar form factors

Three different micelle form factors developed by Pedersen and co-workers, with spherical, elliptical and cylindrical cores and Gaussian coronas, were used.\textsuperscript{27-32} Micelle
form factors $F_{\text{Micelle}}$ contain four different contributions to encounter all interactions from the core, corona and solvent (equation 6.3). The specific terms for the three micelle form factors used in the current study are summarized in Table 6.2.\textsuperscript{27-32}

$$F_{\text{Micelle}} = N\beta_{\text{Core}}^2 F_{\text{Core}}(q) + N\beta_{\text{Brush}}^2 F_{\text{Brush}}(q)$$
$$+ 2N^2 \beta_{\text{Core}} \beta_{\text{Brush}} S_{\text{Core-Brush}}(q) + N(N - 1)\beta_{\text{Brush}}^2 S_{\text{Brush-Brush}}(q)$$  \hspace{1cm} (6.3)

Where $N$ is the number of blocks associated to form the micelle or the aggregation number and $\beta_{\text{Core}}$ and $\beta_{\text{Brush}}$ are the total excess scattering length densities of the core and the shell. The brush corresponds to the polymer chains in the corona. $F_{\text{Core}}$ is the self-correlation term of the core. $F_{\text{Brush}}$ is the self-correlation term of the corona. $S_{\text{Core-Brush}}$ is the cross term between the core and the corona and $S_{\text{Brush-Brush}}$ is the cross term between corona chains. The self-correlation of the core term describes interactions of chains in the core and defines it as a homogeneous core in the center and decaying core chain density at the core corona interface. The self-correlation term of corona describes corona as Gaussian chains and it obeys the Debye function as given in equation 6.2. The cross term between the core and the corona contains information about the interface between the two, which also includes the roughness of the core/corona interface. The cross term between different corona chains reflects the interactions among the corona chains themselves.
### Table 6.2 Contributions to the form factors of block copolymer micelles.

<table>
<thead>
<tr>
<th>Shape</th>
<th>$F_{Core}(q)$</th>
<th>$S_{Core-Brush}(q)$</th>
<th>$S_{Brush-Brush}(q)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>$\Phi^2(qR_{Core})$</td>
<td>$\Phi(qR_{Core})\psi(qR_g)\alpha$</td>
<td>$\psi^2(qR_g)a^2$</td>
</tr>
<tr>
<td>Ellipsoid</td>
<td>$\int_0^{\pi/2} \Phi(qr(R_{Core}, \varepsilon, \alpha)^2 \sin \alpha d\alpha$</td>
<td>$\psi(qR_g) \int_0^{\pi/2} \Phi(qr(R_{Core}, \varepsilon, \alpha))\alpha \sin \alpha d\alpha$</td>
<td>$\psi^2(qR_g) \int_0^{\pi/2} \alpha^2 \sin \alpha d\alpha$</td>
</tr>
<tr>
<td>Cylinder</td>
<td>$\int_0^{\pi/2} \Psi(qR_{Core}, L_{Core}, \alpha)^2 \sin \alpha d\alpha$</td>
<td>$\psi(qR_g) \int_0^{\pi/2} \Psi(qR_{Core}, L_{Core}, \alpha)\Gamma \sin \alpha d\alpha$</td>
<td>$\psi^2(qR_g) \int_0^{\pi/2} \Gamma^2 \sin \alpha d\alpha$</td>
</tr>
</tbody>
</table>

$F_{Core}$ is the self-correlations of core, $S_{Brush-Brush}$ is the cross term between corona chains and $S_{Core-Brush}$ is the cross term between core and corona chains. $\sigma$ is the interface thickness, $\Phi(qR_{Core})=3[\sin(qR_{Core})-qR_{Cor} \cos(qR_{Core})]/(qR_{Core})^3$ is the form factor amplitude of a solid sphere and $\Psi(qR_g)=[1-\exp(-q^2R_g^2)]/q^2R_g^2$ is the form factor amplitude of the brush. In case of spherical and elliptical micelles, $\omega=\sin(q(R_{Core}+dR_{g}))/q(R_{Core}+dR_{g})$. If corona chains stay on top of the core surface $d=1$ and if corona chains penetrate inside the core $0<d<1$. The term $r(R_{Core}, \varepsilon, \alpha)$ is the orientational-dependent radius of the ellipsoid, which is given by $R_{Core}(\sin^2 \alpha + \varepsilon \cos^2 \alpha)^{1/2}$. For cylindrical micelles, $\Gamma=\Delta q, R_{Core}+dR_{g}, L_{Core}+2dR_{g}, \alpha$, where $\Delta q, R_{Core}+dR_{g}, L_{Core}+2dR_{g}$ are radius and length of the cylindrical shell. $\Psi(qL_{Core}, \alpha)=2B_1(qR \sin \alpha)/qL \sin \alpha B_1[\sin(qL \cos \alpha/2)/qL \alpha/2]$ for a cylinder and $B_1$ is the first order Bessel function. $\alpha$ is the angle of the long axis of cylinder/ellipsoid with respect to $q$.

All data analysis was carried out with input parameters including the scattering length density of d-toluene, SiF and PS, calculated theoretically. Rgs of the micelles were estimated from the Guinier region of the patterns and the initial Rg of the coronas were obtained by using the values of Rg of the blocks themselves with an average Kuhn length taken as 18 Å. The dimensions of the core and corona as well as their SLD and the roughness of the boundary were allowed to vary. Best fit results were obtained by minimizing $\chi^2$ less than 1. Attempts to analyze the data with other models including swollen chains when relevant and starlike micelles with either stretched out or homogenous corona did not describe match the data.
Results and Discussion

Toluene solutions of three volume fractions of the SiF block described in Table 6.1 were investigated as a function of temperature and concentration. SANS patterns of a 1.0 wt.% solution of $\phi_{\text{SiF}} = 0.03$ are presented in Figure 6.2a as a function of temperature. The patterns consist of small angle scattering and only slightly change with temperature. There is a clear crossover from $\sim q^{-1.6}$ behavior at intermediate $q$ range to $\sim q^{-1.3}$ at higher $q$ values. At $q$ values below the crossover, the data are best described by a Debye function given in equation 6.2. In this $q$ range the scattering function is dominated by that of the polystyrene in toluene, which is a good solvent for the PS, though it is affected by the SiF block. For a flexible chain, in a good solvent, the slope at intermediate $q$ range is expected to scale as $q^{-1.66}$ corresponding to a fractal dimension $v=0.6$. In this study however the less soluble block is collapsed in comparison to a polymer in good solvent and effects of confinement to a less soluble block, affects the PS chain which is slightly extended, as reflected in the slope at high $q$. Note that the data could not be analyzed with a function that describes a polymer in a good solvent.

The slopes were extracted from the middle $q$ range and the data were plotted in a generalized Kratky plot as shown in Figure 6.2b, where $I(q)q^{1/v}$ is plotted as a function of $q$. In general, $1/v$ provides the fractal dimension of an object and reflects the interface of the polymer and its surroundings. The data collapse into a universal curve at low $q$ with a plateau at higher $q$. The level of the plateau slightly increases with temperature up to the highest temperature, where the slope of the scattering pattern is lower and as a result, the plateau shifts to higher levels. The universal curve provides a first indication that the SiF
segment is not fully exposed to the solvent, and would be in a unimolecular micelle configuration where the PS surrounds the SiF segments. The slight increase in the plateau level with increasing temperature is attributed to changes in the internal conformation of the diblock. At the highest temperature the solvent quality becomes sufficiently high so that the solvent becomes a good solvent for the SiF segment as well.

**Figure 6.2** a) SANS data for a 1.0 wt.% solution of $\phi_{SiF} = 0.03$ in $d$-toluene. The symbols correspond to the experimental data and solid lines are the best fits obtained from a Debye form factor for polymer chains in a good solvent. Data were shifted vertically for clarity. b) Kratky representation of the SANS data.

The $R_g$ values of the polymer molecules, extracted from a Guinier analysis and from the Debye model, as a function of temperature are shown in Figure 6.3. The Debye analysis provides an order of magnitude of the overall scattering object. These dimensions obtained from the Guinier regime and from a full fit are smaller in comparison with the expected values for a Gaussian chain, or for a chain in good solvent as estimated for polystyrene from mean field theory; a difference that could be attributed to excluded volume effects. Using a relation derived experimentally from neutron
scattering by Ragnetti and co-workers \(^{39}\) \(R_g = 0.0155M_w^{0.565}\) we obtain \(R_g \approx 55 \text{ Å}\), if the entire polymer would have consisted of polystyrene in good solvent. The numbers derived in here are lower, leading to the conclusion that the SiF segment is denser than if immersed in good solvent. We attribute the dimensions to the formation of unimolecular micelles, with a more collapsed SiF block surrounded by the PS. The configuration of the micelle is affected by the incompatibility of the two blocks and by the interactions with the solvent.

Figure 6.3 Radius of gyration \((R_g)\) extracted for 1.0 wt.% solution of \(\phi_{\text{SiF}} = 0.03\), as a function of temperature. The open symbols (◊) represent \(R_g\) values extracted from a fit to a Debye function and the solid dots (●) from a Guinier analysis. The inset is a schematic representation of a single molecule micelle, where the dark line in the center represents the SiF block and the surrounding thin line is the PS.

Since the SiF segment is the minority component, less swollen than the PS. As a result we do not detect a direct signature due to the SiF. The dimensions measured together with the solubility patterns measured separately (data not shown) lead to a model
of a unimolecular micelle, in which the SiF is surrounded by the PS. A schematic model is shown in the inset of Figure 6.3.

As the volume fraction of the SiF block increases to \( \phi_{\text{SiF}}=0.16 \) the SANS patterns become more structured as shown in Figure 6.4a. At lower temperatures, the patterns correspond to aggregates whereas with increasing temperature, the patterns become similar to those observed at the lower volume fraction. This small increase in the SiF volume fraction is sufficient to drive the diblock copolymer to form micelles in toluene. The signatures that correspond to the micelles are more pronounced in the generalized Kratky representation with \( \nu=0.67 \), corresponding to the slopes in the middle q range, as shown in Figure 6.4b. With increasing temperature, the peak intensities diminish. Above the critical micelle temperature (CMT), the temperature at which the micelles dissociate, the data appear similar in line shape to those obtained \( \phi_{\text{SiF}}=0.03 \), as shown in the inset of Figure 6.4b. The dimensions obtained from a Debye fit at 70.0°C and 79.5°C corresponds to \( R_g=76 \) Å and \( R_g=65 \) Å. These numbers are larger than expected for one molecule, suggesting that upon dissociation, small clusters remain that eventually dissociate.

The simplest model for a diblock micelle is a spherical star like aggregate with the less soluble block in the core and more soluble one is arranged in a corona. The conformation of the corona depends on the density of the corona chains at the core-corona interface and the interactions with the solvent. At temperatures below 55°C, the data were fit to a form factor of a starlike micelle with a spherical core and a Gaussian
corona, shown as a solid line in Figure 6.4a. The dimensions of the micelles, the aggregation number, the solvent fraction in the core and the roughness of the interface between core and corona, were extracted from the model. The parameters are presented in Figure 6.5.

**Figure 6.4 a** SANS data for a 1.0wt.% of SiF-PS with $\phi_{\text{SiF}} = 0.16$ in d-toluene. Symbols represent the data. The solid lines at 11.0°C, 25.0°C, 40.0°C and 55°C correspond to the best fits to a form factor of a spherical micelle and at 70.0°C and 79.5°C to a Debye form factor. For clarity, the scattering data have been shifted vertically. **b**) Kratky representation of the data at $\nu = 0.6$. Inset correspond to the SANS data for 70.0°C and 79.5°C.

The temperature dependence of the core and the corona sizes are shown in Figure 6.5a. The core size slightly increases with temperature while the corona dimensions decrease. With increasing temperature the core swells, allowing more area per each of the corona chains, resulting in less stretching. The change in solvent fractions inside the core ($X$) as a function of temperature, where $X$ varies from 0.6 to 0.8 is given in Figure 6.5b.
These values are further confirmed by comparing the SLD values of the core obtained from the core using equation 6.4.

\[
SLD_{\text{Fit}} = SLD_{\text{Toluene}}X + SLD_{\text{SiF}}(1 - X)
\]  

(6.4)  

**Figure 6.5** Calculated parameters for \( \varphi_{\text{SiF}} = 0.16 \) as a function of temperature. a) \( R_g \) values extracted for core (●) and corona (◇), b) solvent fraction inside the micelle core and c) aggregation number.
With increasing temperature, solvent quality of the toluene for the SiF block increases driving more solvent into the core, which results in breakdown of the micelles into small clusters and eventually individual chains. The aggregation number calculated for the micelle is around 10 SiF blocks in the core at 25°C and this value decreases with increasing the temperature as shown in Figure 6.5c.

According to mean field theory, for incompatible block copolymer micelles, corona chains stretch away from the core/corona interface to minimize the contact with the core blocks and to reduce the spatial crowdedness closer to the core/corona interface, while at the same time the geometry dictated that more space becomes available for the corona chains away from the core.\(^1\)\(^4\) The length \(L_{\text{Corona}}\) of such a corona chain is given by:

\[
L_{\text{Corona}} \approx f^{1/5} N_{\text{Corona}}^{3/5} b
\]

where \(f\) is the aggregation number and \(N_{\text{Corona}}\) is the number of monomers per corona chain.\(^1\)\(^4\) \(L_{\text{Corona}}\) for diblock copolymer with \(\phi_{\text{SiF}}\) at 0.16 would be ca. 766Å for a highly dense star-like micelle. For the highly swollen cores of the block-co-polymer under consideration, the PS does not follow the mean field prediction for star-like polymers given in equation 6.5 however, the high incompatibility results in extension of the corona chains, away from the core despite the low aggregation number. For this small SiF block, the average area/corona chain of ca. 40nm\(^2\) and it hardly changes with concentration.

Note that despite the low aggregation number the best fit of the experimental data was to a Gaussian corona. This reflects the solvent distribution in the corona, where the
PS remains more dense at the interface with the SiF. Several other micelles with highly swollen cores have been reported in block copolymer formed by poly (oxyethylene) – poly (oxybutylene).\textsuperscript{34,35}

**Figure 6.6** a-SANS data of a 1.0wt.% solution with $\phi_{\text{SiF}}=0.50$ in d-toluene. Symbols represent the data. Solid lines represent the best fits to form factors of elliptical micelle. b, c, Kratky plot of the data with $\nu=1.71$. The plot is broken into two ranges to allow clear visualization of the changes of intensity with temperature.
Increasing the volume fraction of the SiF block results in a shape transformation into micelles that are not spherical. SANS data of 1.0 wt.% solution of $\phi_{\text{SiF}} = 0.50$ diblock copolymers are shown in Figure 6.6a. $I(q)$ as a function of $q$ exhibits a power law dependence of $q^{-1}$ at high $q$, which is characteristic of a cylindrical or an elongated micellar form factor. This exponent may also be observed for highly stretched out chains in the corona, however this possibility is not consistent with the measured dimensions in the Guinier regime. The data were analyzed in terms of both cylindrical and elliptical micelles. The best fits obtained for an elliptical micelle form factor are given in Figure 6.6. A fit of the data to a cylindrical micelles results in short cylinders with length to diameter ratio 3:2. This geometrical proportions and the need to end-cap the cylinders with PS to mask the SiF from the toluene, resulting in elliptical micelles. These two shapes become indistinguishable for short cylinders. The micelles remained stable up to 110$^\circ$C, where the data at high temperatures become more noisy. The Kratky representations of the data is given in Figure 6.6 b and c. The patterns at the lower temperature overlap, where surprisingly with increasing temperature, the intensity of the features increase. This type of increase is characteristics of the formation of well define scattering objects or well-defined interfacial regions within a sample, as will be further discussed.

The concentration dependence of the shape and stability of $\phi_{\text{SiF}}=0.5$ micelles were studied for 0.1 wt.% and 0.5 wt.%, in addition to the 1.0 wt.% solution. Micelles of elliptical shape were observed for all three concentrations throughout the entire temperature range (10$^\circ$C – 100$^\circ$C). The micelles did not dissociate in this temperature
range. The experiment did not exceed 110°C because of the volatility of toluene. $R_g$ values obtained from elliptical form factors are in the same range as the $R_g$ values obtained from the Guinier analysis, which is shown in Figure 6.7a.

$R_g$ values decrease with increasing temperature. The sizes of the micelles vary with the concentration of the diblock copolymer as shown in Figure 6.7b, where largest micelles were observed for the 1.0 wt.% solution and the smallest ones for the 0.1wt.%. However, at higher temperatures, $R_g$ of micelles falls into the same range regardless of the concentration. Relatively large micelles were formed in symmetric SiF-PS system even at 0.1 wt.%, a low concentration in comparison with the size of micelles formed by low segregating diblock copolymer systems such as PS-PI.

The number of SiF blocks in the core, the aggregation number, decreases with increasing temperature as shown in Figure 6.7c. This is in accordance with the decrease in $R_g$ as represented in Figure 6.7b. Decrease in aggregation number with increasing temperature is more steep in a 1.0 wt.% solution of $\phi_{SiF}=0.5$ compared to lower concentrations. This tendency is consistent with a breakdown of micelles into smaller ones due to decreasing solvent incompatibility with the SiF block at higher temperatures. The aggregation number was further evaluated by calculating the number of SiF blocks inside the core as was done for solutions of $\phi_{SiF}=0.16$. Here we assumed the collapsed SiF conformation with Kuhn length of 18 Å due to high incompatibility of SiF blocks and solvent at $\phi_{SiF}=0.5$. 


Figure 6.7  a) Comparison of $R_g$ calculated from Guinier analysis ($\uparrow$) and elliptical ($\Delta$) micelles of 1.0 wt.% solutions. b)-f) calculated parameters using elliptical micelles for $\phi_{Si=0.5}$ with 0.1 wt.% ($\circ$), 0.5 wt.% ($\square$) and 1.0 wt.% ($\Delta$) solutions as a function of temperature.  b) $R_g$ of core, c) aggregation number, d) extended corona chain length, e) solvent fraction in the core and f) $d$, the fraction of corona chains immersed inside the core. The lines have been drawn through the data as a guide to the eye.
The end-to-end distance of the corona chains as a function of temperature is given in Figure 6.7d, where it decreases with increasing temperature. These values are closer to the theoretical end-to-end distance of PS in ϕ=0.5, which is ca. 180Å. The length of the corona chains also depends on the corona chain density at the core/corona interface. A high corona chain density results in increasing the spatial crowding, which causes stretching of the corona chains further away from the core/corona interface. Decreasing the aggregation number results in corona chains with smaller end-to-end distances. In order to quantify the nature of the core-corona interface, a roughness parameter $d$ was introduced.

Total radius of the micelle is defined in terms of $d$ as $R_{(\text{core})} + dR_g(\text{corona})$, where $d=1$ for smooth interfaces and approaches 0 upon increasing the interface roughness. Variation of $d$ as a function of temperature is given in Figure 6.7f. Smaller $d$ values were obtained for the higher concentrations compared to the lower concentrations, which shows the decrease in roughness with decreasing the concentration. Also roughness of the interface decreases ($d$ increases) with increasing temperature. The decrease in the interfacial roughness results in the increase of the intensity in Kratky plot in Figure 6.6b, and c.

The micellar characteristics were further confirmed by comparing the solvent fractions obtained from fitting with the values calculated from SLDs of the SiF blocks and the solvent inside the core, using equation 6.4. Variations of the solvent fraction inside the core with temperature for different concentrations are given in Figure 6.7e. As
temperature increases, the solvent fraction inside the micelle core slightly increases for all concentrations. Micelles in 0.1 wt.% solution has the highest solvent fraction and 0.5 wt.% and 1.0 wt.% have almost the same amount of toluene inside the core.

The area per corona chain as a function of concentration is shown in Figure 6.8a. As expected, as the density of the core becomes more dense, the area/chain decreases. The area per corona chain was calculated as a function of temperature for the 1wt% $\phi_{\text{SiF}}=0.05$, solution. The area/chain increases as the micelles dissociate. Interfacial tension between the core and the corona blocks becomes the dominant energy term over other contributions, which results in driving the interface to a less curved one. This result is consistent with findings by Lodge and coworkers that observed formation of disk like micelles from almost symmetric 1,2-polybutadiene-$b$-poly(hexafluoro propylene oxide) in bis(2-ethylhexyl) phthalate. In these studies, block copolymers consist of rigid blocks, where both rigidity and the high incompatibility play a role in determining the elongated shape of the micelles. The current study however shows that the presence of fluorine dominates even flexible blocks.
Figure 6.8 Area per chain for $\phi_{\text{SiF}}=0.5$ as a function of a) concentration at 10°C and b) temperature for 1wt% solution. The lines have been drawn through the data as a guide to the eye.

These different micelle shapes formed by SiF-PS diblock copolymers are schematically represented in Figure 6.9. The selectivity of the solvent drove the formation of unimolecular micelles whereas the incompatibility of the blocks resulted in micellar shapes with a less curved interface.

Figure 6.9 Schematic representation of self-assembly of the SiF-PS polymers. Red represents the SiF block and blue represents the PS block. a) Unimolecular micelles, b) Spherical star-like micelles and c) elliptical micelles.
Conclusions

The conformation and association of SiF-PS in toluene were investigated by SANS. Incorporation of fluorine into one of the blocks enhances the segregation in block copolymers due to the increasing the incompatibility and rigidity of the polymer. The presence of the siloxane group introduces flexibility to the SiF block, which allows us to exclude the effects of rigidity of the semi-fluorinated block. The study has shown that the enhanced incompatibility drive aggregations at significantly lower concentrations of the diblock in solution in comparison with lower segregation diblocks. At low volume fractions \( \phi_{\text{SiF}} = 0.03 \), individual polymer chains fold into unimolecular micelles, where SiF block was surrounded by the PS. With increasing volume fraction \( \phi_{\text{SiF}} = 0.16 \), SiF-PS associated into highly swollen spherical core-Gaussian shell aggregates below the CMT and transformed into unimolecular micelles at higher temperatures. The symmetric block copolymer formed elliptical micelles with unique temperature stability in comparison with the aggregates formed by diblock-copolymers in lower segregation regime. The micelles consist of a relatively low aggregation number and high amount of solvent in their core. The curvature of the core-corona interface is affected significantly by the volume fraction of the Si-F block. This small angle neutron study have shown that the high segregation of the diblocks derives association at significantly low concentrations observed in low-segregation diblock co-polymers in selective solvent even when both blocks are flexible.
References


CHAPTER 7

Effects of Highly Segregating Random Co-Polymers on the Dispersion of Nano-Particles in Ultra Thin Films

Abstract

The current study investigated the dispersion of nanoparticles (NPs) in new semifluorinated polymers in the ultra thin film regime where the film thickness is comparable to several radii of gyration of the polymer. Semifluorinated polymers are of unique technological significance for coatings where small, highly segregated fluorinated segments control not only the refractive indices and dielectric constants of the polymers but affect their phase diagram. Our study reveals that the unique properties of semifluorinated polymers, including interfacial effects of the polymer coupled with highly segregated segments, affect the dispersion of the NPs. The dispersion of polyhedral oligomeric silsesquioxanes (POSS) NPs and a semi-fluorinated random co-polymer of biphenyl-perfluorocyclobutyl (BPh-PFCB) was investigated using neutron reflectometry. The distribution of two types of NPs was probed, spherical POSS NPs decorated with short alkyl chains and POSS NPs tethered to one chain of the matrix polymer, forming a non-symmetric particle. A wealth of studies of NPs dispersed in homo and diblock-copolymer in the low interaction region, have shown that the dispersion of the NPs is controlled by several factors including the NPs size and shape and often by the interaction of organically grafted layers with the polymer matrix. In highly segregated semi fluorinated random co-polymers, we find that the NP distribution
is affected by segregation of very small blocks that would not have any effects in the low segregation limit. We find that NPs migrate towards interfaces formed in pristine polymer films. When tethered to one chain of the matrix polymer, the POSS NPs not only migrate to the internal interfaces but induce further layering within the thin film. The results demonstrate that the highly segregated nature of fluorinated and protonated segments is fundamental to the dispersion of the NPs.

**Introduction**

Incorporating nanoparticles (NPs) into thin polymeric films has become a major pathway to tune properties of materials enabling a variety of current and potential technologies. Controlled dispersion of NPs, however, the key to tuning properties of polymeric materials, remains a challenge. With the overarching goal to overcome the inherent segregation characteristics of polymers and the tendency of NPs to aggregate, nanoparticles are often grafted with organic chains to enhance their compatibility with the polymers. Bulk and surface studies of the dispersing of NPs had been probed predominantly in homo and diblock co-polymers in the low segregation limit, where the organic chains tethered to NPs are miscible in the polymer matrix. These intensive ongoing efforts have laid the foundations to the understanding of the behavior of organically coated NPs in the flexible and semiflexible homo-polymers, and co-polymers in the low segregation limit.
Of particular technological significance however, are nanocomposites of random
copolymer s in the high segregation limit; among them are semifluorinated polymers.
These polymers consist of highly segregated short fluorinated and protonated segments,
where the fluorinated segments allow tunability of the refractive indices and dielectric
constants together with enhancing chemical stability. The incompatibility between the
fluorinated and protonated segments drives the polymers into the high segregation limit,
in which very short segments are sufficient to induce long range correlations. In contrast
to the recent in-depth understanding of nanocomposites formed by flexible homo-
polymers and block-co-polymers in the low segregation limit, very little is known on the
factors that control the phase diagram of random co-polymers in the high segregation
limit and hardly any knowledge is available regarding the dispersion of very small NPs in
these matrices, either in bulk or in thin films. Counter to distribution of NPs in homo
polymers, we find that in semifluorinated polymers, the high segregation between small
fluorinated and protonated segments affects not only the interfacial structure of the
polymer, but is among the fundamental factors that influence the phase diagram of NPs
in the limit of thin films.

Ongoing wealth of studies\textsuperscript{1-11} of NPs in homo and diblock co-polymers in the low
segregation limit point to several major factors that modulate the dispersion of the
particles, including the size of the NPs with respect to the radius of gyration and the
statistical segments of the polymer, the shape of the NP and the chemical structure, length
and density of organic tethers grafted to the NPs interface. The distribution of the NPs is
a balance between translational and configurational entropic driving forces that often
drive segregation of the NPs, and enthalpy resulting from direct interactions of the organic tethers on the NPs with the polymer matrix. Herein we find that in thin films of a semifluorinated random co-polymer, the mutual incompatibility between very short blocks drive the distributions of small NPs into domain boundaries between protonated and fluorinated segments, and is only slightly affected by organic tethers.

The miscibility of NPs in bulk and in films have studied by Green and co-workers.\textsuperscript{10,17-18} They have shown that miscibility of NPs with a relatively high density of grafted chains, increases with increasing chain length of the grafted layers. They attributed the enhanced dispersion to increased interaction of the NPs grafts with the matrix. They also found that dispersion of the NPs is enhanced with a decreasing size of the NPs and rationalized the enhanced dispersion in terms of translational entropy that would vary with the diameter $D$ of the NP as $D^3$.\textsuperscript{17} They further determined that a mismatch of the symmetry of the grafted monomers and that of the matrix polymers affect the segregation. Further insight into the role of grafting densities has been obtained by Maillard and co-workers\textsuperscript{15} who investigated the dispersion of polystyrene grafted NPs in a polystyrene matrix. They found that the coverage of the NPs drives aggregation of the NPs within the films. Similar findings by Chevigny and co-workers\textsuperscript{16} further emphasized the role of the dimension of the grafted chains, its coverage and the interaction with the matrix. The symmetry of the particles and that of the coating drive different distributions of NPs have been shown by Douglas and Kumar for larger NPs.\textsuperscript{11}

In their efforts to understand the dispersion of NPs in structured polymer films, Matsen and Thompson investigated the effects of particle radius $R$, surface affinity, $\chi N$
(with N being the polymerization number and $\chi$, the Flory-Huggins parameter) using a self-consistent-field. They found that the NP primary location is controlled by its affinity to a specific block. For small NPs and low interactions, NPs migrate across domains with little or no barriers. Increasing $\chi N$ also increases the tendency for the particles to collect at interfaces in order to minimize the unfavorable contact between the A and B blocks. This interfacial trapping was observed by Lin at al. in their study of dispersing 4 nm CdSe NPs grafted with octylphosphine oxide in a poly-styrene-block-poly(2-vinylpyridine) copolymer.

These studies have laid the foundation for elucidating the phase behavior of NPs embedded in homo-polymers and diblock-copolymers in the low segregation limit, and for films thick enough to neglect interfacial effects on the matrix polymer. Significant technologies however, require films to be as thin as possible, for example for coatings for optical transparency and fast electron transfer. These types of current and potential coatings often consist of random co-polymers of highly segregating segments. The need for thin layers, together with the presence of highly segregating segments with significantly different affinities to the interfaces, result in a balance of additional effects that are absent in thicker films formed by polymers in the low segregation limit.

Herein we investigate the phase behavior of ultra-thin random co-polymer films that consist of semifluorinated segments, enriched with NPs. Unlike the dispersion of small NPs with short chain organic coating, in flexible Van-der Walls homo-polymers and di-blocks in the low segregation limit, translational and configurational entropic driving forces dominate the behavior, we found that the interactions of the highly
segregated segments of the co-polymers modulate the enthalpy of the interactions between the polymer molecules themselves.

Specifically, the current study probes the distribution of NPs simultaneously with changes of the structure of thin films, less than 1000 Å, of a random semifluorinated co-polymer, biphenyl- perfluorocyclobutyl (BPh-PFCB). The structure and interfacial behavior of semifluorinated block co-polymers are strongly affected by the high incompatibility of the protonated and fluorinated segments. The fluorinated segments are of a lower surface energy and segregate to the air interface. The high incompatibility between protonated and fluorinated layers drives segregation and induces ordering in the polymers even for short blocks, leading to the formation of internal interfaces. The NP chosen is polyhedral oligomeric silsesquioxane (POSS)\textsuperscript{21-25} shown in Figure 7.1. It consists of a Si-O-Si cage substituted by organic modifying groups on the Si. In the present study we refer to POSS substituted with \textit{iso} butyl groups as POSS. When substituted by a polymer chain on one site we refer to the NP as tethered POSS or t-POSS. The PFCB polymer series are co-polymers with short aromatic blocks bound by the perfluorocyclobutyl (PFCB) group. They form a variety of organized phases from liquid crystalline phases\textsuperscript{26} to surface induced ordered films with periodicities of 10-15Å\textsuperscript{27} with the fluorinated blocks segregating towards the air/polymer interface and the protonated segments segregating to the substrate/polymer interface.
Figure 7.1 The chemical structures of a) a random copolymer of Biphenyl Perfluorocyclobutyl (BPh-PFCB), b) POSS and c) POSS tethered to BPh-PFCB (t-POSS).

Neutron reflectometry (NR) has been used to resolve the distribution of NPs normal to the sample surface supported by AFM to explore the distribution of POSS and POSS tethered to a BPh-PFCB oligomer, in a thin semifluorinated matrix. The study has shown that for an NP on the size of the monomer, the incompatibility between protonated and fluorinated segments traps NPs within the surface induced layers.


**Experimental Section**

**Materials and Thin film preparation**

The BPh-PFCB polymers were synthesized by thermal [2+2] cyclopolymerization of trifluorovinyl biphenyl ethers as described by Iacono et al.\textsuperscript{28} The POSS was synthesized via condensation of commercially available isobutyl POSS triols with acetoxyethyltrichlorosilane and detailed characterization was previously reported.\textsuperscript{28} Polydispersity of BPh-PFCB is ca. 2.1 and that of the tethered (t-POSS) nanocomposite is ca. 3. The glass transition temperature ($T_g$) of the polymer is approximately 140\textdegree C. Solutions were made by dissolving 1wt$\%$ of the polymer and the different POSS in hexafluorobenzene, obtained from Sigma-Aldrich and used as received.

The BPh-PFCB: POSS mole ratio was maintained at 1:1 in both POSS and t-POSS precursor solutions. Films were spin-coated on oxidized silicon wafers and kept under house vacuum at 25\textdegree C for two days to evaporate remaining solvents. For temperature measurements, films were annealed for 12 hours under an N$_2$ environment and cooled to the room temperature.

Atomic force microscopy (AFM) measurements were carried out on a Multimode Nanoscope IIIa in tapping mode. Samples were studied under ambient temperature, pressure and humidity. A vibration isolation system was used to minimize the noise generated from the environment. AFM images were analyzed using nanotech WSxM software (Version 5.0).\textsuperscript{29}
Neutron reflectivity (NR) measurements were performed on the surface profile analysis reflectometer (SPEAR), which is a time-of-flight instrument, covering wavelength (\(\lambda\)) from 1.5 to 16Å, at the Lujan Neutron Scattering Center at Los Alamos National Laboratory. The reflectivity patterns were collected normal to the sample surface as a function of momentum transfer \(q\), where \(q=4\pi\sin\theta/\lambda\) and \(\theta\) is the incident angle of the incoming neutron beam. The data were normalized to the incident beam intensity (\(I_o\)) to obtain reflectivity (\(R\)), where \(R = I/I_o\).

Multilayer recursive Parratt formalism\(^{30}\) was used to model the data, which is available in the Motofit software \(^{30}\) with generic optimization to obtain the best least square fit. Scattering length densities (SLDs) of BPh (1.96x10\(^{-6}\) Å\(^{-2}\)), PFCB (4.59x10\(^{-6}\) Å\(^{-2}\)) and POSS (5.92x10\(^{-7}\) Å\(^{-2}\)) were used as starting values. Data were fit to the minimum number of layers, which are 8 or 9 layers for the current system to provide a physical fit with an accuracy of \(\chi^2 < 0.09\).
Results and Discussion

The result section will first introduce AFM observations of lateral morphology of thin films of the polymer and a representative nanocomposite. The results of neutron reflectometry for the pristine polymer, POSS nanocomposite and t-POSS nanocomposite, will then be presented, followed by comparison of parameters derived from the reflectometry experiments.

Figure 7.2 AFM images of pristine BPh-PFCB (Poly) and t-POSS nanocomposite thin films annealed at 25°C and 140°C. The somewhat ill-defined boundaries of domain within the images are a result of low interfacial energies due to the semifluorinated nature of the polymer.
Formation of continuous films of the polymer, that do not dewet, requires casting from solutions containing at least 1wt% polymer in hexafluorobenzene. This solvent is among the very few that dissolve both the polymer and the NPs. AFM studies of fully continuous films cast from these solutions exhibit homogenous lateral morphology without any distinctive features. While continuous film exhibit featureless images, aggregates are observed in thin, partially wetting domains of the pristine polymer film at 25°C, with average domain sizes of 150-200 Å, as shown in Figure 7.2a. Upon annealing at 140°C, (Figure 7.2b) which is the $T_g$ of the polymer, the domains observed at the thin edges coalesce into larger structures, which readily dewet. These aggregates are depicted by small angle neutron scattering studies in solutions of the polymer, t-POSS and polymer-POSS. The polymer is soluble in the hexafluorobenzene, however the affinity of the two blocks to the solvent remains sufficiently different to drive aggregation even in dilute solutions. These aggregates coalesce into continuous films for slightly thicker films as will be shown in the analysis of the neutron reflectometry measurements.

The nanocomposite of t-POSS / BPh-PFCB thin films behave qualitatively similar to the pristine polymer, as observed in the AFM images in Figure 7.2c and d. The continuous films are featureless and aggregates are detected at the edges of dewetted regimes. The aggregates observed are a bit larger, and slightly less correlated than those of the neat polymer.
Figure 7.3 The reflectivity $R$ and $R(q)q^4$ vs. $q$ as a function of momentum transfer vector $q$ of films annealed at the indicated temperatures. a, b correspond to BPh-PFCB films, c, d to POSS- BPh-PFCB films and e, f for t-POSS BPh-PFCB films. The symbols correspond to the experimental data and the solid lines to the results of the best fitted reflectivity model.
In contrast to studies of “brush” grafted NPs, in homopolymers and co-polymers in the low segregation limit, no lateral association of the NPs is observed at temperatures below the dewetting point. This is particularly surprising in view of prior prominent studies 11,15,16,17 that have shown that small NPs cluster as a network across the films or at the interfaces. In the system under consideration, both the fluorinated segments and the NPs are expected to segregate to the interface. The fluorinated segments tend to migrate to the interface due to predominantly enthalpic interactions.27 The surface composition of semifluorinated polymer liquids is a result of the competition between entropic and enthalpic interactions where at lower temperatures predominantly enthalpic interactions drive the fluorine to the interfaces and with increasing temperature further mixing enhances entropy and drives some of the protonated segments to the interface. This has been clearly shown by Pierce at al. 32 for liquid semifluorinated alkanes. With increasing temperature, the hydrogenated segments, which are smaller and more mobile, migrate to the interface. With both components at the air interface, the NPs do not aggregate.

The distribution of NPs normal to the surface was probed by NR experiments. These measurements followed the distribution of fluorinated and protonated segments in BPh-PFCB while tracking the location of the nanoparticles. Three types of thin films including a pristine polymer, a POSS-polymer thin nanocomposite and t-POSS polymer thin films were all prepared from solutions of identical concentrations, cast under similar conditions. Under identical conditions, the films of different thicknesses were formed with the pristine polymer films were the thinnest and that of t-POSS were the thickest.
We attribute the changes to small differences in viscosity of precursor solutions. All films were sufficiently thick to form homogenous continuous layers.

Representative specular NR data of BPh-PFCB polymer film and two of its nanocomposites as a function of annealing temperature are presented in Figure 7.3a-f. Plotting the data in the form of \( R(q)q^4 \) vs. \( q \); a presentation that takes advantage of the fact that the reflectivity decreases with \( q^{-4} \), reveals details that track the NPs as well as changes in the polymer structure. The decay of the curves of the reflectivity vs. \( q \) plots show that the pristine polymer film is smoother than that of the nanocomposites. For all three films, the thickness decreases following annealing above \( T_g \). The critical angle shifts to higher \( q \) and the intensity of the fringes increases. These changes will be further discussed, following introduction of the full analysis of the data. The data were analyzed accounting for the dimensions of the protonated BPh (~10 Å) and fluorinated PFCB (~6 Å) segments, allowing multiple layers formation normal to the surface.

The reflectometry patterns of the pristine polymers are presented in Figure 7.3a and b. The pristine polymer profiles, derived from the modeled reflectometry, are presented in terms of SLDs in Figure 7.4a. The higher and the lower SLD values in the profiles correspond to the fluorine rich and hydrogen rich domains respectively. At 25°C, traces of layering is observed at the air/polymer and substrate/polymer interfaces where alternating PFCB rich and BPh rich layers with periodicities of ~ 10 – 15 Å appeared closer to the air/polymer interface with more PFCB segments at the polymer-air interface. The solid oxide interface is rich with BPh however layering is less pronounced compared
with the air/polymer interface. Surface induced layering propagates for ~100 Å into the center at both interfaces.

![Image](image.jpg)

**Figure 7.4** a) SLD profiles of BPh-PFCB normal to the thin film surface as a function of annealing temperature. The profiles are presented in units of SLD and are shifted vertically for clarity. Schematic representation of the distribution of BPh and PFCB segments closer to the air/polymer and substrate/polymer interfaces b) before and c) after annealing.

With increasing temperature above $T_g$ of the polymer, the film thickness decreases and the layer boundaries become more defined, as observed from the increase in the amplitude of the fringes. The values of the critical angle shows that the air interface becomes more fluorine rich, as the temperature is elevated above $T_g$. The film remains stable for ~45°C above $T_g$, and then dewets. The enhanced fluorine content at the interface is consistent with the fact that it became extremely hard to detect AFM images above $T_g$. A schematic representation of the polymer film as cast and after annealing is given in Figure 7.4b and c. These results are in agreement with our previous studies on
PFCB polymers\textsuperscript{27}, which have shown the fluorinated segments tend to segregate towards the air/polymer interface and protonated segments move towards the SiO\textsubscript{2} interface.

**Figure 7.5** SLD profiles normal to the thin film surface for BPh-PFCB (Poly) and Poly-POSS systems at the indicated annealing temperatures. The profiles are presented in units of SLD and are shifted vertically for clarity. The x axis is given in absolute value of the distance from the air and solid interfaces.

Two types of NPs were then incorporated into the polymer films: a POSS cages decorated with short isobutyl chains; and t-POSS, a cage decorated on one site with the polymer chain. NR patterns for thin films of POSS/BPh-PFCB thin films (Poly-POSS) are presented in Figure 7.3c-d, together with the best fits obtained from a multilayer model.

The density profiles derived from the best fits are given in Figure 7.5 along with the density profiles of the pure polymer. Similar to the pristine polymer, interfacial layers are observed in as cast films. The air/polymer interface is POSS-rich as shown by the
lower SLD values. Accounting for the SLD values of the polymer however, while the POSS tend to migrate to the interface, both the NPs and significant amount of the polymer remain at the interface. While the POSS NPs migrate towards the interfaces, a close inspection shows that with increasing temperature and mobility of the NPs, their location becomes commensurate with the internal induced layers, where the center of the film consists predominantly of the polymer.

In contrast to the phase diagram of NPs blended in homo polymers,10-11, 15, 17 where NPs grafted with tethers similar in size to the polymer statistical segments cluster, herein the NPs segregate into the interfacial induced layers. The segregation to internal interfaces is consistent with the prediction of Matsen and Thompson.20 They have shown that with increasing $\chi_N$ the tendency for the particles to collect at interfaces in order to minimize the unfavorable contact between the A and B blocks increases. It is though rather unexpected that the NPs will migrate into regions formed by such small segments, and is attributed to the large $\chi$ between the protonated and fluorinated segments.

With the observation that in random co-polymers in the high segregated limit POSS NPs migrate to internal interfaces, the NP was tethered on one site to the matrix polymer chain and the behavior of the thin film of the composite was followed as a function of temperature at temperatures across $T_g$ of the polymer. Herein tethering one chain of the polymer matrix affects not only the interaction of the NP with the matrix, but also influences the effective symmetry of the NP.
The interfacial region of the density profiles normal to the thin film surface a) for BPh-PFCB (Poly) and t-POSS; b) for Poly-POSS and t-POSS, systems annealed at the indicated temperatures. The SLD profiles are shifted vertically for clarity. The x-axes are presented in absolute value from the interfaces.

Reflectometry patterns of t-POSS in BPh-PFCB and their analysis are shown in Figure 7.3e and f. The interfacial regions of the density profiles of t-POSS thin film composites are shown in Figure 7.6 a-b. Similar to blended POSS NPs, the POSS migrates towards the internal interfacial regions, where distinctive layering of the polymer was observed. In contrast to the spherical protonated POSS, t-POSS enhances the layering of the polymer itself. With increasing temperature, these layers become significantly more defined in comparison with the pristine polymer as well as to blended POSS. The thickness of internal layers is slightly increased due to the accumulation of NPs. In contrast to POSS containing thin films where the NPs migrates to surface induced internal interfaces, t-POSS remains distributed across the films, inducing further
layering. The BPh-PFCB tether together with the tendency of the NPs to migrate to internal interfaces, enhanced layering of the nanocomposite.

The changes in the overall thickness of the films, the interfacial composition and internal segregation are compared for the pristine polymer, POSS and t-POSS nanocomposites. The normalized film thicknesses across $T_g$ of the bulk are shown in Figure 7.7a, and the critical angle of the films is shown in Figure 7.7b. The thickness of all three films decrease as the temperature approaches $T_g$ of the polymer. The changes in the thickness of the pristine polymer and t-POSS nanocomposite are rather similar in magnitude whereas the POSS nanocomposite film becomes slightly thinner. The decrease in film thickness is attributed to rearrangements that take place from films that consist of aggregates trapped from solutions to multi-layers, where the high segregation between the fluorinated and protonated segments couples with interfacial forces drive their formation.

The critical angle increases with temperature. The values of the critical edge for the pristine polymer are higher than those of the nanocomposites and increase with temperature. However comparing the values of the pristine polymer with that of the fluorinated segments it becomes apparent that the air interface consists of both fluorinated and protonated segments. This compounded nature of the interface has been observed computationally in semifluorinated alkanes.$^{32}$
Figure 7.7 a) Normalized film thickness as a function of annealing temperature b) critical angle as a function of temperature for Poly (▲), Poly-POSS (♦) and poly t-POSS (■)

While the overall film thickness is hardly affected above $T_g$, internal rearrangements take place. The migration of different species within the film is reflected in changes of the amplitude of the fringes. Figure 7.8 presents the changes of the amplitude of three fringes in the patterns of pristine polymer film, that with POSS, and that with t-POSS. The 1$^{\text{st}}$, 3$^{\text{rd}}$ and 6$^{\text{th}}$ fringes were chosen for each of the films to represent a broad range of dimensions from that of the entire film to that of the polymer segments. The amplitude changes at a different rate (slope of the curve) below and above $T_g$ in all $q$ values. The rate of changes at different dimensions (at different $q$ values) differs for the three films. The rate of changes in the t-POSS nanocomposite pattern, where the NPs are confined to the polymer via the tether, is slower than that of the other films. Further dynamic experiments are required to elucidate the correlation between the structure of the polymer-NP nanocomposites and the specific motions.
Figure 7.8 Amplitude A in units of $Rq^4$, of NR data for 1$^{\text{st}}$, 3$^{\text{rd}}$ and 6$^{\text{th}}$ fringes at the indicated $q$ values as a function of annealing temperature for a) pristine BPh-PFCB polymer, b) Poly-POSS nano composite thin film and c) t-POSS nano composite thin film.

Conclusions

The phase behavior of nanoparticles in highly segregated semifluorinated PFCB polymers was probed by neutron reflectometry, using POSS NPs and POSS tethered to one matrix polymer chain. Neutron reflectometry allowed us to probe dimensions that are comparable to the statistical segment of the polymer and the NPs, taking advantage of the differences in scattering length densities between the fluorinated and protonated segments and probe changes on a length scale that is rarely accessible. In homo and diblock-copolymers in the low segregation limit, small NPs such as POSS, tethered to short chains are expected to either phase segregate or migrate to the interfaces. In thin films of PFCB polymers however, interfacial effects coupled with the inherent segregation of
fluorinated and protonated segments, resulted in layering of the polymer at interfaces. These layers in turn, controlled the dispersion of the NPs. In contrast to the distribution of NPs in polymers at the low segregation limit, in these semifluorinated polymers the NPs tend to align within the interfacial induced layers.

The effects of the highly segregated segments became more pronounced when one polymer chain is tethered to the POSS. Though this asymmetric particle migrates into the surface induced layers, the migration is significantly slower than that of non-tethered particles. In addition, further layering in comparison with the pristine films of the polymers, is observed. Independent of the presence of the NPs, the segregation of the F-segment dominates the behavior of the polymer where the NP distribution is affected by both entropy and the inherent interfacial layering of the polymer. The study revealed that the highly segregating nature of the matrix polymer is fundamental to the dispersion of NPs in this semifluorinated matrix.

References


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CHAPTER 8

Semi-Fluorinated Polymer Mediated Nanoparticle Assembly

Abstract

Dispersion of polyhedral oligomeric silsesquioxanes (POSS) nanoparticles (NPs) modified with short fluorinated grafts in a random copolymer of biphenyl-perfluorocyclobutyl (BPh-PFCB) was studied using neutron reflectometry. Dispersion of NPs in thin films is challenging due to the segregation of NPs to the external interfaces. Introducing fluorinated NPs to a semi-fluorinated polymer will increase the compatibility between the NPs and the fluorinated block and at the same time preference of low surface energy of fluorine drives NPs to the air/polymer interface. The current study has shown that by controlling the interaction of the NPs in highly segregating random copolymers will allow controlling the location of NPs in thin films. BPh-PFCB shows surface induced layers where the fluorinated segments migrated towards the air/polymer interface while protonated segments moved to the substrate/polymer interface. In the blends, POSS cages associated at both external and internal interfaces and center of the film is free of NPs. By modifying the POSS cages with a single matrix polymer chain (t-POSS) enhances the distribution of NPs throughout the thin film and NPs are associated more at the internal polymer interfaces. In contrast to the previous study (chapter 7), more t-POSS associated at the air/polymer interface due to the presence of short fluorinated grafts on NPs.
Introduction

Properties of polymer thin films can be tailored by embedding nanoparticles (NPs) into the system. Such nanocomposites thin films have technological significances in different applications such as organic photovoltaic cells, chemical sensors, hydrophobic and oleophobic coatings and moisture/gas resistant coatings. Controlling the distribution of NPs in polymers is the key to the above property enhancements. However, dispersion of NPs in polymers remains a challenge due to the segregation of NPs to the external interfaces and clustering of NPs within the matrix.

Polyhedral Oligomeric Silsesquioxanes (POSS) NPs, which consists of Si-O-Si polyhedral cage surrounded by organic chains, have been recently utilized to make nanocomposites with controlled surface and bulk properties including control thermal and oxidative resistance, enhances mechanical properties and reduces dielectric constant. Silicon atoms at the corners of the POSS cages can be functionalized with variety of organic ligands, which facilitates the dispersion of NPs in polymer matrix by increasing the compatibility.

Understanding the entropic and enthalpic contributions that govern the distribution of NPs in polymers will allow obtaining nanocomposites with well defined characteristics. The distribution of the NPs is a balance between translational and configurational entropic driving forces that often drive segregation of the NPs, and enthalpy resulting from direct interactions of the organic tethers on the NPs with the
polymer matrix. Several studies have investigated the dispersion of POSS in thin films of homopolymers such as polystyrene and polypropylene, where NPs were segregated to air/polymer and substrate/polymer interfaces providing dewet-resistance thin films. By chemically tethering NPs to block co-polymers will force NPs to follow the segregation tendency of polymers. Zheng et al. obtained multilayered nanocomposites with POSS rich and POSS poor layers using random copolymers of poly-butadiene, where POSS cages were directly attached to the polymer backbone of one of the blocks.

The surface structure of a multicomponent system with different surface energies is not the same as its bulk structure. Such phenomenon is strongly enhances with the presence of fluorinated and hydrogenated segments in the same polymer. Strong incompatibility, which is defined by $\chi N$ where $\chi$ is the Flory interaction parameter and N is the degree of polymerization of the blocks, between fluorinated and hydrogenated blocks drives phase separation of blocks to form specific aggregates. Due to high $\chi$ of the semi-fluorinated polymer, small variation in N results in different bulk structures. Studies have shown that fluorinated blocks are more hydrophobic and prefers medium with lower surface energies compared to the protonated blocks, which results in segregation of fluorinated segments toward the interfaces with lower surface energies. Wynne et al. have shown that by adding small amount of F atoms to the fluorinated block can significantly change the surface energies of the semi-fluorinated polymers and they form well ordered liquid crystalline fluorocarbon domains on the surface of the films. Incompatibility between fluorinated and protonated domains and the segregation
tendency of fluorinated blocks to the air/polymer interface results in multi-layers with F-rich and H-rich domains in semi-fluorinated thin films.\textsuperscript{21}

Studies have shown that in the presence of favorable interactions between NPs and specific blocks of the co-polymers can results in hierarchically ordered structures.\textsuperscript{22-23} Composto \textit{et al.} have shown that segregation of poly(methyl methacrylate) (PMMA) grafted Fe\textsubscript{3}O\textsubscript{4} NPs to the PMMA regions of the polystyrene-\textit{block}-PMMA thin films.\textsuperscript{24} They also discussed the effects of the relative sizes of the matrix polymer and the grafted chains, surface curvature of the NPs and sizes of the NPs to the dispersion of NPs in block copolymers.

The current study follows the distribution of POSS cages modified with short fluorinated groups in thin films of a semi-fluorinated random copolymer of biphenyl perfluorocyclobutyl (BPh-PFCB). The chemical structures of POSS and BPh-PFCB are illustrated in Figure 8.1. Due to the inherent ordering of the polymer and the differences in surface energies of the fluorinated and protonated segments, BPh-PFCB formed surface induced layers with periodicities of 10-15 Å. The fluorinated blocks segregated towards the air/polymer interface while protonated segments migrated towards the substrate/polymer interface. Two different nanocomposites were studied. In one of the nanocomposites, one silicon atom of the POSS cage was chemically tethered to end of the BPh-PFCB (t-POSS) (Figure 8.1c) and the other had free POSS cages in the matrix polymer (Poly-POSS). Neutron reflectometry (NR) has been used to measure the
distribution of different components normal to the sample surface and AFM studies were carried out to follow the changes in surface morphology upon annealing.

In our previous work,\(^{25}\) (chapter 7) we studied the dispersion of POSS cages modified with short protonated groups in BPh-PFCB, where we observed differences in NP dispersion in Poly-POSS and t-POSS systems. In the non tethered system (Poly-POSS), NPs were migrated to the air/polymer and substrate/polymer interfaces as well as to the internal polymer interfaces. When POSS tethered to one chain of the matrix polymer, the NPs not only migrate to the internal interfaces but also induce further layering within the thin film. In contrast to the previous study the preference of NPs to the air/polymer interface is enhanced by introducing fluorinated grafts to the POSS cages.

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\text{Figure 8.1 The chemical structures of a) random copolymer of Biphenyl Perfluorocyclobutyl (BPh-PFCB), b) POSS cages modified with R groups and c) POSS tethered to BPh-PFCB (t-POSS).}
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Experimental section

Materials and Thin film preparation

The BPh-PFCB polymers were synthesized by thermal [2+2] cyclopolymerization of trifluorovinyl biphenyl ethers as described in reference 26. The POSS was synthesized via condensation of POSS triols with acetoxyethyltrichlorosilane and detailed characterization has been reported elsewhere. Polydispersity of the BPh-PFCB is ~2.1 and for the tethered POSS nanocomposite is ~3. The glass transition temperature ($T_g$) of the polymer is around 140°C.

Solutions were made by dissolving 1wt% of the polymer and the different POSS in hexafluorobenzene, obtained from Sigma-Aldrich and used as received. BPh-PFCB: POSS mole ratio was kept at 1:1 in both POSS and t-POSS precursor solutions. Solutions were spin-coated on oxidized silicon wafers and kept under house vacuum at 25°C for two days to evaporate the remaining solvents. For temperature measurements, thin films were annealed under N$_2$ environment for 12 hours and left films inside the oven until temperature falls down slowly to the room temperature.

Atomic force microscopy (AFM) measurements were carried out using Multimode nanoscope IIIa in tapping mode. Samples were studied under ambient temperature, pressure and humidity. A vibration isolation system was used to minimize the noise generated from the environment. AFM images were analyzed using nanotech WSxM software (Version 5.0).
Neutron reflectivity (NR) measurements were performed on the surface profile analysis reflectometer (SPEAR), which is a time of flight instrument covering wavelength (\( \lambda \)) from 1.5 to 16\( \text{Å} \), at Lujan Neutron Scattering Center at Los Alamos National Laboratory. The reflectivity patterns were collected normal to the sample surface as a function of momentum transfer vector \( q \), where \( q = 4\pi \sin \theta / \lambda \) and \( \theta \) is the incident angle of the incoming neutron beam. The data were normalized to the incident beam intensity (\( I_o \)) to obtain reflectivity (\( R \)), where \( R = I/I_o \).

Multilayer recursive Parratt formalism \(^{28}\) was used to model the data, which is available in the Motofit software \(^{29}\) with generic optimization to obtain the best least square fit. Scattering length densities of BPh (1.96\( \times 10^{-6} \text{Å}^{-2} \)), PFCB (4.59\( \times 10^{-6} \text{Å}^{-2} \)) and POSS (2.19\( \times 10^{-6} \text{Å}^{-2} \)) were used as starting parameters. Data were fit to the minimum number of layers, which are 8 or 9 layers for the current system that provided a physical fit with an accuracy of \( \chi^2 < 0.09 \).

**Results and discussion**

Representative AFM images of pristine BPh-PFCB at 25\(^{\circ}\)C and 140\(^{\circ}\)C are shown in Figure 8.2a and b. AFM studies of fully continuous films exhibit homogenous lateral morphology without any distinctive features. While continuous film exhibit featureless images, aggregates are observed in thin, partially wetting domains of the pristine polymer film at 25\(^{\circ}\)C, with average domain sizes of 150-200 \( \text{Å} \). Upon annealing at 140\(^{\circ}\)C, which
is the $T_g$ of the polymer, smaller domains combined to form larger cluster. The observed cluster sizes are comparable with the radius of gyration values of the spherical micelle observed in BPh-PFCB solutions.\textsuperscript{30} Origin of these aggregates is due to the segregation of incompatible fluorinated and protonated blocks in the co-polymer.

Figure 8.2c and d represents the AFM data of the films cast after introducing POSS to the virgin polymer in 1:1 mole ratio. The structure of the aggregates observed in pure polymer at 25°C is changed upon incorporating NPs. Similar to the pure polymer, aggregates of ca. 150Å were observed and they combined to form bigger and more defined aggregates upon annealing at 140°C.

**Figure 8.2** AFM images of pristine BPh-PFCB (Poly) and t-POSS nanocomposite thin films annealed at 25°C and 140°C.
NR was carried out to understand the distribution of components of the co-polymer and to follow the location of NPs perpendicular to thin film surface. BPh-PFCB co-polymer consists of short fluorinated and protonated blocks. As introduced in our previous study\(^\text{25}\) (chapter 7), BPh- PFCB polymer has shown layering closer to the interfaces. Such layering is attributed to the segregation of fluorinated segments towards the air/polymer interface and protonated segments to the substrate/polymer interface due to differences in surface energies. Incompatibility between protonated and fluorinated segments causes internal segregation and facilitates the layering induced at the interfaces.

**Figure 8.3** a) NR patterns of BPh-PFCB as a function of momentum transfer vector \(q\) for thin film annealed at the indicated temperatures. b) NR data and fits of BPh-PFCB in \(R(q)q^4\) vs. \(q\) representation. The symbols correspond to the experimental data and the solid lines to the results of the best fitting model

NR data of BPh-PFCB polymer film as a function of annealing temperature are illustrated in Figure 8.3a. In order to clearly see the changes, NR data were presented in \(R(q)q^4\) vs. \(q\) representation in Figure 8.3b, which enhances the visibility of small
differences in the data. Critical angle slightly moved towered higher $q$ upon annealing indicating rearrangements take place at interfaces. Amplitude of the fringes increases with annealing temperature due to the segregation of protonated and fluorinated segments. These rearrangements cause film to shrink for ca. 40Å.

![Figures](image)

**Figure 8.4** a) SLD profiles of BPh-PFCB normal to the thin film surface as a function of annealing temperature. The profiles are presented in units of SLD and are shifted vertically for clarity. Schematic representation of the distribution of BPh and PFCB segments closer to the air/polymer and substrate/polymer interfaces b) before and c) after annealing.

NR data were analyzed using a multi-layer model considering the formation of alternate layers with fluorine rich and proton rich domains parallel to the thin film surface. During the NR data analysis SLDs of PFCB and BPh and their segment sizes were used as initial parameters. These distributions of different components in the polymer thin films are presented in terms of SLD profiles. Calculated SLD of the fluorinated segment is higher than that of the protonated segment. Therefore, higher and
lower SLD values in the profiles correspond to the fluorine rich and hydrogen rich domains respectively. The SLD profiles of BPh-PFCB thin film are shown in Figure 8.4a. At 25°C layering with periodicities of ~ 10 - 15Å is observed at the air/polymer and the SiO₂/polymer interfaces. The air/polymer interface has more layers than the substrate/polymer interface. These layer thicknesses are matched with the monomer lengths of BPh (~10Å) and PFCB (~6Å). The air/polymer interface is rich with PFCB and SiO₂/polymer is rich with biphenyl groups. Layers get more pronounced upon annealing and they propagated into the film for ~100Å from both interfaces. The flat region in the middle of the profile is due to the presence of homogeneous distribution of fluorinated and protonated segments. These distributions of BPh and PFCB segments in thin film are schematically illustrated in Figure 8.4b and c.

Two types of NPs were introduced to the polymer. Both POSS cages were modified with short fluorinated grafts. In one of the systems, ends of the BPh-PFCB chains were directly attached to one of the silicon corners of the NPs and the rest of the silicon atoms of the POSS modified with short fluorocarbon groups (t-POSS) as shown in Figure 8.1. In the other system fluorinated POSS cages were blended with the virgin polymer (Poly-POSS) in 1:1 mole ratio.

NR data and the best fits for Poly-POSS are shown in Figure 8.5a. Slight changes in the critical angle and the changes in the amplitudes of fringes due to contrast enhancement are clearly observed in Figure 8.5b in $Rq^4$ vs $q$ representation. Figure 8.5c presents the corresponding SLD profiles obtained from the best fitted model along with the profiles for the pure polymer. The thicknesses of the pure polymer film and
nanocomposites are slightly different, which makes the simultaneous comparison of the SLD profiles at both substrate/polymer and air/polymer interfaces difficult. Therefore, zero thickness arbitrarily assigned from both air/polymer and substrate/polymer interfaces. The SLD at the center of the film hardly fluctuated. Therefore that region was excluded from the figure.

![Graphs showing neutron reflectivity patterns and SLD profiles](image)

**Figure 8.5** a) Neutron reflectivity patterns of the thin film of POSS blended with BPh-PF CB (poly-POSS) as a function of annealing temperature. b) Fitted reflectometry data shown in terms of $R_q$. c) SLD profiles of Poly and Poly-POSS normal to the thin film surface as a function of annealing temperature. The profiles are presented in units of SLD and are shifted vertically for clarity. The x axis is given in absolute value of the distance from the air and solid interfaces.
Initially at the air/polymer interface a broad hump was observed at 25°C. Starting from 120°C layering enhanced at the air/polymer interface and the SLD of the surface layer is lower than that of the pure polymer indicating presence of NPs. The substrate/polymer interface is more layered compared to the pure polymer. The SLD next to the substrate/polymer interface is lower than the pure polymer indicating presence of some NPs at that interface. The layer next to that with high SLD is rich with PFCB. The layer on top of that is rich with NPs and upon annealing more NPs segregate to this layer from the center of the film. Therefore we can conclude that the distribution of POSS cages is affected by the layering of the matrix polymer and NPs associated at the external interfaces as well as at the internal polymer interfaces. SLD of the center of the film for the blend is similar to the SLD of the virgin polymer indicating absence of NPs in this region.

Effects of tethering matrix polymer with NPs to the distribution of NPs were followed using t-POSS. NR data and the best fits for thin films of t-POSS are shown in Figure 8.6a. The critical angle slightly moved to higher $q$ upon annealing as shown in Figure 8.6b in $R(q)q^4$ vs $q$ representation, indicating changes in the chemical composition at the interfaces. Amplitude of the fringes increased upon annealing due to the segregation of fluorinated and protonated components.
Figure 8.6 a) Neutron reflectivity patterns of the thin film of t-POSS as a function of annealing temperature. b) NR data and fits in terms of $Rq^4$. c) SLD profiles of BPh-PFCB (Poly) and t-POSS normal to the thin film surface as a function of annealing temperature. The profiles are presented in units of SLD and are shifted vertically for clarity. The x axis is given in absolute value of the distance from the air and solid interfaces.

These NR data were fit to an eight-layer model and the corresponding SLD profiles are compared with SLD profiles of BPh-PFCB in Figure 8.6c. At 25°C t-POSS shows a broad hump at the air/polymer interface and has poor layering at lower temperatures compared to the pure BPh-PFCB. Layer formation is more pronounced after
annealing films above 150°C, which is slightly above the $T_g$ of the polymer. SLD at the air/polymer interface is comparably lower compared to the virgin polymer at temperatures above 150°C indicating presence of NPs on the surface. Similarly, segregation of NPs to the SiO$_2$/polymer interface was observed at temperatures above the $T_g$ of the polymer. The SLD gradient at SiO$_2$/polymer interface, which increases from SiO$_2$/polymer interface towards the center of the film, indicates higher concentration of NPs closer to the interface and lower concentration as moved towards the center of the film. Association of NPs at internal polymer interfaces was also observed in t-POSS system. In this system, NPs are chemically attached to the BPh-PFCB chain, which restricts the motion of NPs. When system is annealed above the $T_g$ of the polymer, polymer chains started to move and NPs inside the polymer matrix get freedom to segregate toward the interfaces. Segregation of NPs to the internal interfaces of BPh and PFCB decreases the SLD contrast that was observed in the pure polymer, which reduces the layering signature of the SLD profiles. SLD at the center of the film is lower in the t-POSS compared to the pure polymer, which confirms the existence of POSS cages at the center of the film.

Amplitudes of the reflectivity fringes are determined by the SLD contrast between different regions in the thin film. Migration of components of the polymer and NPs upon annealing results in change in contrast between domains, which reflect in the amplitudes of the fringes in Figure 8.7. Amplitudes of the 1$^{st}$, 3$^{rd}$ and 6$^{th}$ fringes were chosen to represent a broad range of dimensions from that of the entire film to that of the polymer.
segments. The rate of changes of amplitudes in the t-POSS nanocomposite, where the NPs are confined to the polymer via the tether, is slower than that of the other films.

**Figure 8.7** Amplitude ($A$) in units of $Rq^4$, of NR data for $1^{\text{st}}$, $3^{\text{rd}}$ and $6^{\text{th}}$ fringes at the indicated $q$ values as a function of annealing temperature for a) pristine BPh-PFCB polymer, b) Poly-POSS nano composite thin film and c) t-POSS nano composite thin film.

Comparison of the Poly-POSS and the t-POSS thin films are schematically shown in Figure 8.8. In case of the blend, fluorinated NPs moved to the interfaces even below the $T_g$ of the polymer and show enrichment of NPs especially at the air/polymer interface at all temperatures and some NPs are associated at internal polymer interfaces as show in Figure 8.8a. In t-POSS, NPs are not free to move below the $T_g$ of the BPh-PFCB and shows less segregation of NPs. When annealing temperature increases above the $T_g$ of the polymer, segregation of the NPs increases and enhanced layering was observed as shown in Figure 8.8b. Compared to our previous study of t-POSS with protonated grafts (chapter 7), t-POSS with fluorinated grafts in the current study has less layering and comparably higher NP density at the air/polymer interface.
Figure 8.8 Schematic representations of distributions of POSS cages and components of the BPh-PFCB in a) Poly-POSS and b) t-POSS thin films.

Conclusions

Distribution of POSS cages in a semi-fluorinated random copolymer was followed as a function of annealing temperature. The matrix polymer itself associated into surface induced layers closer to interfaces with the thickness of monomer units. Fluorinated segments migrated towards the air/polymer interface due to the lower surface energy of the fluorine while protonated segment moved towards the SiO$_2$/polymer interface. In the blends (Poly-POSS), NPs segregated to both air/polymer and substrate/polymer interfaces and some NPs associated at internal polymer interface while keeping the center of the film free with POSS cages. When polymer chain is tethered to the NP, POSS has less freedom to move within the thin film due to the confinement of
polymer chain to internal layers, which results in association of NP at internal polymer interfaces more compared to the Poly-POSS. Segregation of NPs to the air/polymer interface is further induced by the short fluorinated grafts on the POSS cages compared to the protonated grafts on POSS as discussed in chapter 7.

References


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CHAPTER 9

Control Dispersion of Water in Thin Films of Semi-Fluorinated Polymer/POSS Nanocomposites

Abstract

The current work investigates the dispersion of D$_2$O molecules in thin films of a semi-fluorinated random copolymer of Biphenyl Perfluorocyclobutane (BPh-PFCB) in the presence of Polyhedral Oligomeric Silsesquioxane (POSS) nanoparticles (NPs). Distribution of solvent molecules was affected by the way that NPs dispersed within the film. In thin films, BPh-PFCB shows layering due to the lower surface energy of the fluorinated component, which migrate towards the air surface, and incompatibility between the BPh and PFCB segments. POSS cages have preference to migrate to the interfaces. By tethering a single matrix polymer chain to NPs enhances the dispersion of POSS cages in the matrix polymer and minimizes segregation to external interfaces. In the pristine BPh-PFCB polymer film, D$_2$O mainly accumulated at the substrate/polymer interface. In nanocomposites, water penetration correlates with the amount of NPs present at the polymer interfaces and the way they distributed within the matrix polymer, where in the presence of dense NP layer at the air/polymer interface minimizes the solvent accumulation in the matrix polymer.
Incorporation of small amount of nanoparticles (NPs) into polymers is used to control the dispersion of solvents in polymers in variety of applications including hydrophobic/oleophobic coatings, material with enhanced barrier properties and selective permeable membranes.\textsuperscript{1-7} Distribution of a given solvent in polymer nanocomposites is governed by the concentration of NPs, how NPs distributed within the matrix polymer as well as the inherent polymer characteristics such as molecular weight of the polymer, glass transition temperature ($T_g$) and modulus of the polymer.\textsuperscript{8-14} The goal of the current study is to understand the effects of different NP distributions on solvent dispersion in polymer thin films.

Solvent distribution in thin film is different from the bulk polymer due to the contribution from interfaces.\textsuperscript{15-16} He et al. has reported that the diffusivity of solvent in thin ionomer films at initial stages are significantly slower compared to the bulk due to interfacial effects.\textsuperscript{16} Polymer chains at the air/polymer interface have less restriction to move compared to the chains near the substrate, which results in more swelling of the film closer to the air/polymer interface with respect to the polymer chains near substrate/polymer interface.\textsuperscript{17} The nature of the interaction between the solvent and the substrate that polymer coated on influence the solvent accumulation at the substrate/polymer interface.\textsuperscript{13-14, 18} For example, hydrophilic substrates such as SiO$_2$ have more water accumulation as film thickness decreases. Accumulation of solvent molecules at the substrate/polymer interface also influenced by the modulus of the polymer chains,
where rubbery polymers reduce the solvent accumulation due to their ability to change the chain conformation depending on the nature of the environment.\textsuperscript{12}

Addition of NPs to the polymer matrix reduces the rate of solvent absorption in nanocomposites.\textsuperscript{8-9} However dispersion of NPs in polymers remains a challenge due to the aggregation tendency of NPs and phase separation from polymers matrix owing to their incompatibilities.\textsuperscript{19} The strategy of confining NPs into specific domains of structured polymers such as block copolymers can be used to make nanocomposites with controlled NP distributions.\textsuperscript{20-22} Theoretical and experimental studies have shown that in the presence of favorable interactions between NPs and specific block of the copolymer result in hierarchically ordered structures.\textsuperscript{20-22} Other factors that control the dispersion of NPs in polymers include the relative sizes of the NPs with respect to block size, grafting chain density on the NP surface and the relative sizes of the grafted chains and the matrix polymer.\textsuperscript{23-25} By controlling above parameters one can achieve a wide variety of NP distributions in copolymer with specific phase separated structures.

Semi-fluorinated polymers are one of the best candidates for providing different morphologies by introducing small variation to the chemical composition of the blocks.\textsuperscript{26} Such phenomenon is observed due to the high incompatibility between fluorinated and protonated segments of semi-fluorinated polymers. Incompatibility between fluorinated and hydrogenated domains and the segregation tendency of fluorinated blocks to the air/polymer interface and hydrogenated blocks to substrate/polymer interface result in multi-layers with F rich and H-rich domains in thin films.\textsuperscript{27} Different solvent distribution may achieve in semi-fluorinated polymer thin films. Presence of fluorine on the surface
provides hydrophobic and oleophobic characters to the surface. Strong segregation between blocks makes strong stretching of polymer chains, which favors the accumulation of solvents at the interfaces between the blocks.

In this study, we focus on the distribution of D$_2$O molecules in nanocomposite thin films of Biphenyl Perfluorocyclobutyl (BPh-PFCB) and Polyhedral Oligomeric Silsesquioxanes (POSS) NPs. POSS, which consists of Si-O-Si inorganic cage surrounded by organic corona chains, has been recently utilized to make nanocomposites with controlled NP dispersion in polymers. In the current study POSS cages were decorated either with short fluorinated or short protonated chains. Due to the differences in surface energies, protonated and fluorinated blocks in the random copolymer segregated into layers with periodicities of 10-15 Å at the air/polymer and substrate/polymer interfaces. Similar phenomenon was observed for a random copolymer of methylstilbene – perfluorocyclobutane by Perahia et al. In our previous studies we have utilized this layering phenomenon to disperse POSS particles into specific interfaces in thin polymer films (chapter 7 and 8). In order to control the distribution of NPs in BPh-PFCB, two sets of nanocomposites were studied. In one of the systems a matrix polymer chain was tethered to one of the corners of the POSS cage (t-POSS) as shown in Figure 9.1c, and the other system had free POSS particles in the matrix polymer (Poly-POSS).

Distribution of D$_2$O molecules in thin films as a function of D$_2$O exposure time was followed by neutron reflectivity (NR) technique, which provides enough contrast
between components of the polymer and the solvent molecules to follow the distribution of D₂O in thin films.

Figure 9.1 The chemical structures of a) random copolymer of Biphenyl Perfluorocyclobutyl (BPh-PFCB), b) POSS cages modified with R groups and c) POSS tethered to BPh-PFCB polymer (t-POSS).

Experimental section

Materials and thin film preparation

The PFCB polymers were synthesized by thermal [2+2] cyclopolymerization of trifluorovinyl biphenyl ethers as described in reference 35. The POSS was synthesized via condensation of POSS triols with acetoxyethyltrichlorosilane and detailed
characterization has been reported elsewhere.\textsuperscript{35} Polydispersity of the BPh-PFCB is $\sim$2.1 and for the tethered POSS nanocomposite is $\sim$3. The glass transition temperature ($T_g$) of the polymer is around 140$^\circ$C. POSS modified with isobutyl side chains were obtained from Hybrid Plastics.

POSS tethered and blended to BPh-PFCB were dissolved in hexafluorobenzene obtained from Sigma-Aldrich and used as received to get 1.0wt\% solutions. In the blend, POSS: BPh-PFCB mole ratio was kept at 1:1. Solutions were spin-coated on oxidized silicon wafers and kept under house vacuum at 25$^\circ$C for two days to evaporate the remaining solvents.

**Neutron Reflectivity Experiment**

NR experiments were performed on the surface profile analysis reflectometer (SPEAR), which is a time-of-flight instrument with the wavelength ($\lambda$) range from 1.5 to 16Å, at the Lujan Neutron Scattering Center at Los Alamos National Laboratory. Specular reflectivity profiles of thin films were collected as a function of momentum transfer vector ($q$) normal to the sample surface, where $q=4\pi\sin\theta/\lambda$. $\theta$ is the angle of the incident neutron beam. The raw data were normalized to the incident neutron beam intensity ($I_0$) to obtain reflectivity ($R$), where $R=I/I_0$.

The samples were kept inside an aluminum chamber. After obtaining the reflectivity profile for the dry samples, 1 ml of D$_2$O was introduced into the chamber without directly touching the thin film and start measuring the time. Then the reflectivity
data were collected as a function of time. The final data set for each of these samples were taken after 8 hours of D$_2$O exposure.

Multilayer recursive Parratt formalism$^{36}$ was used to model the data, which is available in the Motofit software$^{37}$ with generic optimization to obtain the best least square fit. Scattering length densities of BPh ($1.96\times10^{-6}$ Å$^{-2}$), PFCB ($4.59\times10^{-6}$ Å$^{-2}$) and POSS ($2.19\times10^{-6}$ Å$^{-2}$ and $5.92\times10^{-7}$) were used as starting values. Data were fit to the minimum number of layers, which provided a physical fit with an accuracy of $\chi^2 < 0.09$.

**Results and discussion**

Neutron reflectivity data along with the best fitting models for the pure BPh-PFCB are given in Figure 9.2a. Symbols represent the data and solid lines are the best fits obtained by fitting data to a 6-layer model. The 6-layer was the simplest model which allowed us to properly reproduce all the features of the NR spectrum without over parametrizing the problem. The fringes in the reflectivity data are due to the constructive and destructive interferences occurring from different interfaces of the thin film. The film thickness slightly increases with increasing the solvent exposure time indicating swelling due to penetration of D$_2$O molecules into polymer film. Fringes become more visible in D$_2$O exposed samples compared to dry film, which indicates increase in contrast owing to association of D$_2$O molecules at internal interfaces of the polymer. These changes are
more clearly visible in the $R(q)q^4$ representation in Figure 9.2b, a format of data presentation that offers an enhanced visibility of the interference fringes.

**Figure 9.2** a) NR data of the thin film of BPh-PFCB as a function of D$_2$O exposure time. The symbols correspond to the experimental data and the solid lines are the best fitting model. b) NR data in $R(q)q^4$ vs. $q$ representation. c) SLD profiles of BPh-PFCB normal to the thin film surface as a function of D$_2$O exposure time.
SLD distributions normal to the thin film surface of BPh-PFCB as a function of D$_2$O exposure time are given in Figure 9.2c. The SLD of the PFCB segments (4.59x10$^{-6}$ Å$^{-2}$) is higher than that of the BPh (1.96x10$^{-6}$ Å$^{-2}$) segments. Therefore, higher SLD values in the profile of the dry film represent the fluorine rich and the lower SLD regions to the BPh rich domains. Air/polymer interface of the dry film is rich with PFCB and the substrate/polymer interface consists of more BPh segments. These different segregations are attributed to the differences in surface energies of the fluorinated and hydrogenated segments, where lower surface energy of the fluorinated segments drive PFCB segments to the air/polymer interface. In addition to the differences in surface energies, incompatibility between PFCB and BPh enhances the segregation of components, which results in layering. Layering is more pronounced at the air/polymer and SiO$_2$/polymer interfaces and they decay as they penetrate into the center of the film.\textsuperscript{33,34}

Overall SLD of the profiles increased as films were exposed to D$_2$O vapor due to higher SLD of D$_2$O, where the SLD of D$_2$O is 6.33x10$^{-6}$ Å$^{-2}$. This indicates the penetration of D$_2$O molecules throughout the film. However, SLD increments in different areas of the film are not the same indicating uneven distribution of D$_2$O molecules in the film. SLD at the SiO$_2$/polymer interface increased more compared to the other areas of the thin film with solvent exposure time. The thickness of the D$_2$O rich layer at the SiO$_2$/polymer interface is also increased with time. Accumulation of D$_2$O at the SiO$_2$/polymer interface is due to the hydrophilic nature of the substrate. Center of the film has less D$_2$O accumulation. Small amount of D$_2$O accumulated at the air/polymer interface compared to the substrate/polymer interface.
Following sections will introduce the solvent penetration in BPh-PFCB in the presence of NPs. Different NP distributions were achieved in our previous studies by tailoring the interactions between POSS cages and the BPh-PFCB matrix.\textsuperscript{33, 34} Better NP distributions in entire film were achieved when NP decorated with a single matrix polymer chain and they show layering of the NPs at internal polymer interfaces. When NPs are not modified with the matrix polymer, they segregated to the air/polymer and substrate/polymer interfaces more compared to the association at internal interfaces and segregation was enhanced upon annealing the films above the $T_g$ of the polymer. The main objective of the current study is to understand the effects of different NP distributions on the solvent distribution in BPh-PFCB polymer thin films.

First we will focus on the thin films with dispersed NPs or NPs with single polymer tether. These tethered NPs were modified either with short hydrocarbon (t-POSS(H)) or short fluorocarbon (t-POSS(F)) chains. Figure 9.3a and b show the neutron reflectivity data for the t-POSS(H) system as a function of solvent exposure time. The amplitude of the fringes increases with increasing the solvent exposure time indicating increasing SLD contrast due to accumulation of D$_2$O at interfaces. As indicated in Figure 9.3c and d the enhancement of the SLD contrast in t-POSS(F) is comparably smaller indicating less penetration of solvent molecules into the thin film compared to t-POSS(H).
Figure 9.3 a) Neutron reflectivity data of the thin film of t-POSS(H) and c) t-POSS(F) as a function of D$_2$O exposure time. The symbols correspond to the experimental data and the solid lines are the best fits for 6 layer model. b and d are the $R(q)q^4$ representation of data for t-POSS(H) and t-POSS(F) respectively.

Above data were fitted to a 6 layer model and the corresponding SLD distributions along with the SLD profiles for the pure polymer are shown in Figure 9.4. Center of the film has negligible amount of solvent accumulation, therefore those regions
were excluded from the figures. Figure 9.4a shows the SLD profiles as a function of solvent exposure time for t-POSS(H) and matrix polymer closer to interfaces. Water accumulation occurs at both air/polymer and substrate/polymer interfaces of t-POSS(H) as indicated in the SLD profiles. Density of the water at the interfaces is higher and it decreases as goes towards the center of the film (bulk). The amount of the D$_2$O at the SiO$_2$/polymer interface after 8 hours, which is the area difference of the SLD curves at 480 minutes and dry conditions, is smaller in t-POSS(H) compared to the pure polymer. Lower SLD at the air/polymer interface of the dry films of t-POSS(H) compared to the pure polymer indicates the presence of some NPs. Initially the amount of D$_2$O at the air/polymer interface increases with solvent exposure time (up to 10min) and as time goes by those accumulated solvent molecules penetrate towards the substrate/polymer interface. Similar to the pure polymer, less amount of water accumulated at the air/polymer interface of t-POSS(H) compared to the density of D$_2$O layer at the substrate/polymer interface.

Figure 9.4b shows the comparison of SLD profiles of the pure polymer and t-POSS(F). The amount of solvent accumulated at the substrate/polymer interface and the thickness of the D$_2$O rich layer is smaller compared to the polymer and t-POSS(H). Air/polymer interface has less layering in t-POSS(F) and contains NPs, which is indicated by lower SLD region containing fluorinate NPs ($2.19\times10^{-6}$ Å$^2$). This NP rich layer at the air/polymer interface is thicker and denser compared to the t-POSS(H). Density of the NPs at the interface is higher and it decreases as move to the center of the film. This thicker layer of NPs and relatively high hydrophobicity of the fluorinated NPs
compared to the protonated NP might be the reason for the less amount of D$_2$O accumulation at the substrate/polymer interface of t-POSS(F). Hardly any water accumulation was observed at the air/polymer interface of t-POSS(F), which may attributed to the presence of hydrophobic fluorinated NPs on the surface.

**Figure 9.4** Comparison of the interfacial region of the SLD profiles of the pure polymer and a) t-POSS(H) and b) t-POSS(F) as a function of D$_2$O exposure time. The SLD profiles are shifted vertically for clarity. The x-axes are presented in absolute value from the interfaces.

Next we are going to consider the solvent penetration in blends. Similar to the tethered systems, two blends were studied. One of the blends has POSS cages modified with short protonated chains (Poly-POSS(H)) and the other has NPs grafted with short fluorinated chains (Poly-POSS(F)). Figure 9.5a and b represent the reflectivity data for the Poly-POSS(H) as a function of solvent exposure time. Intensity of the fringes slightly increases upon solvent exposure indicating slight increase in SLD contrast, which indicates only a small amount of D$_2$O penetration into the film. $q$ values of the fringes
hardly change indicating hardly any swelling of the film. Figure 9.5c and d show the reflectivity data for the Poly-POSS(F). Minima of the fringes slightly shifted to lower $q$ due to swelling the film upon $\text{D}_2\text{O}$ penetration. Intensity of the fringes also increased compared to the Poly-POSS(H) as a result of solvent accumulation at polymer interfaces.

**Figure 9.5** a) NR data of the thin film of Poly-POSS(H) and c) Poly-POSS(F) as a function of $\text{D}_2\text{O}$ exposure time. The symbols correspond to the experimental data and the solid lines are the best fits for 6 layer model. b) and d) are the $R(q)q^4$ representation of reflectivity data for Poly-POSS(H) and Poly-POSS(F) respectively.
Comparison of SLD profiles obtained from fitting reflectivity data of Poly-POSS(H) and pure polymer are shown in Figure 9.6a. Lower SLD at the substrate/polymer interface of the dry Poly-POSS(H) indicates the presence of NPs at the interface. Hardly any D$_2$O accumulation was observed at the substrate/polymer interface. The air/polymer interface is also rich with NPs and slight accumulation of D$_2$O was observed closer to the thin film surface at longer solvent exposure times.

![Figure 9.6](image)

**Figure 9.6** Comparison of the interfacial region of the SLD profiles of the pure polymer and a) Poly-POSS(H) and b) Poly-POSS(F) as a function of D$_2$O exposure time. The SLD profiles are shifted vertically for clarity. The x-axes are presented in absolute value from the interfaces.

Figure 9.6b shows the comparison of SLD profiles for the Poly-POSS(F) together with the SLD profiles of the pure polymer. Slightly lower SLDs of dry Poly-POSS(F) films at both interfaces compared to the pure polymer indicate presence of some NPs. However the density of NPs at interfaces are smaller compared to the Poly-POSS(H). Slight accumulation of D$_2$O was observed at the SiO$_2$/polymer interface. The layer on top
of that also shows increased SLD indicating accumulation of more D\textsubscript{2}O compared to the substrate/polymer interface and amount of D\textsubscript{2}O in that layer decreases as goes towards the center of the film. This solvent rich layer resides on top of the NP rich layer at the substrate/polymer interface. Therefore NPs at the substrates/polymer interface act as a barrier for D\textsubscript{2}O molecules and minimizes the D\textsubscript{2}O accumulation on the substrate. Compared to the Poly-POSS(H) more D\textsubscript{2}O penetrates inside the Poly-POSS(F) thin films. This might be due to the less density of segregated NPs at the air/polymer interfaces of the Poly-POSS(F) thin films. Also a slight accumulation of D\textsubscript{2}O was observed at the air/polymer interface of the Poly-POSS(F).

In order to compare the amount of D\textsubscript{2}O penetrate inside the thin films, relative change in thickness of the films were extracted. The thickness of the thin film defined as the distance from substrate/polymer interface to the air/polymer interface. The substrate/polymer interface is taken as the center of the roughness at the interface, which is the region of the SLD gradient from SiO\textsubscript{2} to the polymer, and the air/polymer interface is defined as the center of the region that corresponds to the roughness at the air/polymer boundary. Figure 9.7a shows the change in film thickness normalized to the thickness of the dry film as a function of solvent exposure time. Initial rate of relative change in thickness, which is given by the slope at the onset of curves, is the highest in thin films of Poly-POSS(F) and the rate of swelling at the onset decrease in the order of polymer, t-POSS(H), t-POSS(F) and Poly-POSS(H). All the thin films reached towards the steady state after the initial swelling except for the pure polymer, where swelling is progressed at a slower rate.
Figure 9.7 Changes in a) film thickness and b) total area of the SLD profiles normalized to the initial dry film thickness as a function of solvent exposure time for pure polymer (Poly) (♦), t-POSS(H) (■), Poly-POSS(H) (□), t-POSS(F) (●) and Poly-POSS(F) (○) thin films. Lines are drawn as a guide to the eye.

Total D$_2$O uptake was calculated by integrating the area of the SLD profiles between the air/polymer and substrate/polymer interfaces and subtracting the areas at a given solvent exposure time with that of the dry film. In these calculations we assumed that SLD increments occur only due to the association of D$_2$O molecules. These solvent uptake measurements were normalized to the film thicknesses of the dry samples to obtain the relative solvent uptake, which is shown in Figure 9.7b as a function of solvent exposure time. Rates of solvent absorption at the onset of diffusion is similar for both polymer and Poly-POSS(F) films and are the highest. Both tethered POSS films have the intermediate rates and Poly-POSS(H) has the lowest. According to Figure 9.7b, amount of D$_2$O accumulated in nanocomposite films are smaller than that of the pure polymer. Similar behavior was observed for the pure polymer as observed in relative change in thickness measurement, where accumulation of D$_2$O continues at slower rate at longer
solvent exposure times. As thin films are exposed to longer time, rearrangements may take place in above thin films, which may reduce the accuracy of the area measurement of the SLD profiles.

These measurements indicates the relative similarities of the pure polymer and Poly-POSS(F) at the onset of swelling and effect of NPs at interfaces on minimizing the water uptake in thin polymer film. We expected Poly-POSS(F) thin films to behave as similar to the Poly-POSS(H) where more NPs were observed at the air/polymer interface, which was not the case in this study. High solvent uptake in Poly-POSS(F) may attributed to the less density of NPs at the air/polymer interface indicating POSS cages were kinetically trapped inside the thin film during the spin coating process.

**Conclusions**

The current study has shown that the distribution of solvent molecules in polymer thin films is affected by the density of NPs accumulated at the interfaces. In BPh-PFCB, D$_2$O mainly accumulated at the SiO$_2$/polymer interface due to the hydrophilic nature of the silicon substrate. Thin films with dispersed NPs or less accumulation of NPs at air/polymer interface results in high D$_2$O uptake similar to the pure polymer. Accumulation of NPs at the substrate/polymer interface minimizes the solvent accumulation at the substrate as observed in Poly-POSS(F) system. Dense NP layer at the
air/polymer interface act as a barrier to D$_2$O molecules and minimizes the solvent accumulation in thin films.

**References**


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CHAPTER 10

Summary

The major goal of this research is to understand the factors that control the distribution of NPs in polymers and role of NPs in modifying the structure and properties of the polymeric matrices.

1. Nanocomposites of PA6 and montmorillonite NPs made by chaotic blending

1.1 Chaotically blending of NPs into PA6 changed the stable α crystalline form of PA6 into the meta-stable γ form.

1.2 The correlation between the chaotic advection parameter (N), the concentration of NPs and the structure obtained were investigated. In low NP concentrations, the fraction of γ crystalline form increased with increasing N. At higher NP concentrations, surface forces of the NPs dominate the crystalline packing of the PA6 chains and N hardly affected the α/γ crystalline ratio.

1.3 In nanocomposites NPs were oriented along the extrusion direction and long axis of PA6 chains orient perpendicular to the NP surfaces.

1.4 Annealing and stretching of chaotically blended films caused polymer chains to rearrange into stable α configuration and changed the orientation of the long axis of the polymer chains parallel to the NP surface.
1.5 The $\alpha/\gamma$ and crystalline/amorphous ratios increased significantly with degree of stretching. Stretching enhanced the ordering along the $\alpha(002)$ crystalline plane.

1.6 Incorporation of water into nanocomposite films increases the $\alpha/\gamma$ crystalline fraction and this transformation was more significant in nanocomposites made at higher Ns.

1.7 In chaotically blended nanocomposite films amorphous and crystalline domains formed stacks.

2. Semi-fluorinated block-copolymers assemblies in solution

2.1 Semi-fluorinated block-copolymer of polytrifluoro propyl methylsiloxane-$b$-polystyrene (SiF-PS) associated into micelles in toluene, which is a good solvent for PS and a poor solvent for the SiF. Fluorine introduced rigidity to the block, which affects the shape of the micelles. Presence of siloxane group in the SiF block provides flexibility to overcome the rigidity effects of fluorine.

2.2 Association takes place at very low volume fractions of the SiF block compared to block copolymers in the low segregation limit.

2.3 At low volume fractions of the SiF block ($\phi_{SiF}=0.03$), unimolecular micelles were observed. Spherical micelles were observed at $\phi_{SiF} = 0.16$ below the critical micelle temperature (CMT) and they transformed into unimolecular micelles at higher temperatures.
2.4 Elongated micelles were observed at symmetric volume fractions of the blocks. These micelles show unique temperature stability compared to the diblock copolymers micelles in lower segregation regime.

3. Dispersion of NPs in semi-fluorinated polymer thin films

3.1 The semi-fluorinated random copolymer of biphenyl-perfluorocyclobutyl formed surface induced layers of fluorine rich and proton rich domains due to the incompatibilities of the blocks and preference of PFCB to the air/polymer interface and BPh to the substrate/polymer interface.

3.2 POSS NPs modified with short fluorinated or protonated chains migrated to internal surface induced interfaces in contrast to block copolymers in lower segregation limit where NPs were segregated to the external polymer interfaces due entropic effects.

3.3 The tendency of NPs to migrate to the external interfaces was further reduced by grafting the NPs with a single matrix polymer chain. These modifications induced layering at the center of the film compared to the pure polymer and blends.

3.4 Fluorinated grafted layer on t-POSS force NPs to associate at air/polymer interface more compared to the t-POSS with protonated grafts.

3.5 Distribution of water molecules in POSS/BPh-PFCB thin films is governed by the density of NPs accumulated at the air/polymer interface.
APPENDICES

Appendix A: Copyright permission letter for chapter 6

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I am preparing the following work for publication:

Article/Chapter Title: Self-Assembly of a Semi-Fluorinated Diblock Copolymer in a Selective Solvent

Journal/Book Title: Self-Assembled and Flow Induced Nano-Structures in Polymer Nanocomposites

Editor/Author(s): Dilru R. Ratnaweera

Publisher: Clemson University

I would very much appreciate your permission to use the following material:

Journal/Book Title: Soft Matter

Editor/Author(s): Dilru R. Ratnaweera, Umesh M. Shrestha, Naresh Osti, Stephen Clarson, Ken Littrell, Dvora Perahia

Volume Number: 8
Year of Publication: 2012

Description of Material: The title of the paper is "Self-assembly of a semi-fluorinated diblock copolymer in a selective solvent", a small angle neutron scattering study of semi-fluorinated diblock-copolymer in toluene solution

Page(s): 2176-2184
Any Additional Comments : 

I am a graduate student at Clemson University. This is one of my own studies, which was recently published in Soft Matter and I am the first author of the paper. I would like to get permission from RSC to include this paper in my PhD dissertation.

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