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Structure-Property Relationships in the Formation of Polyphenylsulfone Molecular Composites and Nanocomposites

Paul Joseph Jones
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STRUCTURE-PROPERTY RELATIONSHIPS IN THE FORMATION OF
POLYPHENYLSULFONE MOLECULAR COMPOSITES AND NANOCOMPOSITES

by

Paul Joseph Jones

Abstract of a Dissertation
Submitted to the Graduate School
of The University of Southern Mississippi
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ABSTRACT

STRUCTURE-PROPERTY RELATIONSHIPS IN THE FORMATION OF POLYPHENYLSULFONE MOLECULAR COMPOSITES AND NANOCOMPOSITES

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May 2010

As the constituent phases in a polymer composite approach the molecular level, specific phenomena occur that can lead to significant changes in material properties when only minimal quantities of the additive are incorporated into the polymer matrix. Molecular composite and nanocomposites are state-of-the-art polymeric materials that contain nanostructured additives effectively dispersed within polymer matrices. The properties of molecular composites and nanocomposites are directly related to the interactions of the nanostructured additive and the polymer matrix. Subtle changes to the nanostructured additive can have profound effects on the ultimate properties of the composite material. Therefore, understanding the structure-property relationships in these systems represents a fundamental step in the realization of these advanced materials.

A molecular dispersion of rigid-rod and flexible coil macromolecules is known as a molecular composite. Similar to carbon or glass fiber composites, strain in a molecular composite is transferred to a stiff reinforcing agent with a high aspect ratio. However, in a molecular composite the reinforcing agent is a rigid macromolecule, and these materials are inherently homogeneous, transparent, possess a single coefficient of thermal expansion and are potentially recyclable. The degree of mechanical reinforcement in a molecular composite is directly related to the modulus and aspect ratio of the rigid-rod
macromolecule as well as its state of dispersion within the flexible coil matrix. In the first portion of this dissertation, semi rigid-rod macromolecules having phenylketone substituted para-phenylene and unsubstituted meta-phenylene recurring units (i.e. SRPs) at two different ratios are blended by rapid coagulation from solution with polyphenylsulfone (PPSU), and the resulting effects on miscibility, morphology and nanomechanical properties are assessed. Initially, the nanomechanical behavior of an SRP having a completely sp$^2$ hybridized backbone was demonstrated in comparison to conventional high performance engineering thermoplastics as a function of polymer rigidity via nanoprobe instrumentation techniques. Next, various light scattering techniques were employed to obtain key molecular and structural parameters of the SRPs and PPSU in dilute solution, which were related to polymer conformation, theoretical entropic and enthalpic contributions, and predicted blend compatibility. Miscibility was investigated using thermal analysis techniques to monitor the glass transition as a function of blend composition. The bulk and surface morphologies of these blends were analyzed via atomic force microscopy (AFM) to confirm a homogeneous morphology or determine the mechanism of phase separation, and the mechanical properties of these blends were evaluated using nanoindentation. Finally, an understanding of the relationship between the ratio of substituted para and unsubstituted meta recurring units in the SRP copolymer backbone to miscibility, morphology and nanomechanical properties in blends (or molecular composites) with PPSU was developed.

A polymer nanocomposite is broadly defined as a polymeric composite material in which one of the phases has dimensions less than 100 nm. These materials are not new since polymer blends often have dimensions much less than 100 nm. However, polymer
composites containing nanofillers have experienced a recently renewed interest from the scientific community due to the potential for these materials to exhibit not only superior mechanical properties, but also elevated thermal and dimensional stability and an array of other property improvements at relatively low additions of nanofiller. A special class of nanofillers is polyhedral oligomeric silsesquioxane (POSS®) nanostructured chemicals. POSS molecules with their hybrid organic/inorganic structure, well defined three-dimensional architecture and mono-disperse particle size have been the subject of a great deal of both academic and scientific interest for their potential to increase the strength and modulus of a polymer matrix without the negative side effects to processing observed with many traditional fillers. In fact, significant enhancements in the rheological and melt flow behavior of amorphous polymers have been observed with only minimal additions of POSS. These enhancements depend upon the interactions of POSS with the amorphous matrix based on the chemical structure of POSS. However, few detailed studies of these relationships have been performed, and the mechanism of this behavior has not been clearly defined. In the second portion of this dissertation improvement in the melt processing and rheological behavior of an amorphous polymer, PPSU, and the resulting thermomechanical properties of the nanocomposite by the addition of different types of POSS at various loading levels is discussed. The relationship of POSS chemical structure to the final properties of the nanocomposite materials was defined in terms of the difference in solubility parameters of POSS and PPSU, the dispersion of POSS within the PPSU matrix and the phase transformations POSS undergoes as a function of temperature.
In these studies many new nanoprobe characterization techniques were adapted and utilized for the advanced characterization of polymer films, specifically AFM. Recent advances in these characterization techniques have made possible the direct imaging of molecular events with sub-nanometer resolution. When applied to polymer films they can provide a wealth of knowledge that could not be obtained otherwise. In the Appendix of this dissertation a description of one of these techniques applied to stimuli-responsive polymer systems is included, in which current sensing AFM was used to identify the actuation mechanism in perfluorosulfonated ionic membranes.
DEDICATION

This dissertation is dedicated to my loving parents, Scott and Deloris Jones.
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\[ \gamma_{12} = \gamma_1^d + \gamma_2^d + \gamma_1^p + \gamma_2^p - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \]  

\[ \lambda_{21} = \gamma_1 - \gamma_2 - \gamma_{12} \]  

\[ W_{ad} = \gamma_1 + \gamma_2 - \gamma_{12} \]  

\[ E_c = \frac{E_m \cdot (1 + \xi \eta V_f)}{(1/\eta V_f)} \quad \text{with} \quad \eta = \frac{(E_f / E_m - 1)}{(E_f / E_m + \xi)} \]  

\[ E_c = E_f V_f + E_m V_m \]  

\[ E_c = \frac{E_f E_m}{E_m V_f + E_f V_m} \]  

\[ i_\mu \bigg/ I_0 = \frac{2\pi^2 \bar{n}^2}{\lambda^4 r^2} \frac{2(1 + \cos^2 \theta)c}{(1/V_i)\partial(\partial \mu_1 / \partial c)_{T,P}} \]  

\[ - \frac{1}{V_i kT} \left( \frac{\partial \mu_1}{\partial c} \right)_{T,P} = N \left( \frac{1}{M_w} + 2A_2c + 3A_3c^2 + ... \right) \]  

\[ \frac{i_\mu}{I_0} = \frac{2\pi^2 \bar{n}^2}{N\lambda^4 r^2} \left( \frac{1}{M} + 2A_2c + ... \right) \]  

\[ R_o = \frac{Kc}{1/M + 2A_2c + ...} \]  

\[ K = \frac{2\pi\bar{n}_0^2}{N\lambda^4} \left( \frac{\partial \mu_1}{\partial c} \right)^2 \]  

\[ \frac{Kc}{R_o} = \frac{1}{M} + 2A_2c \]  

\[ \frac{Kc}{R_o} = \frac{1}{M_w P(\theta)} \]
\[ \frac{1}{P(\theta)} = 1 + \frac{16\pi^2}{3\lambda^2} R_G^2 \sin^2 \frac{\theta}{2} + \ldots \] 

\[ \frac{Kc}{R_o} = \left( \frac{1}{M_w} + 2A_2 \right) \left( \frac{1}{M_w} + \frac{16\pi^2}{3\lambda^2} R_G^2 \sin^2 \frac{\theta}{2} \right) \] 

\[ \chi_0 = 0.5 - \rho_j \phi V \lambda \] 

\[ \ln \left( \frac{p}{p_0} \right) = \ln \phi^2 \phi + \chi^2 \phi \] 

\[ D_H = \frac{kT}{3\pi \eta D} \] 

\[ S = \frac{dP}{dh} \] 

\[ A = \frac{\pi}{4} \left( \frac{S}{E_r} \right)^2 \] 

\[ H = \frac{P_{\text{max}}}{A} \] 

\[ \frac{dh}{dP} = \frac{\sqrt{\pi}}{2} \frac{1}{\sqrt{A/E_r}} \] 

\[ \Delta z_i = \Delta z_p - \Delta z_i \cos(10^\circ) \] 

\[ \eta_0 = \eta(0)[1 + 2.5\phi + \ldots] \] 

\[ H = \frac{P_{\text{max}}}{A} \] 

\[ \frac{1}{E_r} = \frac{dP}{dh} \frac{2A^{1/2}}{\pi^{1/2}} \] 

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CHAPTER 1

INTRODUCTION

Molecular composites are a special class of polymer blends, where organic macromolecules with a rigid-rod structure serve as reinforcing elements within a flexible polymer matrix. Unlike carbon or glass fiber composites, there is no interface between the reinforcing elements and the matrix in a molecular composite when a uniform dispersion of the reinforcing macromolecules is achieved, and hence, these materials are inherently homogeneous. In addition to having elevated strength-to-weight ratios, improved dimensional and thermal stability and increased toughness, these types of molecular composites are transparent, have smooth surfaces and a single coefficient of thermal expansion. The concept of molecular composites arose in the late 1970s and early 1980s, but their success has been limited due to the fundamental problem associated with their development, obtaining a uniform dispersion of the rigid-rod macromolecule in the flexible polymer matrix. Barriers to obtaining this uniform mixture range from mechanical mixing limitations to inherent thermodynamic incompatibility of the two components. Therefore, understanding the phase behavior of rigid-rod and flexible coil polymer systems and the factors that govern the formation of molecular composites with uniform compositions becomes vital in the realization of these advanced materials.

Small modifications to the structure of rigid-rod macromolecules have profound effects on the composite properties. Recent developments in the rigid-rod macromolecular structure by copolymerization of monomers containing organic substituents and non-symmetric monomers have led to materials exhibiting greater
solubility in organic solvents as well as improved melt processability. The primary goal of this research is to determine the effects of molecular structure, specifically the degree of substitution and linearity of the semi rigid-rod polymer, on the formation of molecular composites, through a study of copolymers of phenylketone substituted \( p \)-phenylene with \( m \)-phenylene blended with amorphous polyphenylsulfone (PPSU).

Polymer nanocomposites are defined as blends containing nanofillers with at least one dimension that is smaller than 100 nm. Nanocomposites have been the subject of intense research interest due to their potential to achieve the high strength and modulus of traditional composites without their negative side effects, such as reduced processability and impact strength. Recent studies have indicated that incorporation of low loadings of spherical nanoadditives actually improves processability. The mechanism of this behavior, however, is not well understood, and the aggregation tendency of most nanofillers complicates the study of their behavior. A secondary objective of this research is to determine the dispersion and aggregation behavior of organic/inorganic polyhedral oligomeric silsesquioxane (POSS) nanostructured chemicals in an amorphous PPSU matrix, and to define the relationship of POSS structure to rheological and mechanical properties in the resultant polymer nanocomposite.

A range of light scattering, rheological, thermomechanical and microscopy techniques have been employed to pursue these objectives, with specific focus on nanoprobe techniques for determination of morphological features at the nanoscale. A description of advanced nanoprobe techniques applied to complex polymer systems to understand the dynamic behavior of polymer films on a molecular level is included in the Appendix.
Rigid-Rod Polymers

In order to understand the mechanism of reinforcement in a molecular composite, it is necessary to understand the nature of the reinforcing element or rigid-rod polymer. The underlying principle associated with the exceptionally high strength and stiffness of rigid-rod polymers is how they undergo single chain deformation. For polymeric single chain deformation the strain associated with flexible coil polymers is generally attributed to covalent bond angle rotation, while the strain associated with rigid-rod polymers is generally attributed to covalent bond angle bending and bond angle stretching. The energy required for single chain deformation by bond angle bending is approximately ten times higher than that required for bond angle rotation, and that required for bond angle stretching is up to one hundred times greater. The amount of strain associated with covalent bond angle bending and stretching rather than covalent bond rotation is proportional to the persistence length and Young’s modulus of the macromolecule. One rigid-rod polymer, aromatic polyester, has a calculated and experimental persistence length of approximately 10 nm, and it exhibits a Young’s modulus close to 100 GPa. Rigid-rod polymers with higher persistence lengths exhibit much higher values for Young’s Modulus. For example, poly($\text{p}$-phenylenebenzobisthiazole) (PBZT) has a persistence length of 64 nm and a Young’s modulus greater than 300 GPa.

Although rigid rod polymers exhibit extraordinary mechanical properties, their commercial application is limited due to challenges in production, solubility and processing. An ideal rigid-rod polymer that has received much attention for its simplistic structure and potentially inexpensive synthesis is poly($\text{p}$-phenylene) (PPP). The theoretical persistence length of PPP has been calculated to be 22 nm, and its Young’s
modulus has been estimated as high as 456 GPa. Therefore, significant efforts have been focused on the synthesis of PPP. However, these attempts were unsuccessful due to the extremely poor solubility of PPP. After incorporation of only 6 to 10 repeat units, PPP precipitates from solution, and a low molecular weight product with an irregular structure is produced.

The poor solubility of rigid-rod polymers is not due to enthalpic interactions but a result of configurational entropy. The highly linear and rigid nature of these polymers makes them susceptible to nematic phase ordering in solution brought upon by steric forces between the rods. The development of nematic order can be illustrated thermodynamically by analyzing the partition function for a binary lyotropic system consisting of rods in an athermal solvent. \( Z_M \) is the product of both the combinatorial \( Z_{comb} \) and the orientational \( Z_{orient} \) partition functions.

\[
Z_M = Z_{comb} \cdot Z_{orient}
\]

\[
Z_M = Z_{comb} \cdot Z_{orient} = \left( \frac{1}{n_p!} \right) \prod_{j=1}^{n_p} v_j \prod_y \left( \frac{w_j n_p}{n_{py}} \right)^{n_{py}}
\]

\[
Z_{comb} = \frac{(n_r + y \cdot n_p)!}{n_r! n_p! (n_r + x_r n_p)^{n_p(n_r+1)}}
\]

\[
Z_{orient} \approx \left( \frac{v_j}{x_r} \right)^{2n_p}
\]

\( n_p \) = total number of lattice site filled with rigid segments

\( n_{py} \) = number of rods disorientated from the preferred axis marked by \( y \)

\( v_j \) = number of situations accessible to molecule \( j \) with orientation \( y \)
\( w_y \) = fraction of solid angle associated with \( y \)

\( n_s \) = number of vacant sites respectively filled with solvent molecules

\( x_r \) = axial ratio of solute

\( \bar{y} \) = average value of the disorder index, \( y \)

Using Sterling’s approximation the factorials in Eq. I-2 can be replaced to yield Eq. I-5.

\[
- \ln Z_M = n_s \ln v_s + n_p \ln \left( \frac{v_p}{x_r} \right) + n_p \ln(\bar{y} - 1) - \\
(n_s + \bar{y} n_p) \ln \left[ 1 - v_p \left( 1 - \frac{\bar{y}}{x_r} \right) \right] - 2n_p \ln \left( \frac{\bar{y}}{x_r} \right)
\]  

(I-5)

\( v_p \) = volume fraction of rodlike solute

\( v_s \) = volume fraction of solvent

The state of minimum free energy results from a balance of both combinatorial and orientational equilibrium and occurs when \( Z_M \) is maximized. As the \( x_r \) or concentration of the solute is reduced \( Z_{\text{orient}} \) is maximized. Under these conditions, \( Z_{\text{orient}} \) dominates \( Z_M \), leading to a state of complete disorder. However, as the \( x_r \) of the solute increases a maximum value for \( Z_M \) occurs by parallel orientation of the rods, resulting in an ordered nematic solution.\(^{35}\) Therefore, for a given \( x_r \) the formation of an ordered nematic solution occurs when the volume fraction of rods in solution exceeds a critical value \( \phi_{r,c} \).

\[
\phi_{r,c} = \frac{8}{x_r} \left( 1 - \frac{2}{x_r} \right)
\]

(I-6)
Under dilute solution conditions the solution will be isotropic. Once $\phi_{r,c}$ is reached the solution will be become biphasic with an isotropic phase and an ordered phase existing simultaneously. When $\phi_{r,c}$ is surpassed the entire system forms a nematic phase. The minimum $x_r$ required for the formation of a stable nematic phase has been estimated to be $6.42$.\textsuperscript{36} This result is very interesting since PPP precipitates from solution with a degree of polymerization of only 6 to 10.

In addition to poor solubility, the melt processing of rigid-rod polymers is highly complicated. Rigid-rod polymers often exhibit thermotropic liquid crystalline behavior. The liquid crystalline order that develops among the mesogenic units hinders processing of these materials by substantially increasing viscosity. The liquid crystalline order that develops will eventually melt at high temperatures, but these temperatures often exceed the degradation temperature of the polymer itself.\textsuperscript{37} This has limited the commercial use of rigid-rod polymers primarily to films or fibers processed from dilute solutions.

Developments in rigid-rod polymers for more general application have predominantly focused on preventing the formation of anisotropic phases and increasing the solubility of rigid-rod polymers. The most important factor in determining the degree of anisotropic phase ordering in rigid rod polymers is free volume. A small increase in free volume can relax the steric constraints associated with rigid rod polymers and destabilize the anisotropic phase.\textsuperscript{35} One effective method for increasing free volume as well as the solubility associated with rigid rod polymers is incorporation of monomers containing short side chains into the polymer backbone structure.\textsuperscript{38,39,40,41,42} This is exemplified in the previously discussed case of polyphenylene. Polyphenylene containing phenyl side groups can reach a molecular weight of up to 2000 and remain
soluble in organic solvents. In addition to side chains on the polymer backbone, introduction of non-linear co-monomers into the polymer backbone can effectively increase free volume thereby reducing the propensity of the rigid-rod polymers to form anisotropic phases.

The first commercial rigid rod polymers displaying both solubility and melt processability were introduced under the trade name Parmax®. Today these polymers are known as PrimoSpire® and are produced by Solvay Advanced Polymers. They are synthesized by the co-polymerization of 1,3-dichlorobenzene and 2,5-dichlorobenzophenone at various ratios to yield the general structure shown in Figure I-1. They have a fully aromatic backbone containing both meta and para linkages as well as benzoyl side groups that impart solubility, and they do not display any liquid crystalline characteristics. Since these polymers contain meta linkages they are not classified as true rigid rods but are more accurately described as semi-rigid rods. Because they display high strength and modulus without fiber reinforcement they are often referred to as self-reinforced polymers (SRPs). These transparent, amorphous polymers are inherently thermally and dimensionally stable and do not begin to degrade until they are heated well above 500°C. They have been shown to possess mechanical properties far superior to known thermoplastics (see Figure I-2) and can even be compared to structural metals (see Figure I-3). The mechanical performance of SRPs make them excellent candidates as reinforcing elements for blends with flexible polymers. If homogeneous blends of this nature could be produced, they would be regarded as molecular composites.
Polymer Blends

As the need for polymeric materials with enhanced properties grows the ability to create new polymeric materials by blending represents a valuable alternative to new polymer synthesis. Polymer blends alone currently make up 30% of the entire polymer market.

It is well known that, regarding the mixing of thermoplastics, incompatibility is the rule and miscibility and even partial miscibility is the exception. Since most thermoplastic polymers are immiscible in other thermoplastic polymers, the discovery of a homogeneous mixture or partially miscible mixture of two or more thermoplastic polymers is, indeed, inherently unpredictable with any degree of certainty.

Flory explains,

“It is well known that, regarding the mixing of thermoplastics, incompatibility is the rule and miscibility and even partial miscibility is the exception. Since most thermoplastic polymers are immiscible in other thermoplastic polymers, the discovery of a homogeneous mixture or partially miscible mixture of two or more thermoplastic polymers is, indeed, inherently unpredictable with any degree of certainty.”

Therefore, understanding the factors that lead to miscibility (or immiscibility) becomes a fundamental step in the process of creating new materials.

The basic thermodynamic relation that governs the mixing of different materials is Gibb’s free energy of mixing \((\Delta G_m)\) given by the relationship:

\[
\Delta G_m = \Delta H_m - T\Delta S_m
\]

where \(\Delta H_m\) is the enthalpy of mixing; \(T\) is temperature, and \(\Delta S_m\) is the combinatorial entropy of mixing. When \(\Delta G_m\) is negative the two substances will spontaneously mix, and when \(\Delta G_m\) is positive mixing will not occur, resulting in phase separation.

Typically, a positive enthalpy can be offset by the increase in entropy upon mixing. In
In the case of polymers, the free energy of mixing of a binary polymer blend can be modeled using the classical Flory-Huggins theory:

\[
\frac{\Delta G_m}{V} = B \phi_A \phi_B + RT \left( \frac{\rho_A \phi_A \ln \phi_A}{M_A} + \frac{\rho_B \phi_B \ln \phi_B}{M_B} \right)
\]

\[
\frac{\Delta H_m}{V} = B \phi_A \phi_B
\]

\[
\frac{\Delta S_m}{V} = R \left( \frac{\rho_A \phi_A \ln \phi_A}{M_A} + \frac{\rho_B \phi_B \ln \phi_B}{M_B} \right)
\]

where \( V \) is the total volume of the system; \( B \) is the binary interaction density parameter; \( R \) is the ideal gas constant, \( \phi_i \) is the volume fraction of component \( i \); \( \rho_i \) is the density of component \( i \), and \( M_i \) is the molecular weight of component \( i \). The enthalpic term of Eq. I-8 can also be rewritten in terms of Hildebrand solubility parameters.

Substitution of these parameters in Eq. I-8 yields:

\[
\frac{\Delta G_m}{V} = (\delta_A - \delta_B)^2 \phi_A \phi_B + RT \left( \frac{\rho_A \phi_A \ln \phi_A}{M_A} + \frac{\rho_B \phi_B \ln \phi_B}{M_B} \right)
\]

where \( \delta_i \) is the solubility parameter of component \( i \). From analysis of Eqs. I-8 and I-11, it is clear that immiscibility in polymer blends arises due to the high molecular weight of their components. As molecular weight is increased, the entropic terms of Eqs. I-8 and I-11 diminish, and only small enthalpic contributions can lead to phase separation.

The phase behavior of a solution or polymer blend can be described by an upper critical solution temperature (UCST) or a lower critical solution temperature (LCST). Generally, solvent-solvent and polymer-solvent systems exhibit UCST behavior, meaning that they form a single, stable phase above a certain critical temperature. Polymer-polymer mixtures typically exhibit LCST behavior, meaning that they undergo phase
separation above a critical temperature (see Figure I-4). The spinodal curve shown in Figure 1-4 encloses the unstable regime associated with a polymer blend. It is formed by the position where the second derivative of \( \Delta G_m \) with respect to the volume fraction of the individual components of the blend is equal to zero.

\[
\left( \frac{\partial^2 \Delta G_m}{\partial \phi^2} \right)_{T,P} = 0
\]  \hspace{1cm} (I-12)

Although the system may possess a negative \( \Delta G_m \), if Eq. I-12 possesses a negative value the system is classified as unstable, and compositional fluctuations can develop leading to phases that are rich in either of the blend components.\(^{56}\) The binodal curve shown in Figure I-4 is defined by the equilibrium phase boundary between the single phase and two phase regimes, where the chemical potential of an individual component is equal in both phases. Between the spinodal and binodal curves the system is classified as metastable. Outside the binodal boundary the system is classified as stable, and only a single phase is observed. The critical point occurs when the binodal and spinodal curves intersect.

The interfacial tension \( \gamma_{12} \) between polymer 1 and polymer 2 has a strong effect on both miscibility and blend stability. It is an indication of the intermolecular interactions that occur between blend components. High values of \( \gamma_{12} \) inhibit miscibility, and as \( \gamma_{12} \) approaches zero miscibility is promoted.\(^{57}\) Interfacial tension is expressed in terms of the polar and dispersive contributions of the surface tensions of pure components as:

\[
\gamma_{12} = \gamma_1^d + \gamma_2^d + \gamma_1^p + \gamma_2^p = \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}
\]  \hspace{1cm} (I-13)
where $\gamma_i^d$ and $\gamma_i^p$ are the dispersive and polar components of polymer i, respectively.

Based on the surface tensions of polymer 1 ($\gamma_1$) and polymer 2 ($\gamma_2$), the spreading coefficient ($\lambda_{21}$) can be calculated as:

$$\lambda_{21} = \gamma_1 - \gamma_2 - \gamma_{12} \tag{I-14}$$

If $\lambda_{21}$ is positive, polymer 2 can spread over polymer 1. The converse of this statement also holds true. However, if the absolute value of the difference between $\gamma_1$ and $\gamma_2$ is less than $\gamma_{12}$ then neither polymer will spread over the other. The surface tension of the individual components also determines the reversible work required to develop an interface, known as the work of adhesion ($W_{ad}$), by the relation:

$$W_{ad} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{I-15}$$

In order to create a stable, miscible polymer blend $\gamma_{12}$ and $W_{ad}$ must be minimized, while $\lambda_{21}$ and $\lambda_{12}$ must be maximized. Ultimately, similarities in surface tension between the components of a blend favor miscibility by minimizing interfacial tension and the work of adhesion, while maximizing spreading. When blends are prepared by solution casting the surface tension of the individual components determines which component will be enriched at the surface. Typically, the component with the lower surface free energy will be enriched at the surface in order to minimize polymer-air surface tension.

Phase separation in a polymer blend occurs when the phase boundaries of Figure I-4 are traversed by compositional or temperature fluctuations. There are two primary mechanisms by which phase separation can occur. These are spinodal decomposition and nucleation and growth. Spinodal decomposition occurs in the unstable region of the phase diagram, while nucleation and growth only occurs in the metastable region. The
phase separated regions that develop by spinodal decomposition become enriched in one component of the blend as the polymers diffuse from regions of low concentration to regions of higher concentration. Systems exhibiting spinodal decomposition yield co-continuous phase separated morphologies. The phase separated regions formed by nucleation and growth have a constant concentration but increase in size over time. The morphology generally associated with nucleation and growth consists of isolated regions of phase separation dispersed within a homogeneous matrix.

Molecular Composites

The most attractive feature of molecular composites is the reinforcing potential of the flexible polymer matrix by rigid-rod molecules. As previously stated, flexible coil polymers generally alleviate strain by rotational movements of the polymer molecule, while rigid-rod molecules alleviate strain by deformation of bond angles and distances, leading to much higher values for both strength and stiffness. Reinforcement in blends containing these two types of polymers occurs by transferring the strain to the rigid-rod molecule. The degree of molecular reinforcement is generally predicted using the equations established for macroscopic fiber reinforced systems, according to the Halpin-Tsai equation:

\[ E_c = \frac{E_m \cdot (1 + \frac{\xi V_f}{\eta V_f})}{(1/\eta V_f)} \quad \text{with} \quad \eta = \frac{(E_f / E_m - 1)}{(E_f / E_m + \xi)} \]

where \( E \) refers to modulus; \( V \) is volume fraction; \( \eta \) is a reduced property; \( \xi \) is an empirical parameter related to the aspect ratio of the reinforcing agent, and the subscripts \( c, m, \) and \( f \) refer to composite, matrix, and fiber. As \( \xi \) approaches infinity, or the aspect
ratio of the reinforcing element approaches infinity, the upper limit of molecular
reinforcement predicted by the Halpin-Tsai equation becomes the rule of mixtures.

\[ E_c = E_f V_f + E_m V_m \]  \hspace{1cm} (I-17)

Conversely, as \( \xi \) approaches zero the lower limit for the composite modulus is predicted.

\[ E_c = \frac{E_f E_m}{E_m V_f + E_f V_m} \]  \hspace{1cm} (I-18)

From a simple analysis of the equations above it is apparent that maximizing the aspect
ratio by decreasing the diameter of the reinforcing agent is the most practical way to
maximize reinforcement without changing the reinforcing agent. This leads one to
conclude that a single molecule fiber is the most effective reinforcing agent (see Figure I-5).

Although blending rigid-rod polymers with flexible thermoplastics to form a
molecular composite has the potential to create new materials with high increases in
modulus and strength, difficulties in dispersing the rigid-rod polymers within the flexible
matrix have prevented their commercial development. In 1978 Flory extended his lattice
model of nematic fluids to include rods and coils dispersed in an athermal solvent. 62 He
predicted similar behavior occurs when rods are mixed with flexible coils and when rods
are in solution. He showed that the phase separation or high incompatibility observed in
rigid-rod and flexible coil blends is driven by entropic considerations. This is often
referred to as entropic demixing. Early work by Ciferri and coworkers 63 in 1984
confirmed this behavior experimentally. The phase behavior of a tertiary system
consisting of a rigid-rod polymer, unfractionated poly(\( \rho \)-benzamide) (PBA), a random
coil polymer, polyacrylonitrile (PAN), and a diluent consisting of N,N-
dimethylacetamide + 3% LiCl was studied. Above a critical concentration the system became biphasic. It was found that only a small isotropic phase existed containing the lower molecular weight fraction of PBA and PAN, while a nematic phase formed containing the high molecular weight PBA species.

Efforts to improve dispersion in rigid-rod and flexible coil polymer systems have focused on modification of the rigid-rod polymer architecture through synthesis of either graft or block copolymers. Graft copolymers generally have a rigid backbone with flexible side chains, and block copolymers consist of both rigid and flexible segments. The concept behind these routes is that covalent bonds between rigid and flexible units will prevent phase separation. In 1993 Evers and coworkers$^{64}$ exhibited the success of the graft copolymer approach by the introduction of flexible thermoplastic poly(ether ketone) (PEK) side-chains onto the rigid-rod poly(\(p\)-phenylenebenzobisthiazole) (PBZT) backbone. It was found that the flexible side chains effectively suppressed formation of anisotropic phases containing the rigid-rod polymers. In addition, it was shown that the frequency of the PEK side chains along on the PBZT backbone played a more important role in preventing the formation of ordered phases than the length of the PEK side chains.$^{65}$ One of the most successful molecular composites developed was a triblock copolymer consisting of 30% rigid-rod PBZT and 70% semi-flexible coil poly(2,5(6)benzimidazole). Morphology was examined by X-ray scattering and transmission electron microscopy. PBZT segments were found to be well dispersed with lateral dimensions less than 3 nm. The modulus and tensile strength of the molecular composite were measured to be 100 GPa and 1.7 GPa, respectively.$^{10}$
In addition to modification of polymer architecture, rapid coagulation from solution (solution casting) to obtain a homogeneous mixture has yielded successful results. This approach relies on controlling the phase separation kinetics of polymers through temperature and concentration by limiting diffusion. For molecular composite systems that exhibit homogenous behavior in dilute solution, rapid evaporation of the solvent can essentially lock the system into a homogeneous, glassy state before thermodynamic equilibrium is reached. Rapid coagulation of solutions of SRP with polyimide, polycarbonate, and polysulfone has yielded transparent films indicating a significant degree of compatibility. However, molecular composites prepared in this manner may undergo a demixing process when subjected to elevated temperatures resulting in phase separated blends. In this research the preparation of molecular composites is explored using a combination of polymer architecture modification and rapid coagulation.

Light Scattering

To understand the influence of polymer architecture on miscibility and morphology, the dilute solution properties of rigid rod/amorphous polymers are investigated in this thesis using light scattering techniques. Specifically, the radius of gyration (\(R_g\)), weight-average molecular weight (\(M_w\)) and second virial coefficient (\(A_2\)) are obtained using static light scattering (SLS), while the hydrodynamic diameter (\(D_H\)) is measured using dynamic light scattering (DLS). The information obtained from light scattering provides a measure of the polymer’s conformation in solution as well as its interactions with the solvent. Based upon the strength of interactions between the polymer and the solvent the enthalpic contribution upon mixing can be estimated, while
the entropic contribution can be estimated from polymer conformation. In addition this information can be used to optimize the conditions used during solution casting.

SLS is based upon the principle of polarization of particles by electromagnetic radiation. Under the influence of electromagnetic radiation, the electrons of a particle experience a force in one direction while the nucleus of the particle experiences a force in the opposite direction producing a dipole moment. If the electromagnetic radiation is in the form of a light beam then an oscillating dipole is produced, and the oscillating dipole becomes a source of electromagnetic radiation scattering in all directions as a spherical wave.72,73

Two effects occur when a polymer solution is excited by electromagnetic radiation in the form of a laser, non-ideal solution behavior and destructive interference caused by large particle size. Einstein74 and Debye75 accounted for the effect of non-ideal solution behavior in Eq. I-19 by relating the partial molal volume of the solvent \( V_i \) to the dependence of the chemical potential of the solvent \( \mu_i \) on the concentration \( c \) of the solute:

\[
I_\theta = \frac{2\pi^2\tilde{n}^2(\partial n / \partial c)^2(1 + \cos^2 \theta)c}{\lambda^2r^2[-(1/V_i k T)(\partial \mu_i / \partial c)_{T,P}]}
\]

where \( I_\theta \) is the intensity of the scattered unpolarized incident light; \( I_0 \) is the intensity of the incident light; \( \tilde{n} \) is the refractive index of the solution; \( d\tilde{n} / dc \) represents the change in refractive index with respect to concentration; \( \theta \) is the scattering angle; \( \lambda \) is the wavelength of incident light; \( r \) is the distance of observation; \( T \) is temperature; \( P \) is pressure, and \( k \) is Boltzman’s constant. In a dilute solution the chemical potential can be expressed in terms of concentration as a power series by:
\[-\frac{1}{V_i k T} \left( \frac{\partial \mu_i}{\partial c} \right)_{T,p} = N \left( \frac{1}{M_w} + 2A_2 c + 3A_3 c^2 + \ldots \right) \]  

(I-20)

where \( N \) is Avogadro’s number, and \( A_3 \) is the third virial coefficient and so on. \( A_2 \) is a measure of the strength of the interactions between the solvent and the solute. \( A_3 \) and higher order terms are generally assumed to be negligible. Eq. I-19 can now be written as:

\[
\frac{i_\theta}{I_0} = \frac{2\pi^2 \bar{n}^2 (\bar{n}/c)^2 (1 + \cos^2 \theta)c}{N A_4 r^2 \left( \frac{1}{M} + 2A_2 c + \ldots \right)} \]  

(I-21)

In a dilute solution \( \bar{n} \) can be replaced by the refractive index of the solvent \( (\bar{n}_0) \). The quantity measured in a light scattering experiment is known as Rayleigh’s ratio \( (R_\theta) \):

\[
R_\theta = \frac{Kc}{1/M + 2A_2 c + \ldots} \]  

(I-22)

where

\[
K = \frac{2\bar{m}_0^2 (\bar{n}/c)^2}{N \bar{\lambda}^4} \]  

(I-23)

Rayleigh’s ratio is independent of the scattering angle and when used to measure molecular parameters is written as Eq. I-24.

\[
\frac{Kc}{R_\theta} = \frac{1}{M} + 2A_2 c \]  

(I-24)

When light is scattered by large particles \( (R_g > \lambda/20) \), scattered light from different parts of the particle travel different path lengths to the detector and result in destructive interference. Therefore, the intensity of scattered light by large particles is less than that by small particles (see Figure I-6). No destructive interference is observed at \( \theta = 0^\circ \), but
as the scattering angle is increased, interference increases as well. This is accounted for by introducing the scattering function \( P(\theta) \), which is the ratio of the actual amount of scattered light to the amount of light that would be scattered if the particles were small (no interference). Rayleigh’s ratio remains the key quantity measured, but is now expressed as Eq. I-25.

\[
\frac{Kc}{R_g} = \frac{1}{M_w P(\theta)} \tag{I-25}
\]

with

\[
\frac{1}{P(\theta)} = 1 + \frac{16\pi^2}{3\lambda_s^2} R_g^2 \sin^2 \frac{\theta}{2} + \ldots \tag{I-26}
\]

Accounting for the effects of large particle size and non-ideal solution behavior as well as truncating higher order terms, Rayleigh’s ratio can be related to scattering angle and concentration by Eq. I-27.

\[
\frac{Kc}{R_g} = \left( \frac{1}{M_w} + 2A_c \right) \left( 1 + \frac{16\pi^2}{3\lambda_s^2} R_g^2 \sin^2 \frac{\theta}{2} \right) \tag{I-27}
\]

Performing a light scattering experiment to measure the intensity of scattered light at various angles and concentrations allows \( M_w, A_2 \) and \( R_g \) to be measured simultaneously by construction of a Zimm plot (see Figure I-7). Extrapolating the data to \( c = 0 \) provides a measure of \( R_g \), and extrapolation to \( \theta = 0^\circ \) provides a measure of \( A_2 \).

Both extrapolations intercept the y-axis at \( 1/M_w \).\(^{76,77,78}\)

Since the \( A_2 \) is measure of the strength of interactions between the solute and the solvent it can be used to calculate the Flory-Huggins (\( \chi_0 \)) interaction parameter at infinite dilution by the simple relationship:\(^{79}\)
\[ \chi_0 = 0.5 - \rho_j V_i A_2 \]  

where \( \rho_j \) is the density of the polymer, and \( V_i \) is the solvent molar volume. When \( \chi_0 \) is less than 0.5 the solvent is referred to as a “good” solvent for the polymer. When \( \chi_0 \) is equal to 0.5 the solvent is referred to as a “theta” solvent, and when it is greater than 0.5 the solvent is regarded as “poor”. If the polymer is in a “good” solvent it can be assumed that the Flory-Huggins interaction parameter is independent of solute concentration, and the Flory-Huggins interaction parameter is equal to that at infinite dilution.\(^5\) Using the data from SLS, the vapor pressure of a polymer solution (\( p \)) can now be calculated as:

\[ \ln \left( \frac{p}{p^0} \right) = \ln \phi + \chi \phi^2 \]  

where \( p^0 \) is the pure solvent vapor pressure, and \( \phi \) and \( \chi \) are the volume fractions of the solvent and polymer, respectively.\(^7\) Using the relationship expressed in Eq. I-29 the conditions for solvent evaporation can be maximized during solution casting by estimating the vapor pressure of the polymer solution. If the solvent is removed too fast and the solution boils, then the resulting film will have a poor surface, exhibiting what is typically known as “orange peel”. However, if the solvent is removed too slowly, phase separation may occur.

Brownian motion of particles in solution due to the impact by solvent molecules is measured by DLS, and is defined by the translational diffusion coefficient (\( D \)). Larger particles move slower than smaller particles. The particle size measured by DLS is the hydrodynamic diameter, \( D_H \), and is related to \( D \) by the Stokes-Einstein equation:

\[ D_H = \frac{kT}{3\pi \eta D} \]  

(I-30)
where $\eta$ is the viscosity of the solvent. The diameter measured in this manner is the same as that of a sphere with the same translational diffusional coefficient.\textsuperscript{80,81}

The conformation of the polymer in solution can be determined from the angular dependence of light scattering from solution.\textsuperscript{82} However, this method is not applicable to low molecular weight polymers because the angular variation of light scattering for rods and coils deviates significantly only at higher molecular weights. Another indication of polymer conformation is the ratio of $R_G$ to $R_H$.\textsuperscript{83} The theoretical ratio of $R_G / R_H$ for a hard sphere is 0.778. Random coil polymers demonstrate ratios in the range of 1.27–2.05, while rod-like polymers show ratios greater than 2.2.\textsuperscript{84,85,86,87,88,89}

Atomic Force Microscopy

In the past many studies of molecular composites were limited to X-ray diffraction and transmission electron microscopy to obtain morphological information. Recent advances in nanoprobe characterization techniques, such as atomic force microscopy (AFM), have made possible the imaging of polymer structures with Angstrom level resolution. AFM has become an indispensable tool in the morphological characterization of polymer blends and composites for its ability to directly image surface topography and compositional heterogeneities as well as measure localized mechanical, electrical, magnetic, thermal and adhesive surface properties through tip-sample interactions. AFM was developed by Binnig and coworkers\textsuperscript{90} in 1986 and applied to polymers\textsuperscript{91} in 1988. It makes use of a sharp probe having a typical radius of curvature of 10 nm for surface profiling. Interactions of the probe tip and cantilever with the sample surface are the main factors influencing the imaging of polymers. These forces are amplified by focusing a laser onto the reflective backside of the cantilever. The laser
signal is reflected to a segmented photodiode detector (SPDD). As the tip profiles the surface the laser signal moves accordingly on the SPDD. The voltages from the SPDD are used to construct a three-dimensional topographical image of the sample surface and provide feedback that controls the vertical motion of the stage or cantilever (see Figure I-8).92

The two most common AFM operational modes are contact and oscillatory (tapping) modes. During contact mode the tip is brought into contact with the sample surface until a set deflection of the cantilever is achieved, and this deflection is maintained while scanning. The tip-sample force is a product of the cantilever stiffness and its deflection. For most polymeric samples the forces generated between the tip and the sample during contact mode are too high and cause damage to the sample surface. Therefore, oscillatory mode is preferred when imaging polymeric samples to maintain the integrity of the surface.93 In oscillatory mode the tip is oscillated at or near its resonant frequency and only comes into contact with the surface once during its oscillatory cycle, producing a drop in amplitude of the cantilever. In oscillatory mode the level of tip sample forces generated is determined by the stiffness of the cantilever as well as the ratio of the set-point amplitude (A_{sp}) to the amplitude of a free-oscillating cantilever (A_0). As A_{sp}/A_0 is decreased the force applied to the sample is increased. This increase in force is extremely useful in resolving surface heterogeneities having different energy dissipative characteristics.

The motion of the cantilever can be modeled as a harmonic oscillator. Monitoring the amplitude and phase of the cantilever allows a three-dimensional image to be constructed based on the shift in phase of the cantilever as it interacts with different
regions of the sample surface. Attractive forces cause a low frequency phase shift in the
oscillation of the cantilever, while repulsive forces cause a high frequency phase shift
(see Figure I-9). By measuring the phase shift with constant excitation force, differences
in probe-tip sample interactions produce compositional contrast in a heterogeneous
sample in what is known as a phase image.\textsuperscript{94} Contrast in the phase image arises from
differences in mechanical energy dissipation between the tip and the sample.\textsuperscript{95,96}
Applying high tip sample forces in the intermittent contact regime (hard tapping), softer,
more viscous, energy dissipative components appear as darker features in the phase
image, while harder, more elastic, components appear brighter.\textsuperscript{97}

Adhesive forces are extracted from surfaces by measuring tip-sample interactions
using a force curve (see Figure I-10).\textsuperscript{98,99,100} Force curves are generated by monitoring
the deflection of the cantilever with respect to the motion of the vertical piezo. To
generate a force curve the tip is lowered towards the surface. It experiences a small
attractive force that pulls the tip to the surface, and the cantilever bends downward. The
surface is indented by the tip, and the tip is finally lifted from the surface. The force
required to pull the tip from the surface is regarded as a measure the adhesive force of the
surface.\textsuperscript{101,102} The cantilever follows Hooke’s law, where the force applied to the surface
is the product of the spring constant and the deflection of the cantilever. The deflection
of the cantilever is converted from a voltage signal on the SPDD to an actual
displacement in length by indentation on a hard surface such as sapphire where there is
virtually no indentation of the sample surface. This conversion factor is known as the
deflection sensitivity and has units of nm/V. Once the deflection sensitivity of the
cantilever is known, reliable and accurate adhesive force measurements can be made.
Nanoindentation

Measuring mechanical properties using nanoindentation has significantly progressed over the past decade. Localized mechanical property information can be obtained at rapid rate, and nanoindentation is an ideal method for measuring the properties of films and other substances when only small quantities are available. A stiff probe, usually composed of diamond, is forced into the surface. Load, displacement, and time are monitored. The applied load (P) is plotted versus displacement (h) to generate a force curve, and measurements of stiffness (S), hardness (H) and reduced modulus (E_r) are made from the linear portion of the retraction curve based on the contact mechanics of an axisymmetric indenter with an elastically isotropic half space. These relationships are shown below:

\[
S = \frac{dP}{dh}
\]  
(I-31)

\[
A = \frac{\pi}{4} \left( \frac{S}{E_r} \right)^2
\]  
(I-32)

\[
H = \frac{P_{\text{max}}}{A}
\]  
(I-33)

\[
\frac{dh}{dP} = \frac{\sqrt{\pi}}{2} \frac{1}{\sqrt{A}} \frac{1}{E_r}
\]  
(I-34)

where \( P_{\text{max}} \) is the maximum applied load, and \( A \) is the contact area between the indenter and the sample surface. For accurate measurements, the contact area of the indenter with the sample surface should be measured as a function of depth by indenting a sample with known modulus to generate a tip area function. Using the relationships in Eqs. I-31 and I-32, this can easily be accomplished. Analysis of the force curve can also provide
valuable information on creep, elastic recovery and plastic deformation that the material experiences.\textsuperscript{104,105} An AFM can be used for measurements of this nature.\textsuperscript{106,107} However, due to the angle of the cantilever with respect to the sample surface and non-vertical engagement of the sample surface, AFM nanoindentation experiments are generally limited to qualitative comparisons between two materials or phases within an immiscible blend.\textsuperscript{108,109} For quantitative measurements an indenter with a vertical indentation cycle is more suitable.\textsuperscript{110,111} A typical force curve is shown in Figure I-11a. The maximum applied load is maintained for a short period of time in order to remove what is known as the “nose effect” that happens when further displacement occurs after the tip has began retracting from the sample surface (see Figure I-11b). This effect can lead to highly inaccurate measurements if it is not taken into account.\textsuperscript{112,113}

The applications of nanoindentation can be extended to measuring the thickness of thin films. By monitoring the force curve as the indenter penetrates the sample surface an increase in the slope of the extension curve will appear as the indenter comes into contact with the substrate. This technique has been shown to compare well with results from ellipsometry when measuring the thickness of polyelectrolyte multilayers.\textsuperscript{114} The displacement of the piezoelectric actuator ($\Delta z_p$) and tip deflection ($\Delta z_t$) are related to the indentation displacement ($\Delta z_i$) by:

$$\Delta z_i = \Delta z_p - \Delta z_t \cos(10^\circ)$$  \hspace{1cm} (I-35)

where $\Delta z_i$ is multiplied by $\cos(10^\circ)$ to account for the angle of the probe relative to the sample surface. It should be noted that the tip must actually penetrate the surface rather than only deform it elastically. Therefore, this method is particularly applicable to soft, hydrated samples or biological films.
Nanocomposites

The fundamental material properties of polymer composites undergo a significant change as the size of their constituent particles approach the nanometer scale. Typically nanofillers (such as clays, silica and carbon nanotubes) greatly enhance the composite’s strength and modulus but produce a large increase in viscosity that complicates melt processing. However, as the size of the nanoparticles in the polymer matrix approach the molecular level, deviations from theory for hard-sphere-filled suspensions (Eq. I-37)\(^{115}\) may occur. This theory predicts a monotonic increase in zero-shear-rate viscosity (\(\eta_0\)) as the particle volume fraction (\(\phi\)) increases.

\[
\eta_0 = \eta(0)[1 + 2.5\phi + \ldots]\quad (I-36)
\]

This was observed by Zhang and Archer\(^{116}\) in their study on the viscoelastic properties of poly(ethylene oxide) (PEO) filled with 12 nm silica particles. At very low loadings (approximately 2 vol %) the linear viscoelastic properties were enhanced considerably. In the work of Mackay el al.,\(^{117}\) polystyrene (PS) melts were filled with 5 nm highly-crosslinked PS nanoparticles, and decreases in viscosity up to 50% were reported. While the exact mechanism of these dramatic reductions in viscosity is not known, it has been suggested that low additions of nanoparticles result in an increase in free volume that is responsible for the observed viscosity reductions.\(^{118}\)

Polyhedral oligomeric silsesquioxane (POSS) nanostructured chemicals are a unique class of nanoparticles with a hybrid organic-inorganic structure, well defined three-dimensional architecture and mono-disperse particle size. POSS molecules consist of a Si-O-Si inorganic cage, surrounded by an organic corona, represented by substituents “R”. The inorganic cage, with structure \((\text{SiO}_{1.5})_n\) where \(n=8, 10\) or 12, may be a fully
condensed “closed” or “open” structure (see Figure I-12). The diameter of these nanoparticles ranges from 1 to 3 nm, depending on the composition of the cage. The organic substituents can be tailored to provide a wide range of different properties. They can also be modified to increase compatibility with a specific polymer matrix or made reactive to allow co-polymerization with a spectrum of monomers.

Incorporation of POSS molecules into a polymer matrix can proceed by copolymerization or physical blending methods. While most studies have focused on synthesis of POSS copolymers, relatively few studies have been performed on melt blended systems. Recent work has shown that when POSS dissolves into the polymer matrix, deviations from the theory for hard-sphere-filled suspensions occurs. Investigations of melt-mixed systems containing POSS and polypropylene, high density polyethylene and poly(methyl methacrylate) indicate that rheological behavior is related to the compatibility of the POSS molecule with the thermoplastic matrix and to the POSS loading level. At low concentrations POSS was shown to dissolve into the polymer matrix producing a strong decrease in viscosity. At higher concentrations the solubility limit of POSS was reached, and agglomeration occurred leading to an increase in viscosity.

Studies in our own and other research laboratories have demonstrated the propensity of POSS to segregate to the surface of a polymer matrix. The POSS/polymer nanocomposites exhibited reduced friction and melt viscosity, and improved nanomechanical properties, abrasion resistance and hydrophobicity. The level of property improvement was related to the extent of segregation and POSS molecular aggregation. Aggregation appears to be related to POSS concentration and solubility in
the polymer matrix. An alternative explanation for observed enhancement in melt processability is the surface segregation resulting in lubrication by POSS aggregates. Furthermore, it has been suggested that melting temperatures and relative viscosities of the polymer and POSS molecules may play a role.¹⁴⁸ These factors, however, do not fully explain the observed rheological behavior of POSS nanocomposites, and the mechanism of rheology modification is not understood. In this thesis the role of POSS structure on dispersion and aggregation in a polyphenylsulfone matrix is investigated, and its effect on rheological and mechanical properties of the resultant nanocomposite is defined.

Motivation and Contribution of Current Research

Identification of the molecular parameters of nanoadditives (semi rigid-rod polymers or hybrid nanostructured chemicals) and their mechanism of operation in determining the ultimate properties of composite materials is necessary for the development of these advanced materials. Minor adjustments to the additive structure can mean the difference between a high performance composite and a useless material. Understanding how additive structure impacts interaction with the polymer matrix will permit efficient use of these costly materials enabling the development of successful molecular composites and nanocomposites.

The majority of studies pertaining to molecular composites have focused on using strictly linear macromolecular reinforcing agents. This highly linear, rodlike macromolecular structure inherently leads to the development of anisotropic phases. However, little research has been performed on “kinked” or semi rigid-rod structures containing organic substituents. The outstanding mechanical and thermal properties of
SRP polymers make them excellent candidates for use as reinforcing elements in a thermoplastic matrix for the development of molecular composites. By understanding the fundamental influence of copolymer composition (i.e., ratio of substituted para to unsubstituted meta recurring units in the polymer backbone) on miscibility, morphology and mechanical properties of molecular composites, the development of these materials can be greatly facilitated. This study examines the inherent mechanical properties of SRP polymers and polyphenylsulfone (PPSU). Information obtained from dilute solution properties is used to understand the complex relationship between enthalpic and entropic contributions during blending. SRP polymers are solution blended with PPSU and cast into films. Miscibility is investigated using standard thermal characterization techniques such as differential scanning calorimetry. The interfacial tension and surface segregation in the blends are studied by measuring the surface tension of the pure components and blends though contact angle measurements, while AFM is employed to image the resulting morphologies. Furthermore, the nanomechanical properties of the blends are measured using nanoindentation to obtain information about modulus and hardness.

POSS nanostructured chemicals have effectively reduced the melt viscosity of certain amorphous thermoplastics. This has been shown to occur when POSS dissolves into the polymer matrix as well as in the presence of strong phase segregation, but the relationship of POSS structure to this phenomenon and the mechanism(s) of flow enhancement remain unknown. This study seeks to evaluate how POSS structure relates to compatibility and phase segregation within a PPSU matrix and how these factors affect the rheological performance and thermomechanical properties in the resulting nanocomposite. Compatibility is predicted by calculation of solubility parameters for
selected POSS chemicals. The rheological properties of POSS/PPSU composites and enhancements in melt flow are observed by a combination of capillary rheometry and monitoring of process conditions. Mechanical performance of these composite materials is evaluated by subjecting them to a series of standardized tensile tests to measure their modulus, strength and elongational properties while thermal analysis techniques are employed to monitor glass transition behavior as well as thermal degradation. The dispersion and aggregation behavior POSS chemicals and the resulting morphology is analyzed by optical microscopy and related to the observed changes in nanocomposite properties.

This dissertation is composed of six chapters. Chapter II outlines the overall research goals and specific objectives of this research. Chapter III establishes the mechanical and viscoelastic properties of SRP compared to commercially available polymers. Chapter IV explores the dilute solution properties of PPSU and two different grades of SRP to understand how their structural parameters can contribute to or hinder the development of molecular composites. The relationships between copolymer architecture and miscibility, morphology and nanomechanical properties of the resulting blends are established in this chapter. Chapter V probes the influence of the structure of POSS molecules on the rheological and mechanical performance of melt blended PPSU nanocomposites. Chapter VI provides future recommendations for further understanding of the complex relationships established by this research. Finally, advanced AFM characterization techniques developed to understand the morphology and dynamic responses of polymer films are included in the Appendix of this document. In this section conductive AFM techniques used to identify the mechanism of actuation present
in perfluorosulfonated ionic (PFSI) membranes by probing their response under the influence of electrical fields is described.
Tables and Figures

**Figure I-1.** Generalized chemical structure of SRP copolymer.

*Diagram showing the chemical structure of SRP copolymer.*

**Figure I-2.** Comparison of SRP specific tensile modulus to polysulfone (PSU), polyetherimide (PEI), polyetheretherketone (PEEK), polyimide (TPI), polyamideimide (PAI), polyphenylene sulfide (PPS), thermoplastic polybenzimidazole (TP-PBI) (Adapted from ref. 47 p. 1067).

*Graph comparing the tensile modulus of different polymers, with SRP showing the highest value.*
Figure I-3. Comparison of SRP specific yield strength and tensile modulus to structural metals 316 stainless steel (316 SS), 6061-T6 Aluminum (Al 6061), 7075-T6 Aluminum (Al 7075), 6A1-4V Titanium (Ti6A1-4V) (Adapted from ref. 47 pp. 1067-8).
Figure I-4. Illustration of LCST and USCT behavior for binary polymer solutions or blends (Adapted from ref. 56 p. 12).
Figure I-5. Schematic illustration of Halpin-Tsai description with matrix modulus of 1 GPa and fiber modulus of 50 GPa and varying aspect ratio of fiber.
Figure I-6. Scattering intensity as a function of scattering angle for small and large particles.
Figure I-7. Typical Zimm plot.

\[ \frac{Kc}{R_\theta} = \frac{1}{M_w} + 2A_c \theta \]

\[ \frac{Kc}{R_\theta} = \frac{1}{M_w} + \frac{16\pi^2}{3\lambda^2} R_G^2 \sin^2 \frac{\theta}{2} \]
Figure I-8. General schematic of atomic force microscope.
Figure I-9. Amplitude versus frequency and phase versus frequency relationships for harmonic oscillator with resonant frequency $\omega_0$. Attractive forces cause a low-frequency shift of these curves (---), repulsive forces cause a high-frequency shift (---) (Adapted from ref. 92 p. 15).

Figure I-10. Generalized force curve (a) cantilever approach (b) jump to contact (c) extension portion of force curve (d) retraction portion of force curve (e) adhesive release.
Figure I-11. Load versus displacement curves from nanoindentation (a) load controlled indent with hold time at maximum load (b) load controlled indent with no hold time at maximum load displaying “nose” effect.

Figure I-12. Representative POSS structures (a) condensed “closed” cage dodecaphenyl POSS (b) “open” cage trisilanolphenyl POSS.
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CHAPTER II
OBJECTIVES OF RESEARCH

As the dimensions of the reinforcing element in a polymer matrix approach the molecular level, specific phenomena occur that lead to remarkable improvements in modulus and strength of the composite material even at low volume fractions. The principal factor leading to this behavior is a substantial increase in the surface area to volume ratio of the reinforcing element that maximizes interfacial interactions with the polymer matrix. Because the cost of these materials is so high, it is imperative that they be used in an efficient manner. Therefore, understanding the factors that control effective dispersion of these materials on the molecular level becomes paramount in taking full advantage of their potential in an economical fashion.

Molecular dispersions of molecules with rigid-rod structures in flexible macromolecules (molecular composites) represent a new class of reinforced plastic materials that offer distinct advantages over carbon or glass fiber composites. Unlike anisotropic carbon or glass fiber composites, reinforcement in a molecular composite occurs at the molecular level resulting in an isotropic material. Therefore, molecular composites are inherently homogeneous materials that have smooth surfaces and are potentially recyclable. Also, the aspect ratio of the reinforcing element in a composite is directly related to the degree of reinforcement. By maximizing the aspect ratio, the maximum reinforcement is achieved through: (1) increasing the length of the reinforcing element, and (2) decreasing the diameter of the reinforcing element. In a molecular composite the diameter of the reinforcing element is reduced to that of a single molecule, providing the greatest opportunity for reinforcement of the polymer matrix. The
difficulties associated with effective production of molecular composites arise from the nature of the rigid-rod macromolecule. The strong tendency of rigid-rod macromolecules toward alignment during conventional processing methods leads to the development of anisotropic order through a process known as entropic demixing. This causes rigid-rod polymers to be insoluble in organic solvents and highly incompatible with flexible coil polymers. When phase separation occurs in a rigid-rod/flexible coil polymer blend an anisotropic phase rich in the rigid-rod component coexists with an isotropic phase containing the flexible coils. Interfacial area is minimized, and the full reinforcing potential of the rigid-rod macromolecule is not achieved. Recently developed semi rigid-rod macromolecules have exhibited both solubility in organic solvents and isotropic properties in the solid state through modification of the polymer’s structure. This was accomplished by the development of a copolymer containing a mixture of phenylketone substituted para-phenylene and unsubstituted meta-phenylene recurring units (i.e., self reinforced polymers (SRPs)). The substituted para recurring units impart solubility to the semi rigid-rod macromolecule in organic solvents while the unsubstituted meta recurring units form “kinks” that serve to disrupt the formation of anisotropic order. The ultimate properties of the copolymer strongly depend on the ratio of substituted para to unsubstituted meta recurring units in the polymer backbone. Understanding this complex relationship will provide valuable insight into the phase behavior and degree of reinforcement that can be expected from these macromolecules in blends with flexible polymers.

Addition of nanostructured materials (such as nano silica) to a polymer matrix provides a potential avenue for increasing mechanical properties of the composite
without reducing processability, in contrast to behavior observed in blends reinforced with micro-fillers. In fact, significant enhancements in material processing have been observed for polymer nanocomposites with low loadings of nanostructured additives when the dimensions of the additives approach the molecular scale. Polyhedral oligomeric silsesquioxanes (POSS\textsuperscript{®}) are a special class of silica-based nanostructured chemicals that have been shown to provide significant processing improvements in selected systems. POSS molecules are hybrid organic-inorganic structures, monotonic in size, consisting of a silicon oxide cage with a corona of organic substituents. A wide variety of organic substituents can be incorporated in the corona, providing opportunities for promoting solubility and improving dispersion within a specific polymer matrix.

While dramatic processing improvements have been achieved in some polymer systems, other composites show minimal or no improvements, and the factors controlling rheology enhancements are not well understood. We hypothesize that the key to attaining desired performance in POSS/polymer nanocomposites relies on developing an understanding of the factors that control molecular level dispersion and POSS aggregation in the polymer matrix.

Nano-scale dispersion is required for successful development of both molecular composites and nanocomposites. This research is comprised of two segments, both involving study of molecular level dispersion in an amorphous polymer matrix. The primary objective of this research is to determine the structure/property factors that govern the effective production of molecular composites in semi rigid-rod/amorphous polymer systems. The second research segment involves study of the effects of POSS structure and dispersion on nanocomposite rheology and mechanical performance.
key goals are to perform a fundamental investigation of the molecular parameters of recently commercialized semi rigid-rod copolymers and polyphenylsulfone (PPSU) to determine the factors controlling production of reinforced homogeneous blends (molecular composites), and to understand the influence of the ratio of substituted para to unsubstituted meta recurring units in the copolymer backbone on miscibility, morphology and mechanical properties. In addition, it is of considerable interest to determine the factors controlling successful production of POSS/polymer nanocomposites and relate these factors to rheological and mechanical performance.

The specific goals of this research are to:

1. Demonstrate the nanomechanical behavior of semi rigid-rod copolymers, having complete sp² hybridization in their backbone, in comparison to conventional high performance amorphous thermoplastics with flexible spacers in their backbone as a function of polymer rigidity via nanoprobe instrumentation techniques.

2. Determine the molecular parameters in dilute solution (weight-average molecular weight, radius of gyration, second virial coefficient and hydrodynamic radius) of individual SRPs having different ratios of substituted para and unsubstituted meta recurring units and PPSU using light scattering techniques, and to relate these molecular parameters to polymer conformation, theoretical enthalpic and entropic contributions and predicted blend compatibility.

3. Develop an effective blending strategy for SRPs and PPSU by rapid coagulation from dilute solution using results from light scattering studies and cast blends.
(4) Predict miscibility using bulk thermal characterization techniques (i.e.,
differential scanning calorimetry) to measure glass transition behavior as a
function of copolymer and blend composition.

(5) Analyze bulk and surface morphologies of blends using nanoprobe
microscopy to determine the mechanism of phase separation or confirm
homogeneous morphology.

(6) Evaluate mechanical properties (i.e., modulus and hardness) of blends
using nanoindentation techniques and compare to predictions for mechanical
properties of molecular composites.

(7) Develop an understanding of the relationship between the ratio of
substituted para and unsubstituted meta recurring units in the SRP copolymer
backbone to miscibility, morphology and nanomechanical properties in blends (or
molecular composites) with PPSU.

(8) Identify suitable nanostructured chemicals (POSS) based on minimal
differences in calculated solubility parameters and thermal stability for
nanocomposite formation.

(9) Determine enhancements in melt processing of PPSU by addition of POSS
nanostructured chemicals of different compositions at varying loading levels.

(10) Demonstrate the rheological and thermomechanical property effects of
POSS addition to PPSU as a function of POSS composition and loading level.

(11) Assess dispersion of POSS within the PPSU matrix in relation to solubility
parameters and the resulting effects on rheological, mechanical and thermal
properties.
Fulfillment of these objectives has required the application of advanced nanoprobe techniques that have been utilized in polymers only recently. These powerful techniques have permitted the direct imaging of molecular events with sub-nanometer resolution and have become an indispensable tool in polymer characterization. The versatility of these methods allows them to be applied to a wide range of polymeric systems and to provide a wealth of information that could not be gained otherwise. The Appendix of this document describes advanced nanoprobe techniques that have been employed to understand the complex and dynamic response of polymer films to various stimuli. Current sensing AFM to identify the mechanism of electrical actuation in perfluorinated ionomer based artificial muscles is discussed.

By understanding the principles that govern the phase behavior and mechanical reinforcement in semi rigid-rod/amorphous polymer molecular composites, the development of the materials can be greatly facilitated. In addition, the relationships established can be applied to the intelligent design of other reinforced molecular composite systems. With regards to nanocomposites containing POSS and PPSU, there have been relatively few studies that investigate material processing, rheology, and thermomechanical properties. This research represents one of the first systematic studies that probes the influence of POSS architecture on all of these areas. Ultimately, identifying the key molecular parameters in these systems and their relationship to the final properties of the composite materials is the overall goal of this research.
CHAPTER III
NANOMECHANICAL CHARACTERISTICS OF A COPOLYMER BASED ON BENZOYL-1,4-PHENYLENE AND 1,3-PHENYLENE

Abstract

Surface mechanical properties of a copolymer based on benzoyl-1,4-phenylene and 1,3-phenylene were evaluated using nanoprobe investigation techniques and compared to the properties obtained at the macroscale. These copolymers are commonly referred to as self-reinforced polymers (SRPs) because of their intrinsic high strength and modulus without addition of any reinforcing agent. Specimens were prepared solvent casting and compression molding. Surface mechanical properties and film thickness were measured by nanoindentation. Immediately after indentation the resulting indents were imaged. Nanoindentation of SRP, polycarbonate (PC), and polyetherimide (PEI) demonstrated superior surface hardness and modulus of SRP copolymers.

Introduction

Poly(paraphenylene) is a rigid rod polymer that in theory should possess ultra high strength and stiffness due to the rigid nature of its backbone, consisting exclusively of phenylene linkages. However, during the polymerization reaction only 6 to 10 repeat units are incorporated into the polymer chain before it precipitates from solution. Incorporation of a comonomer with benzoyl substituents renders the copolymer soluble and a copolymer with a high molecular weight and intrinsic viscosity can be produced (Figure III-1). The strength and stiffness of the material is retained by the rigid phenylene linkages throughout the backbone, while the side group attachment gives the polymer its solubility. Linear copolymers of 1,4-phenylene with benzoyl-1,4-
phenylene, however, remain difficult to process via traditional melt processing techniques such as injection molding. Incorporation of 1,3-phenylene comonomer yields a copolymer with improved melt processability, but somewhat reduced modulus. These copolymers are commonly referred to as self-reinforced polymers (SRPs) because of their intrinsic high strength and modulus without addition of a reinforcing agent.

Compared to most linear polymers, which possess a more coil-like structure, SRPs have reduced conformational and rotational motion. This inhibits their ability to flex and produces a much stiffer material. The strength of SRPs is also directly related to the aspect ratio of the rod-like segments of the polymer molecule, with a higher aspect ratio yielding a stronger material. The solubility, stiffness, and melt processability of the copolymers can be specifically tailored by adjusting the copolymer composition. The SRP used in this study is a commercially available copolymer with approximately 15 mole % 1,3-phenylene and 85 mole % benzoyl-1,4-phenylene.

SRPs are amorphous polymers that can be processed by both solution and melt techniques into transparent, amorphous films and plaques. SRPs exhibit dramatically increased strength, modulus and hardness properties in comparison to traditional engineering thermoplastics, as exhibited in reported properties for commercial SRP, polyetherimide (PEI) and polycarbonate (PC) polymers of similar molecular weights (Table III-1). Additionally, SRPs have been demonstrated to form miscible blends with polycarbonate with intermediate modulus levels, providing potential opportunity for more easily processable high strength transparent materials. Their ultra high strength, hardness and strength to weight ratio make SRPs of interest for applications ranging from light weight structural components to protective films and coatings. In particular, their
demonstrated dielectric capabilities\textsuperscript{6,10} combined with their high strength and hardness, indicate their potential for thin film and micro/nanoelectronic applications. For these types of applications, it is critical to understand not only the bulk mechanical properties, but also surface nanomechanical performance of the materials and how these properties correlation from the nano to macroscale. Nanomechanical properties of SRP were evaluated in comparison to PEI and PC polymers, and their surface properties compared to reported bulk mechanical properties. The widely used engineering thermoplastics PEI and PC were chosen as reference comparative materials for evaluating SRP performance, and to provide materials with varying rigidity (SRP stiffness > PEI > PC). SRP, PEI and PC grades of similar molecular weights were chosen to minimize performance differences based on molecular weight.

Nanoindentation techniques are emerging as effective methods for measurement and prediction of thin film properties, including friction, wear, surface roughness, adhesion, lubrication, hardness, and modulus.\textsuperscript{11,12,13} Indentation characterization is a valuable method for evaluating the nanoscale response of materials. These methods are used to determine local hardness and modulus on the surface of a material. Measurements are based on a force curve generated as a stiff probe penetrates the material surface. A force curve plots the applied load to the probe with respect to displacement into the specimen, and information about modulus, hardness, elastic recovery, and plastic deformation is obtained.\textsuperscript{14} Property measurements are based on the contact mechanics of an axisymmetric indenter with an elastically isotropic half space, developed by Oliver and Pharr.\textsuperscript{15} Hardness values ($H$) are calculated as:

$$H = \frac{P_{\text{max}}}{A}$$  \hspace{1cm} (III-1)
where $P_{\text{max}}$ is the maximum applied load, and $A$ is the contact area between the probe and the specimen. Reduced modulus ($E_r$) values are taken from the slope ($dh/dP$) of the unloading portion of the force curve and are dependant upon the contact area by the relation:

$$\frac{1}{E_r} = \frac{dh}{dP} \frac{2A^{1/2}}{\pi^{1/2}}$$  \hspace{1cm} (III-2)

where $h$ is the depth of penetration, and $P$ is the applied load. In this paper properties measured at both the nanoscale and macroscale are compared to assess the translation of properties from the molecular to macroscopic level, of particular interest for assessing performance for advanced thin film applications.

**Experimental**

**Materials**

Materials were used as received unless noted otherwise. SRP resin and compression molded discs were supplied by Mississippi Polymer Technologies, Inc. (MPT) Bay St. Louis, MS. The SRP copolymer evaluated, PARMAX® 1200, has Mw of 30,000 as measured by light scattering. The SRP is produced on commercial scale at MPT facilities via a proprietary process. PC (LEXAN® 144R) and PEI (ULTEM® 1000) molded discs were provided by GE Plastics. The PC Mw measured by light scattering (absolute method) is reported as 26,300, while the relative Mw determined by GPC using polystyrene standards is reported as 57,000. PEI relative Mw measured by GPC using polystyrene standards is reported as 52,000, so actual molecular weight is presumably in the range of 20,000 to 30,000.
**Sample Preparation**

Solution cast films of SRP were prepared using a draw down bar on a glass plate. SRP was dissolved in 1-methyl-2-pyrrolidinone at ten weight percent for solution casting. After application to a glass plate the solvent was removed in a vacuum oven. Vacuum pressure was adjusted from -20 to -30 inches Hg, and the temperature was increased from room temperature to 150°C at a rate of 30°C per hour. The films were allowed to remain in the vacuum oven for a minimum of ten hours at 150°C and -30 inches Hg. After removal from the vacuum oven, the films were placed in a convection oven at 205°C to drive off any remaining solvent.

**Nanoindentation**

Indentation were made using a MultiMode AFM (Digital Instruments, Santa Barbara, CA) and a Triboindenter (Hysitron, Inc., Minneapolis, MN). The probe used with the MultiMode was a steel cantilever mounted with a diamond tip, having a force constant of 162 N/m and resonant frequency 63.8 kHz. Deflection sensitivity of the cantilever was calibrated on a sapphire surface. The Triboindenter was operated with a three-sided diamond (Berkovich type) tip, which was calibrated on fused silica.\(^\text{20}\)

Nanoindentation using a MultiMode AFM was performed on solvent cast SRP films and extruded PC films. Deflection sensitivity of the cantilever was determined from indenting an impenetrable sapphire surface. A 4x4 array of indents spaced by 750 nm with the applied load increasing by equal increments of 3.4 µN from 13.7 µN to 23.9 µN along each row was made into PC and SRP surfaces. Immediately after indentation the arrays were imaged.
Nanoindentation of SRP, PC, and PEI compression molded discs was performed using a Triboindenter mounted with a Berkovich tip. A single indentation sequence was used for all three specimens. The applied force was linearly ramped from 0 to 8 milliNewtons over a period of 10 seconds with a 16 second hold time at the maximum force and removed linearly over a period of 10 seconds.

Results and Discussion

Nanoindentation studies were performed on SRP samples to determine comparative hardness and elasticity of thin films and surfaces at nanoscale in relation to bulk measurements. SRP and PC films were analyzed via AFM nanoindentation techniques, as described in the experimental section. In this study, an indent array was created by indenting increasing levels of force on the film surface. The same array was applied to both SRP and PC, and as observed in Figures III-2 and III-3, indentation depth and deformation of the surface is substantially greater for the PC film. The maximum indentation depth is extracted from the force curve obtained during the indentation process. The maximum occurs when the tip is at the highest deflection and maximum z-piezo travel (Figure III-2).

Maximum indentation depths for each level of applied force are given in Table III-2. For the lowest levels of applied force indentation depth is two times greater for PC than SRP, increasing to 3:1 indentation depths for PC compared to SRP at higher levels of force. Residual indentation depth is determined by imaging the films in tapping mode after completing the indentation array (Figure III-3). As seen for maximum penetration depth, PC exhibits two to three times greater residual indentation depth than SRP, with the difference in indentation depths increasing with increasing applied load (Table III-2).
Percent recovery is defined as the difference in maximum penetration depth and residual indentation depth divided by the maximum indent depth. Average recovery for both materials is 70 – 75%. Thus, although plastic deformation is substantially higher for the PC film, elastic recovery is similar for the two amorphous polymers.

Nanomechanical analysis of compression molded SRP, PEI and PC samples was performed using the Hysitron Triboindenter to determine surface hardness and reduced modulus via the methods described in the introduction and experimental section. As seen in Figure III-4, penetration of the diamond tip as well as are dramatically greater for both PEI and PC in comparison to SRP. As was observed in AFM measurements, penetration depth is three to four times higher for PC than for SRP for the same loading force. Plastic deformation is approximately two times greater for PEI and three times greater for PC than for SRP, under the same load. Reduced modulus and hardness data for the molded samples are summarized in Table III-3. Reduced modulus measured via the nanoindentation method exhibits the same trends observed in bulk testing, with SRP demonstrating a reduced modulus that is more than twice that of PEI and almost three times that of PC. When the reduced modulus at the nanoscale is compared to flexural modulus measured at the macroscale, the SRP shows an increase in properties based on the ratios of the reduced modulus and flexural modulus of the SRP to that of PEI and PC. Similarly, nanoscale hardness evaluations display the trends observed in macroscale Rockwell hardness tests, with substantially greater hardness for the SRP molded sample. The observed nano and macro scale properties follow expected trends, with hardness and modulus increasing with increasing chain stiffness. SRP exhibits highest modulus and strength due to the high proportion of *para*-phenylene linkages and restricted rotational
movement along the main chain,\textsuperscript{21} followed by PEI\textsuperscript{22,23} and finally PC\textsuperscript{24}. Thus the incorporation of \textit{meta}-phenylene linkages in the SRP copolymer, at least at the copolymer level tested, provides improved processability while maintaining high surface hardness and modulus for SRP in comparison to traditional engineering thermoplastics. These findings indicate the potential utility of SRPs for thin film applications requiring high strength and modulus. The ultra high hardness and modulus exhibited by SRPs in nanoindentation evaluations indicate their greater resistance to plastic deformation, scratching, and wear as well as resistance to local penetration on application of external force.

Conclusions

Copolymers based on benzoyl-1,4-poly(p-phenylene) and 1,3-phenylene are readily processed via solution and melt processing techniques. In nanoindentation studies, SRP molded samples demonstrated one and a half to two times the surface hardness and reduced modulus of traditional engineering thermoplastics, while maintaining similar elastic responses. These improved nanomechanical properties contribute to more resistance to wear, deformation and local penetration. The high modulus and surface hardness of these thin films indicates their potential utility for advanced thin film applications.

Acknowledgements

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are also due to Mississippi Polymer Technologies, Inc, (Bay St. Louis, MS) and GE Plastics for providing the polymer samples, and Dr. Sergei Magonov (VEECO Industries, CA) for valuable discussions and inputs during this study.
Tables and Figures

Table III-1
*Bulk Mechanical Properties of SRP Vs Traditional Engineering Thermoplastics.*

<table>
<thead>
<tr>
<th></th>
<th>SRP (MPa)</th>
<th>PEI (MPa)</th>
<th>PC (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural modulus</td>
<td>8300</td>
<td>3510</td>
<td>2340</td>
</tr>
<tr>
<td>ASTM D790</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile stress at yield</td>
<td>207</td>
<td>110</td>
<td>62</td>
</tr>
<tr>
<td>ASTM D630</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rockwell hardness</td>
<td>80B</td>
<td>109M</td>
<td>109M</td>
</tr>
<tr>
<td>ASTM D785</td>
<td>(B scale)</td>
<td>(M scale)</td>
<td>(M scale)</td>
</tr>
</tbody>
</table>

Table III-2
*Maximum Indentation Depth, Residual Indentation Depth, and Percent Recovery of SRP and PC.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Force (µN)</th>
<th>Max. indent depth (nm)</th>
<th>Residual indent depth (nm)</th>
<th>Percent recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRP</td>
<td>13.7</td>
<td>63</td>
<td>15</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>17.1</td>
<td>68</td>
<td>18</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>20.5</td>
<td>62</td>
<td>21</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>23.9</td>
<td>81</td>
<td>23</td>
<td>72</td>
</tr>
<tr>
<td>PC</td>
<td>13.7</td>
<td>140</td>
<td>26</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>17.1</td>
<td>156</td>
<td>40</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>20.5</td>
<td>180</td>
<td>42</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>23.9</td>
<td>190</td>
<td>64</td>
<td>66</td>
</tr>
</tbody>
</table>

*Each value is an average of the values from 4 indents.*
Table III-3
*Reduced Modulus and Hardness for SRP, PEI and PC Molded Samples Obtained via Hysitron Triboindenter Nanoindentation.*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reduced modulus (GPa)</th>
<th>Hardness (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRP</td>
<td>10.2</td>
<td>688</td>
</tr>
<tr>
<td>PEI</td>
<td>4.6</td>
<td>357</td>
</tr>
<tr>
<td>PC</td>
<td>3.6</td>
<td>188</td>
</tr>
</tbody>
</table>

*Figure III-1. Generalized chemical structure of a copolymer of benzoyl-1,4-phenylene and 1,3-phenylene.*
Figure III-2. Force curves for (A) SRP and (B) PC indentation.

Figure III-3. Tapping mode images for (A) SRP and (B) PC indent arrays. Height scale is set to 150 nm.
Figure III-4. Force curves for SRP, PEI, and PC compression molded samples from Triboindenter.
References


7 PARMAX® 1200 SRP Technical Data Sheet http://www.mptpolymers.com, accessed 1/06.


16 Communicated by MPT.


CHAPTER IV
EFFECTS OF CHAIN CONFORMATION ON MISCIBILITY, MORPHOLOGY AND MECHANICAL PROPERTIES OF SOLUTION BLENDED SUBSTITUTED POLYPHENYLENE AND POLYPHENYLSULFONE

Abstract

The effects of polymer conformation and degree of substitution on miscibility, morphology and mechanical properties of solution blended systems containing polyphenylsulfone and copolymers of phenylketone substituted p-phenylene with m-phenylene were studied. Static and dynamic light scattering studies were performed to obtain the z-average root mean square radius of gyration, second virial coefficient, weight average molecular weight and hydrodynamic radius. Solution blends of polyphenylsulfone with phenylene copolymers yielded free standing films. Blend miscibility was assessed by glass transition behavior, morphology was analyzed using atomic force microscopy and mechanical properties were measured using nanoindentation. Copolymer composition determined miscibility. Miscible blends exhibited homogeneous morphologies while immiscible blends displayed unique, heterogeneous morphologies. Polymer conformation in solution, rather than enthalpic contributions, was the primary determinant of miscibility. Successful reinforcement was achieved in blended systems.

Introduction

Molecular composites are blends containing rigid-rod polymers that act as reinforcing agents dispersed within a flexible polymer matrix. When no interface exists between the reinforcing fibers and the polymer matrix, molecular composites can also be
referred to as homogeneous composites.\textsuperscript{1} According to composite theory, successful mechanical reinforcement is described by the rule of mixtures and occurs when the aspect ratio of the reinforcing component is greater than one hundred.\textsuperscript{2} Development of molecular composites has the potential to provide new materials with increased strength to weight ratios and improved dimensional and thermal stabilities. Composite performance is driven by the molecular level reinforcing agent and its interaction with the matrix.\textsuperscript{3,4} A primary challenge in developing useful composites of this type is the dispersion of the rigid-rod polymer within the flexible matrix. Unlike blends of coiled polymers where compatibility can be achieved by offsetting an unfavorable enthalpy of mixing with a favorable entropy of mixing, blends containing rigid-rod and coiled polymers most often suffer from a highly unfavorable mixing entropy due to differences in conformation. As a result of steric forces, rigid-rod polymers form an ordered phase, excluding the coiled polymers. This effect, commonly referred to as entropic demixing, most often leads to unstable or incompatible blends even when favorable enthalpy of mixing exists between the rigid-rod and coiled polymers.\textsuperscript{5,6,7} In order to create a molecular composite, the thermodynamic effects of entropic demixing must be counteracted by altering the rigid-rod polymer to allow incorporation of the coiled polymer in the rigid phase.\textsuperscript{8,9,10,11} Increasing the free volume associated with the rigid-rod phase has been shown to relax the steric constraints and inhibit the formation of an ordered state. Effective methods for increasing free volume include modification of the rigid-rod polymer through side group attachment and introduction of nonlinear monomers into the polymer backbone.\textsuperscript{12}
The rigid-rod polyphenylenes investigated in this study are copolymers of para-phenylene substituted by a phenylketone group and meta-phenylene, with the generalized structure shown in Figure IV-1. These transparent, amorphous polymers have been classified as self reinforcing polymers (SRPs) for their high strength and modulus without the addition of reinforcing agents.\textsuperscript{13,14} SRPs are inherently both thermally and dimensionally stable and have been shown to possess mechanical properties far superior to known high performance thermoplastics.\textsuperscript{15,16,17} Their mechanical performance makes them excellent candidates as reinforcing elements when blended with flexible polymers. Miscible blends of this nature are classified as molecular composites. Although SRPs have typically exhibited low melt compatibility with other polymers, high levels of miscibility have been reported for SRP/polyetherimide (PEI) blends.\textsuperscript{18} Studies of tertiary melt blends containing SRP, polyetheretherketone (PEEK), and polyphenylsulfone (PPSU) demonstrated that PPSU increases compatibility between SRP and PEEK \textsuperscript{19}. While less industrially viable, solution blending provides a more effective means for creating homogenous blends of SRPs. Solution blends of SRP with polyimide, polycarbonate, and polysulfone yielded transparent films.\textsuperscript{15,20} Formation of optically clear films provides evidence of blend miscibility, but complicated processes that occur during solution casting often alter the state of mixing. Deviation from a state of thermodynamic equilibrium in solution cast films is due to the diffusion kinetics of the polymers in solution, the solubility of the polymers in solution and the surface free energy of the blend components. Non-homogenous films can be produced from polymers that usually form miscible blends if the solution becomes trapped in a state of immiscibility based on the tertiary solvent-polymer-polymer phase diagram.\textsuperscript{21,22}
Conversely, a homogenous film can be produced from immiscible polymers if the solvent is removed at such a rate that the polymers cannot kinetically diffuse into a state of thermodynamic equilibrium before solidification occurs. Immiscible polymer blends will often display an enrichment of one component at the surface. Typically, the component with the lower surface free energy will be enriched at the surface in order to minimize polymer-air surface tension, and the component with the lower solubility will deposit on the substrate first due to solvent effects.

In this study, solution blends of two SRP copolymers with PPSU and their films are investigated to determine miscibility and molecular reinforcement properties. Static and dynamic light scattering techniques are used to obtain information about the physical dimensions and intermolecular interactions of the two different SRP copolymers and polyphenylsulfone (PPSU) in solution. Surface free energies are measured using contact angle goniometry. Miscibility is characterized by observing the glass transition behavior of the blends, and the morphology is imaged by atomic force microscopy (AFM). The mechanical performance of the blends is assessed using nanoindentation and compared to the upper limit of mechanical reinforcement predicted by the rule of mixtures.

Experimental

Materials

PPSU and two variations of SRP (SRP-A and SRP-B) were supplied by Solvay Advanced Polymers, L.L.C. in powder form. The SRPs are copolymers of phenylketone substituted \textit{para}-phenylene with \textit{meta}-phenylene. SRP-A contains a low amount (less than 25 mol\%) of m-phenylene recurring units, and SRP-B contains a higher amount of m-phenylene (40 - 60 mol\%). Both copolymers are commercially available under the
trade name PRIMOSPIRE®. The reported tensile moduli for SRP-A and SRP-B are 8.3 and 5.5 GPa, respectively. PPSU has a reported tensile modulus of 2.3 GPa.25

Anhydrous 1-methyl-2-pyrrolidone (NMP), anhydrous toluene, and a 5,000 molecular weight polystyrene standard were obtained from Sigma-Aldrich. Anhydrous solvents were supplied in sealed bottles and only opened immediately prior to solution preparation. In each case that a polymer solution or solvent was filtered, an inorganic membrane filter (Anotop 25, Whatman, Maidstone, UK) was used.

Sample Preparation

For light scattering measurements all glassware was rinsed with filtered ethanol and dried prior to use to remove any dust collected. Polymer powders were dried in a vacuum oven at 120°C for 1 hour prior to dissolution. Stock solutions were prepared by adding 1 gram of dry polymer to a 100 mL volumetric flask. NMP is a hygroscopic solvent, and precautions were taken to minimize water absorption by limiting its exposure to the laboratory environment. To remove dust NMP was drawn from a sealed container into a syringe and then added to the flask through a 0.02 µm pore size filter. The polymers were dissolved under nitrogen. The stock solution was added to a scintillation vial through a 0.2 µm pore size filter and diluted solutions were prepared by adding NMP to the same vial through a 0.02 µm pore size filter. Using the same scintillation vial to dilute a polymer solution during light scattering minimizes error due to variations in the scintillation vial since it also serves as the measurement chamber during batch measurements. The least concentrated polymer solutions used during static light scattering (SLS) measurements were used for dynamic light scattering (DLS) measurements. Each solution was stored in a desiccation chamber after preparation.
Solution cast polymer films were prepared by mixing stock solutions at 10 wt% in different ratios to make blended solutions. The blended solutions were applied to glass plates and placed into a vacuum oven at 30°C and an absolute pressure of approximately 20 kPa to prevent rapid flashing of the solvent. The temperature was increased at a rate of 30°C per hour until 150°C was reached. Pressure was gradually reduced each time the temperature was increased until the maximum vacuum was achieved around 1-2 kPa. The films were left in the vacuum oven overnight and placed in a convection oven at 205°C for 1 hour to remove any remaining solvent.

*Light Scattering*

The z-average root mean square radius of gyration ($<R_G^2>$), weight average molecular weight ($M_w$), and second virial coefficient ($A_2$) of the polymers in NMP were measured by SLS techniques using a multi-angle photometer DAWN DSP (Wyatt Technologies Corp, Santa Barbara, CA) in batch mode. This instrument uses a He-Ne laser with wavelength ($\lambda$) of 632.8 nm as the excitation source. Scintillation vials served as the batch cell, and 11 fixed angle detectors between 44° and 147° were used to collect the scattered light. An absolute calibration of the photometer was carried out using anhydrous toluene filtered through a 0.02 µm pore size filter into a clean scintillation vial. The individual photodiodes were normalized using an isotropic scattering solution. The isotropic scattering solution was a narrow molecular weight polystyrene standard (most probable molecular weight of 5,000) in toluene. Polystyrene having this molecular weight in toluene has a radius of gyration ($R_G$) of approximately 2.3 nm and behaves as an isotropic light scattering solution. The differential refractive index of each polymer in NMP was measured by a refractometer (Bausch and Lomb), and NMP filtered through a
A 0.02 µm pore size filter was used to establish the baseline. SLS data is linearly fitted using Zimm formalism, where \( K^* c / R_{\text{theta}} \) is plotted versus \( \sin^2(\theta/2) \). \( K \) is an optical constant, \( c \) is solution concentration in g/mL, \( R_{\text{theta}} \) is Rayleigh’s ratio, and \( \theta \) is the scattering angle. In each figure the data is extrapolated to both \( \theta = 0^\circ \) and \( c = 0 \). The inverse of the intercept of each extrapolated line is the weight average molecular weight, \( M_w \). The limiting slope of the line projected to \( \theta = 0^\circ \) at constant \( c \) gives the second virial coefficient \( (A_2) \). Due to the polydisperse nature of the polymers investigated the limiting slope of the line projected to \( c = 0 \) at constant \( \theta \) gives the \( z \)-average root mean square radius of gyration \( \langle R_g^2 \rangle_z \). The relationship between \( R_G^2 \) and \( \langle R_G^2 \rangle_z \) is given by eqn 1.

\[
\langle R_g^2 \rangle_z = \frac{\sum w_i M_i R_G^2(i)}{\sum w_i M_i}
\]  

(IV-1)

The hydrodynamic radii (\( R_h \)) of the polymers in NMP were measured by DLS using a Malvern Instruments Zetasizer Nano series instrument equipped with a He-Ne laser operating at a wavelength of 632.8 nm, an avalanche photodiode detector with a high quantum efficiency, and an ALV/LSE-5003 multiple tau digital correlator electronics system.

**Differential Scanning Calorimetry**

For neat and blended samples the glass transition (Tg) was measured using a Thermal Analysis Instruments Q100 DSC under nitrogen at a flow rate of 50 mL/min. A heating rate of 10°C/min was applied from room temperature to 230°C. The samples were held at 230°C for 1 min then quenched to 50°C. A heating rate of 10°C/min was applied until 230°C, and the Tg was determined from the second heating scan by the
temperature on the curve half way between the tangent lines drawn above and below the transition region.

**Contact Angle Goniometry**

Contact angle measurements were conducted via the sessile drop technique using a Ramé-Hart goniometer coupled with DROP-image® data analysis software. The static contact angle formed by drops of HPLC grade water (11 µL) and diiodomethane (DiiM) (2 µL) was measured on each polymer surface immediately after deposition. Ten droplets of each test fluid were analyzed at different locations on each polymer surface. The solid-vapor surface energies ($\gamma_{SV}$) of the pure components and blends are calculated from the measured contact angles ($\theta$) of water and diiodomethane on the polymer surfaces using the Owens-Wendt model given by eqn. 2.28. This model contains both a dispersive energy component ($\gamma_{SV}^d$) that accounts for van der Waals forces and a polar energy component ($\gamma_{SV}^p$) accounting for dipole-dipole, induced dipole and hydrogen bonding forces.

$$\gamma_{SV} = \gamma_{SV}^d + \gamma_{SV}^p$$  \hspace{1cm} (IV-2)

The polar and dispersive components of the Owens-Wendt model are found by combining Good’s and Young’s equations in eqn. 3, where the only unknowns are $\gamma_{SV}^d$ and $\gamma_{SV}^p$. The contact angles of water and diiodomethane on each polymer surface are used to solve for the polar and dispersive energy components of each solid polymer surface by eqn. 3.29

$$\left(1 + \cos \theta \right) \cdot \frac{\gamma_{LV}^p + \gamma_{LV}^d}{2 \cdot \gamma_{L}^d} = \sqrt{\gamma_{SV}^d + \sqrt{\gamma_{SV}^p}} \cdot \frac{\gamma_{LV}^p}{\gamma_{LV}^d}$$  \hspace{1cm} (IV-3)
In the above equation $\gamma_L$ is the surface tension of the test fluid, and $\gamma_{LV}^P$ and $\gamma_{LV}^d$ are the polar and dispersive components of the surface tension of the test fluid.

**Atomic Force Microscopy**

AFM micrographs were collected with an Agilent 5500 AFM (Agilent Technologies, Santa Clara, CA) in alternating current mode using an etched silicon probe with a nominal resonant frequency of 275 kHz (RTESP, Veeco Instruments, Santa Barbara, CA). The scan rate was kept at 0.5 Hz, and images are an array of 512x512 data points. Data were processed using Gwyddion version 2.7 software to remove artifacts and improve image quality by applying plane leveling, line correction, and scar removal operations. AFM studies were performed under ambient conditions in a temperature (27°C) and humidity (40-45%) controlled room. Multiple areas were imaged for each sample, and representative images are presented. Height and phase images of the pure component and blend surface morphologies were obtained on the film surfaces without further sample preparation. Measurements of root mean square roughness ($R_{rms}$) values were taken from AFM micrographs over an area of 625 $\mu$m$^2$ and calculated using Gwyddion version 2.7 software.

Bulk morphologies of blended systems were investigated by AFM analysis of microtomed surfaces. The films were embedded in a thermally cured epoxy resin. The cured epoxy surrounding the film was trimmed away to expose a small surface containing the film cross section. The surfaces were cut with a diamond knife using a microtome to obtain surfaces that were smooth on a nanoscopic level. After the cross sectional surface of the embedded film was located using an optical microscope, the cantilever was placed
directly over the location, and height and phase micrographs were obtained simultaneously.

**Nanoindentation**

Hardness and reduced modulus values for all samples were calculated from load-displacement curves generated by displacement controlled indents using a Hysitron Triboindenter (Hysitron, Minneapolis, MN) with a Berkovich diamond probe tip. A trapezoidal displacement profile with a 5 second hold at the maximum displacement and displacement rate of 10 nm/sec was applied to the samples. Ten indents were made in each specimen made at a maximum depth of 100 nm. The shape of the tip was modeled by making a series of indents in a fused quartz standard with depths ranging from 80-280 nm. Using the known value for the reduced modulus of fused quartz and the measured contact depth, $h_c$, area was fitted to a six parameter function of $h_c$ using eqn. 4 to give the tip area function, $A(h_c)$, in nanometers by the relation:

$$A(h_c) = C_0 * h_c^2 + C_1 * h_c + C_2 * h_c^{1/2} + C_3 * h_c^{1/4} + C_4 * h_c^{1/8} + C_5 * h_c^{1/16}$$

(IV-4)

where $C_{0-5}$ are the parameters for the area function. Load-frame compliance was measured in a similar manner by making indents in a fused quartz standard. Total compliance is plotted versus $1/(P_{max})^{1/2}$, and the intercept is the load-frame compliance.30

**Results and Discussion**

**Solution Properties**

In Figure IV-2 static light scattering (SLS) data are linearly fitted using Zimm formalism, where $K*c/R_{\theta}$ is plotted versus $\sin^2(\theta/2)$. There is good agreement for $M_w$ from extrapolation of angular and concentration data, and parallel lines are observed at different concentrations and angles. The conformation of the polymer in solution can
be determined from the angular dependence of light scattering from solution.\textsuperscript{31} However, this method was not applicable to the polymers under investigation because the angular variation of light scattering for rods and coils deviates significantly only at higher molecular weights. Therefore, dynamic light scattering (DLS) was employed to measure the hydrodynamic radius (R\textsubscript{h}). The ratio of \(<R_G>_z\) to R\textsubscript{h} provides a measure of polymer conformation in solution.\textsuperscript{32} The theoretical ratio (\(<R_G>_z/R_h\)) for a hard sphere is 0.778. Random coil polymers demonstrate ratios in the range of 1.27-2.05, while rod-like polymers show ratios greater than 2.2.\textsuperscript{33,34,35,36,37,38}

Data from SLS and DLS are summarized in Table IV-1. SRP-A has a M\textsubscript{w} of 32,000, SRP-B has a slightly higher molecular weight of 34,000 and the molecular weight of PPSU is 26,000. The \(<R_G>_z/R_h\) values for the polymers indicate that each adopts a rodlike conformation when dissolved in NMP. SRP-A has the most extended conformation followed by PPSU and then SRP-B. SRP-A is expected to have a more extended conformation than SRP-B due to the greater number of para linkages between phenylene units in the copolymer backbone, while SRP-B contains a greater number of meta backbone linkages that reduce its degree of linearity. The reduced linearity in SRP-B results in a reduction in the \(<R_G>_z\) in comparison to that of SRP-A, even though SRP-B has a greater molecular weight. The reduced degree of linearity of SRP-B is expected to provide an increased ability to form homogeneous blends with PPSU by increasing the free volume of the SRP phase. This increase in free volume relaxes the steric constraints associated with the SRP phase and helps prevent entropic demixing.

The second virial coefficient (A\textsubscript{2}) measured from SLS is reported in Table IV-1. It reflects the strength of the interaction between the polymer and NMP and is used to
calculate the polymer-solvent interaction parameter as concentration approaches zero ($\chi_0$) of the system by the following relation:\(^{39}\)

$$\chi_0 = 0.5 - \rho^2 V A_2$$  \hspace{1cm} (IV-5)

where $\rho$ is the density of the polymer and $V$ is the solvent molar volume. Polymer-solvent interaction decreases in the order PPSU$>$SRP-A$>$SRP-B. These results compare well with observations from dissolution of the polymers in NMP. PPSU dissolved in a short time at room temperature with stirring at a concentration of 1 gram PPSU per 100 mL of solution. At the same concentration both SRPs required elevated temperatures to dissolve, but SRP-B required the most time. The increased solubility of SRP-A in NMP compared to SRP-B is explained by the higher benzoyl substitution in SRP-A which provides increased interaction with the solvent. The similarities of the $\chi_0$ values calculated from the $A_2$ indicate a low enthalpy of mixing for PPSU with SRP.\(^{40}\)

**Bulk Properties of Pure Components and Blends**

Blends were first assessed for miscibility by a visual inspection of films cast from blend solutions. PPSU, SRP-A and SRP-B polymers produce transparent, amorphous films when solution cast. The films are free standing with thicknesses greater than 25 $\mu$m. The difference in refractive index between PPSU and the SRPs is greater than 0.01, and thus a valid assumption concerning miscibility can be made by optical inspection.\(^{41,42}\)

Films prepared from blends containing PPSU and SRP-B appear transparent over the entire range of compositions, indicating that a homogenous blend is produced during solution casting. Films prepared from blends containing PPSU and SRP-A are transparent at 20 wt% concentrations of the minor component, but those with an SRP-A
content between 40 and 60 wt% have a cloudy appearance, indicating the presence of compositional heterogeneities.

The glass transition behavior of polymer blends is an indication of bulk blend miscibility. A single, well-defined glass transition is characteristic of a miscible blend, while multiple glass transitions indicate that the blend components possess phase separation or are only partially miscible.\textsuperscript{43} Two conditions must be met for assessment of miscibility by a single glass transition. The blend must contain at least 10 to 20 wt% of the minor component, and the difference in the glass transition of the two components must be at least 20°C.\textsuperscript{44,45} Both of these conditions are satisfied in this study with the minor component content being greater than 20 wt% and the difference in the glass transitions between the SRP and PPSU being greater than 55°C. Glass transition behavior is summarized in Table IV-2. Blends containing SRP-B and PPSU show a single, well-defined glass transition over the entire composition range, and blends of SRP-A and PPSU where the minor component is 20 wt% also show a single glass transition. Blends containing SRP-A and PPSU where the minor component content is approximately 40 wt% display two glass transitions indicating an immiscible blend.

A simple and convenient method to predict the temperature of the glass transition when there are weak polymer-polymer interactions is application of the Fox equation:\textsuperscript{46}

\[
\frac{1}{T_g} = w_1 \frac{1}{T_{g1}} + w_2 \frac{1}{T_{g2}}
\]  

(IV-6)

where \(T_g\) is the glass transition temperature of the blend and \(w\) refers to the weight fraction. The subscripts 1 and 2 refer to the components of the blend. Blends of SRP-B and PPSU follow the Fox equation well, but those containing SRP-A and PPSU display significant deviations. Although blends containing SRP-A where the minor component is
20 wt% display a single $T_g$ the actual temperature of the $T_g$ is weighted towards the major component of the blend.

Microtomed samples were analyzed by AFM to investigate the bulk morphology of blended systems. AFM images of the SRP-A/PPSU film cross sections are shown in Figure IV-3. These films exhibit bulk morphologies characteristic of metastable and unstable blends. The 20/80 (3a,b) and 80/20 (3g,h) SRP-A/PPSU blends display isolated regions of phase separated components that are dispersed in a predominantly homogeneous continuous phase. The 40/60 (3c,d) and 60/40 (3e,f) SRP-A/PPSU blends display co-continuous morphologies with larger phase dimensions [47]. Micrographs of the 40/60 and 60/40 SRP-B/PPSU blends are shown in Figure IV-4. In contrast to the morphologies observed in the SRP-A/PPSU blends, the morphologies of SRP-B/PPSU blends appear homogeneous with no evidence of phase separation or compositional fluctuations.

*Surface Properties of Pure Components and Blends*

The surface properties of polymer blends often deviate from those observed in the bulk. Differences in surface energy between the pure components of the blend lead to surface enrichment of the lower energy component. This phenomenon increases the concentration of one component at the surface and can induce phase separation in a metastable blend by creating large fluctuations in concentration over the polymer surface. The measured contact angles, surface free energies and surface roughness ($R_{rms}$) values for the pure components and the blends are shown in Table IV-3. Standard deviations were calculated following propagation of uncertainty method and are shown in parenthesis next to the measurement or calculation.
SRPs exhibit slightly lower surface energy than PPSU indicating that a small driving force exists for surface enrichment of SRP in SRP/PPSU blends. The surface free energy of the blends is consistently lower than that of the pure components. Blends containing SRP-B and PPSU that displayed miscible characteristics according to bulk analysis techniques show only a small drop in surface free energy with respect to the pure components, while blends containing SRP-A and PPSU that displayed immiscible bulk characteristics display a significant drop in surface free energy.

The drop in surface free energy is correlated with surface roughness. Roughness and compositional heterogeneities present on blend surfaces can increase the observed contact angles of test fluids by inhibiting spreading, leading to a reduction in measured surface free energy. The roughness induced by surface phase separation in SRP-A/PPSU blends (Figure IV-7) is responsible for the lower measured surface free energy in these blends. SRP-B/PPSU blends (Figure IV-6) have a lower degree of roughness and thus show only a moderate drop in surface free energy. The pure component surfaces (Figure IV-5) have the lowest degree of surface roughness and are free of large compositional heterogeneities. The smooth, pure component surfaces give the most accurate assessment of the surface free energy.

The surface topographies of neat films of PPSU, SRP-A, and SRP-B are presented as AFM height images in Figure IV-5. The different polymers exhibit similar surface morphologies with low degrees of $R_{\text{rms}}$. The surfaces are composed of predominantly homogenous features with isolated heterogeneities, appearing as bright spots. In the homogenous region of the surfaces the features are approximately 30 to 60 nm in diameter with heights ranging from 0.1 to 2 nm. The isolated heterogeneities are larger,
having diameters ranging from 75 to 150 nm and heights on the order of 10 nm in each case. Due to the tight packing of the surface features in the neat films and the ratio of their diameter to height, it is apparent that both homogenous and heterogeneous features are not spherical, but possess either a cylindrical or disk shape. However, the distinction between cylinders and disks cannot be made without knowledge of the morphology below the surface, and the exact nature of the heterogeneities remains unknown. A possible explanation is that they are nanoscopic crystallites that form on the surface during solution casting and are predominately composed of low molecular weight polymer species.

Blends of SRP-B and PPSU (Figure IV-6) show surface morphologies similar to those of the pure components. Small bright features are observed, but there is no evidence of phase separation in the blends. These surfaces exhibit low degrees of roughness attributed to the small bright features rather than high levels of roughness caused by phase separation or metastability. These blends appear primarily homogeneous and display miscible characteristics.

Blends of SRP-A and PPSU demonstrate completely different surface morphologies that are strongly dependent upon blend composition, representative of metastable and immiscible blends. Figure IV-7 shows AFM height images that are representative of the different morphologies exhibited for blends containing 20, 40, 60, and 80 wt% SRP-A. The blend containing 20 wt% SRP-A (Figure IV-7a) has a continuous granular morphology with surface roughness of 10.9 nm. The granules show evidence of coalescence into structures having extended dimensions of 300 to 400 nm.
and widths of approximately 100 nm. Although the appearance of coalesced particles indicates the initial stages of phase separation, a clear interface between regions of SRP-A and PPSU is not apparent. When the fraction of SRP-A is increased to 40 wt% (Figure IV-7b) phase separation is evident, and a clear interface is observed between domains of SRP-A and PPSU. This surface exhibits well defined island structures above a pitted surface. These islands have a height of up to 50 nm and diameters between 100 and 500 nm, while the pits are up to 200 nm wide with a depth of 30 nm. The 60 wt% SRP-A blend (Fig. 7c) displays a continuous, elevated surface with large pits, but no interface is observed between elevated regions and pits. The surface has an R_{rms} of 5.09 nm. The 80 wt% SRP-A (Fig. 7d) blend has a surface morphology and roughness similar to that of the pure components.

**Nanomechanical Properties of Films**

The experimental values for hardness (H) and reduced modulus (E_r) presented in Fig. 8 are calculated by the contact mechanics relationships developed by Oliver and Pharr. The relationships for H and E_r are given by equations 7 and 8, respectively as:

\[ H = \frac{P_{\text{max}}}{A(h_c)} \]  \hspace{1cm} (IV-7)

\[ \frac{1}{E_r} = \left( \frac{\partial h_c}{\partial P} \right) * 2 * \left( \frac{\sqrt{A(h_c)}}{\sqrt{\pi}} \right) \]  \hspace{1cm} (IV-8)

where P is applied load, and P_{\text{max}} is the maximum applied load. The error bars associated with each data point represent one standard deviation based on ten indentation measurements. The anticipated degree of mechanical reinforcement, predicted by the rule of mixtures, is indicated by a solid line on each graph in Fig. 8. The linearity of the data for all systems in Fig. 8 indicates that their mechanical performance follows the rule of mixtures well. SRP-A has higher H and E_r than SRP-B, and blends containing SRP-A
exhibit the same trend. The standard deviations associated with SRP-A blends are nearly two times greater than those observed for SRP-B blends, indicating higher surface heterogeneity for the SRP-A blends. The increase in surface heterogeneity indicates phase segregation of the SRP-A component at the surface. We explain this behavior by migration of the SRP during the final stages of solution casting. At the final temperature of solvent removal, 205°C, the lower T_g SRPs are able to undergo long range segmental motion and are driven towards the surface.

*Relation of Copolymer Structure to Miscibility, Morphology and Nanomechanics of Blends*

Light scattering measurements of A_2 and χ_o parameters revealed more similar values for SRP-A and PPSU than SRP-B and PPSU. Thus SRP-A is expected to have a lower enthalpy of mixing with PPSU than SRP-B. However, based on T_g measurements as well as bulk and surface morphology images, SRP-B is more compatible with PPSU than SRP-A. This can be explained in terms of chain conformation and flexibility. Light scattering measurements reveal that all three polymers adopt rod-like conformations in NMP, with SRP-A having the most extended conformation, followed by PPSU, and with SRP-B having the least extended conformation. The SRP backbone structure, formed by a combination of *meta*-phenylene and *para*-phenylene recurring units, possesses some degree of flexibility related to the number of meta linkages present. The PPSU molecule demonstrates increased flexibility due to the presence of sulfone and ether linkages in the backbone. As the solution becomes concentrated PPSU deforms to accommodate restrictions placed on it by the highly rigid SRPs. From light scattering measurements the ratio of R_{g2}/R_h of SRP-B is much closer to PPSU than that of SRP-A. Blends
containing SRP-A are more susceptible to entropic demixing. The more extended structure of SRP-A excludes PPSU from penetrating into the rigid phase by restricting the conformational freedom of PPSU. This leads to incompatible, heterogeneous blends of SRP-A and PPSU. SRP-B has a more kinked and less extended conformation that is more similar to that of PPSU than SRP-A. There is less restriction on the conformational freedom of PPSU leading to compatible, homogenous blends.

Based on the lower surface energy calculated for the SRPs, surface enrichment of SRP is favored for the blends. Surface roughness and compositional heterogeneities lead to lower measured surface free energy for the blends in comparison to their pure components. AFM studies indicate surface enrichment of SRP-A in the solution cast films. In addition to surface free energy contributions, the method of solvent removal can have strong effects on the resulting morphology. In contrast to typical solution casting experiments, a high boiling point solvent is used in this system, and the casting procedure requires an extended time period at elevated temperatures. Initially, solvent removal is rapid and thermodynamically driven to reach vapor liquid equilibrium by reduced pressures. At this point polymer diffusion is limited, and the system can become locked in a state that deviates from thermodynamic equilibrium. Once the majority of the solvent has been removed, the residual solvent is removed by a diffusive mechanism that is controlled by temperature. At this point phase separation begins to occur in SRP-A blended systems. During this stage the high aspect ratio of SRP-A favors kinetic diffusion to form a separate phase from PPSU. Evidence for this is presented in both bulk and surface morphology images of SRP-A/PPSU blends. In contrast to SRP-A, the more kinked and lower aspect ratio SRP-B limits kinetic diffusion of the molecule,
leading to more compatible and stable blends over the entire composition range, and homogeneous bulk and surface morphologies are observed for SRP-B/PPSU blends.

Phase segregation is further evidenced for SRP-A/PPSU blends by nanoindentation measurements. While all blends display exceptional nanomechanical performance that is closely predicted by the rule of mixtures, SRP-A blends exhibit substantially higher standard deviations in measured properties than SRP-B blends. Because of the scale of measurement, nanoindentation is sensitive to the degree of dispersion in a blend. Immiscible blends display regions that vary in local composition at the nano to micro level, while miscible blends have uniform composition and dispersion. For nanoindentation studies of a completely immiscible system, a bimodal distribution of mechanical properties is expected, with the average close to that predicted by the rule of mixtures. In contrast, homogeneous blends are expected to yield uniform distributions of property measurements with low standard deviations. This is evidenced by the phase-segregated SRP-A blends yielding standard deviations twice the level of those observed for the homogeneous SRP-B blends.

Conclusions

The molecular conformation, degree of linearity, and solubility of SRP and PPSU polymers in NMP were investigated by static and dynamic light scattering techniques. It was confirmed that the polymers exist as extended rods in solution, and NMP is a good solvent. In contrast to predictions based on the similarity of $\chi_0$ values, thermal analysis by DSC shows that SRP-B is more miscible with PPSU than SRP-A. This illustrates that the miscibility of these systems is driven by configurational entropy rather than intermolecular interactions. The higher aspect ratio, more rigid SRP-A copolymer
formed phase separated and metastable blends with PPSU as observed in the bulk and surface morphology images from AFM. SRP-B copolymer, with its greater chain flexibility through higher meta-linkage content, formed a molecular composite. Phase separation in SRP-B/PPSU blends was not detected in the bulk or at the surface by AFM, and the blends appeared well mixed and homogeneous.

Surface segregation of the SRP-A copolymer was indicated through surface morphology and nanomechanical property characterization. The microstructure that develops below the surface in incompatible blends depends strongly upon blend composition and film formation methods. Study of the three dimensional morphologies produced in these systems revealed the complicated relationship between morphology and mechanical reinforcement, while probing localized features in the systems provided information about local composition. The observed increase in mechanical properties at the surface of the films and development of complicated surface morphologies indicate the potential for the formation of PPSU/SRP blends that exhibit synergistic properties based on nano/microphase separation. Thermal, nanomechanical, and morphological characterization show that stable reinforced PPSU/SRP blends can be created and tailored through control of SPR copolymer architecture.

Acknowledgments

Partial funding from Solvay Advanced Polymers is gratefully acknowledged. This work was also supported by the major research instrumentation program of the National Science Foundation under Award Number DMR-0421403 and through instrumentation supported by the Office of Naval Research, Award No. N00014-07-1-1057.
**Tables and Figures**

**Table IV-1**  
*Summary of SLS and DLS Measurements for SRP-A, SRP-B and PPSU.*

<table>
<thead>
<tr>
<th></th>
<th>SRP-A</th>
<th>SRP-B</th>
<th>PPSU</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$</td>
<td>32,000</td>
<td>34,000</td>
<td>26,000</td>
</tr>
<tr>
<td>$&lt;R_G&gt;_z$ (nm)</td>
<td>22.5</td>
<td>19.1</td>
<td>18.6</td>
</tr>
<tr>
<td>$R_h$ (nm)</td>
<td>6.3</td>
<td>8.0</td>
<td>8.5</td>
</tr>
<tr>
<td>$&lt;R_G&gt;_z/R_h$</td>
<td>3.6</td>
<td>2.4</td>
<td>2.9</td>
</tr>
<tr>
<td>$A_2<em>10^3$ (mol</em>mL/g²)</td>
<td>1.67</td>
<td>1.59</td>
<td>2.31</td>
</tr>
<tr>
<td>$\chi_0$</td>
<td>0.265</td>
<td>0.283</td>
<td>0.233</td>
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**Table IV-2**  
*Glass Transition Behavior of Neat and Blended Films Cast from 10 wt% Polymer Solutions Measured by DSC and Their Relation to the Fox Equation.*

<table>
<thead>
<tr>
<th>Mass Fraction PPSU</th>
<th>Mass Fraction SRP-A</th>
<th>Mass Fraction SRP-B</th>
<th>Glass Transition (°C)</th>
<th>Predicted Glass Transition (°C)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.000</td>
<td>0.000</td>
<td>161</td>
<td>161</td>
</tr>
<tr>
<td>0.220</td>
<td>0.780</td>
<td>0.000</td>
<td>159</td>
<td>173</td>
</tr>
<tr>
<td>0.418</td>
<td>0.582</td>
<td>0.000</td>
<td>159, 210</td>
<td>184</td>
</tr>
<tr>
<td>0.623</td>
<td>0.377</td>
<td>0.000</td>
<td>160, 211</td>
<td>196</td>
</tr>
<tr>
<td>0.808</td>
<td>0.192</td>
<td>0.000</td>
<td>211</td>
<td>207</td>
</tr>
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<td>0.000</td>
<td>0.000</td>
<td>1.000</td>
<td>164</td>
<td>164</td>
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<tr>
<td>0.205</td>
<td>0.000</td>
<td>0.795</td>
<td>174</td>
<td>174</td>
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<tr>
<td>0.407</td>
<td>0.000</td>
<td>0.593</td>
<td>185</td>
<td>185</td>
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<tr>
<td>0.606</td>
<td>0.000</td>
<td>0.394</td>
<td>195</td>
<td>196</td>
</tr>
<tr>
<td>0.805</td>
<td>0.000</td>
<td>0.195</td>
<td>209</td>
<td>208</td>
</tr>
<tr>
<td>1.000</td>
<td>0.000</td>
<td>0.000</td>
<td>220</td>
<td>220</td>
</tr>
</tbody>
</table>

a Theoretical glass transition predicted by Fox equation.
Table IV-3
Contact Angles, Surface Free Energies, and Roughness for Pure Polymers and Blends.

<table>
<thead>
<tr>
<th></th>
<th>$\theta_{\text{water}}$ (deg.)</th>
<th>$\theta_{\text{DiiM}}$ (deg.)</th>
<th>$\gamma_{SV}$ (mJ/m$^2$)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Components</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SRP-A</td>
<td>70.7 (0.5)</td>
<td>29.5 (1.7)</td>
<td>50.8 (0.3)</td>
<td>0.60</td>
</tr>
<tr>
<td>SRP-B</td>
<td>71.3 (0.8)</td>
<td>30.2 (2.9)</td>
<td>50.3 (0.5)</td>
<td>1.85</td>
</tr>
<tr>
<td>PPSU</td>
<td>70.1 (0.5)</td>
<td>26.2 (1.3)</td>
<td>52.0 (0.5)</td>
<td>0.77</td>
</tr>
<tr>
<td>Blends</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20/80 SRP-A/PPSU</td>
<td>91.7 (1.6)</td>
<td>54.0 (2.0)</td>
<td>33.7 (0.6)</td>
<td>10.9</td>
</tr>
<tr>
<td>40/60 SRP-A/PPSU</td>
<td>82.4 (0.4)</td>
<td>26.2 (1.0)</td>
<td>47.9 (0.2)</td>
<td>10.7</td>
</tr>
<tr>
<td>60/40 SRP-A/PPSU</td>
<td>93.1 (0.6)</td>
<td>56.6 (1.1)</td>
<td>32.2 (0.2)</td>
<td>5.09</td>
</tr>
<tr>
<td>80/20 SRP-A/PPSU</td>
<td>95.2 (1.3)</td>
<td>56.2 (2.0)</td>
<td>32.0 (0.5)</td>
<td>1.64</td>
</tr>
<tr>
<td>20/80 SRP-B/PPSU</td>
<td>80.0 (0.6)</td>
<td>26.1 (0.7)</td>
<td>48.6 (0.3)</td>
<td>0.72</td>
</tr>
<tr>
<td>40/60 SRP-B/PPSU</td>
<td>79.1 (0.2)</td>
<td>25.1 (0.6)</td>
<td>49.1 (0.1)</td>
<td>0.71</td>
</tr>
<tr>
<td>60/40 SRP-B/PPSU</td>
<td>82.6 (0.7)</td>
<td>27.5 (1.5)</td>
<td>47.4 (0.3)</td>
<td>0.92</td>
</tr>
<tr>
<td>80/20 SRP-B/PPSU</td>
<td>82.5 (0.6)</td>
<td>27.4 (1.6)</td>
<td>47.5 (0.3)</td>
<td>1.93</td>
</tr>
</tbody>
</table>

Figure IV-1. Generalized chemical structure of SRP copolymer.
Figure IV-2. Zimm plots: (a) SRP-A (b) SRP-B (c) PPSU.
Figure IV-3. AFM height (left) and corresponding phase (right) images of blends containing SRP-A and PPSU: (a) 20/80 SRP-A/PPSU, Z-scale = 30 nm; (b) 20/80 SRP-A/PPSU, Z-scale = 90°; (c) 40/60 SRP-A/PPSU, Z-scale = 20 nm; (d) 40/60 SRP-A/PPSU, Z-scale = 60°; (e) 60/40 SRP-A/PPSU, Z-scale = 15 nm; (f) 60/40 SRP-A/PPSU, Z-scale = 60°; (g) 80/20 SRP-A/PPSU, Z-scale = 30 nm; (h) 80/20 SRP-A/PPSU, Z-scale = 120°. The above images were taken on the cross sectional surfaces of the solution cast blends. Each image is 5 μm x 5 μm.
Figure VI-4. AFM height (left) and corresponding phase (right) images of blends containing SRP-B and PPSU: (a) 40/60 SRP-B/PPSU, Z-scale = 20 nm; (b) 40/60 SRP-B/PPSU, Z-scale = 60°; (c) 60/40 SRP-B/PPSU, Z-scale = 20 nm; (d) 60/40 SRP-B/PPSU, Z-scale = 60°. The above images were taken on the cross sectional surface of the solution cast blends. Each image is 5 μm x 5 μm.
Figure IV-5. AFM height images of neat polymer films: (a) PPSU (b) SRP-A (c) SRP-B. In all height images the vertical axis (Z-scale) is set to a 10 nm data scale.
Figure IV-6. AFM height images of solution cast polymer blends containing SRP-B and PPSU: (a) 20/80 SRP-B/PPSU, Z-scale = 10 nm; (b) 40/60 SRP-B/PPSU, Z-scale = 10 nm; (c) 60/40 SRP-B/PPSU, Z-scale = 20nm; (d) 80/20 SRP-B/PPSU, Z-scale = 25 nm.
Figure IV-7. AFM height images of solution cast polymer blends containing SRP-A and PPSU: (a) 20/80 SRP-A/PPSU, Z-scale = 75 nm; (b) 40/60 SRP-A/PPSU, Z-scale = 100 nm; (c) 60/40 SRP-A/PPSU, Z-scale = 50nm; (d) 80/20 SRP-A/PPSU, Z-scale = 20 nm.
Figure IV-8. Reduced modulus for (a) SRP-A/PPSU blends (b) SRP-B/PPSU blends and hardness for (c) SRP-A/PPSU blends (d) SRP-B/PPSU blends measured by nanoindentation. Error bars represent one standard deviation based on 10 measurements.
References


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CHAPTER V
RHEOLOGICAL AND THERMOMECHANICAL PROPERTIES OF MELT PROCESSED POLYHEDRAL OLIGOMERIC SILSESQUIOXANE/POLYPHENYLSULFONE NANOCOMPOSITES

Abstract

Two structurally and chemically different polyhedral oligomeric silsesquioxane (POSS) molecules with different solubility parameters, condensed dodeca-phenyl POSS and open cage trisilanophenyl POSS, were melt blended with polyphenylsulfone (PPSU) and the resulting effects on material processing, rheology and thermomechanical properties investigated. Process monitoring and capillary rheometry revealed enhancements in processing melt flow and reduction in nanocomposite viscosity with only a small addition of POSS. No measurable effect on the glass transition temperature or molecular weight of PPSU was observed, while small improvements in thermal degradation behavior were obtained on incorporation of POSS. As modulus increased, reductions in other measured tensile properties were observed at high incorporations of POSS. Analysis of nanocomposite fracture behavior and surface morphology provided evidence for surface phase segregation of both types of POSS. The degree of interfacial adhesion in the POSS/polymer composite was related to predicted solubility parameters.

Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are a unique class of nanoparticles with a hybrid organic-inorganic structure, well defined three-dimensional architecture and mono-disperse particle size. They are the subject of intense scientific and commercial interest due to their potential to provide enhanced properties on incorporation
in a polymer matrix. POSS molecules consist of a Si-O-Si inorganic cage, surrounded by an organic corona, represented by substituents “R”. The inorganic cage, with structure (SiO_{1.5})_n where n=8, 10 or 12, may be a fully condensed “closed” or “open” structure.\(^1,2\)

The diameter of the nanocages ranges from 1 to 3 nm, depending on the composition of the molecule.\(^3\) The organic substituents can be tailored to provide a wide range of properties. They can also be modified to enhance compatibility with a specific polymer matrix\(^4,5,6\) or made reactive to allow copolymerization with a spectrum of monomers.

Incorporation of POSS molecules into a polymer matrix can proceed by copolymerization or physical blending methods. While most studies have focused on synthesis of POSS copolymers,\(^7,8,9,10,11,12,13,14,15,16\) relatively few studies have been performed on melt blended systems.\(^17,18,19\) Investigations of melt-mixed systems reveal a correlation between nanocomposite rheological behavior and POSS composition and loading level. This behavior deviates from the classical theory for hard-sphere-filled suspensions, which predicts a monotonic increase in viscosity with an increase in particle loading.\(^20\) Joshi et al.\(^21\) performed an investigation into the rheological and viscoelastic properties of melt-mixed high density polyethylene (HDPE)/POSS composites. They report that low POSS concentrations (0.25 to 0.5 wt %) reduce complex viscosity, while higher concentrations cause complex viscosity to increase. This behavior was attributed to the limited solubility of POSS in HDPE at low concentrations, while above the solubility limit POSS agglomeration occurred, and viscosity increased. Kopesky et al.\(^22\) reported a minimum in the zero-shear viscosity at low POSS loadings (less than 5 vol%) in melt-mixed polymethyl methacrylate (PMMA) POSS blends. Two different types of flow regimes were proposed for melt-mixed POSS systems. In the low concentration
regime POSS is molecularly dispersed, and viscosity is reduced. In the higher concentration regime, after the solubility limit has been reached, crystallization and agglomeration of POSS occur, and the system behaves as a hard-sphere-filled suspension. Zhou et al.\textsuperscript{23} reported a minimum in complex viscosity at a POSS concentration of 1 wt% for physically blended systems containing POSS and polypropylene (PP). Cole-Cole plots indicate fine dispersion at POSS concentrations below 1%, with POSS aggregation at concentrations higher than 1%. Studies of other types of nanoparticles (approximately 10 nm and below) show that weak polymer-particle interactions cause the behavior of the system to deviate from the classical theory for hard-sphere-filled suspensions, resulting in a strong decrease in viscosity at low concentrations followed by an increase in viscosity at higher concentrations.\textsuperscript{24,25} For the purpose of this paper this phenomenon will be referred to as the “nanoparticle effect”.

Studies in our own and other research laboratories have demonstrated the propensity of POSS to segregate to the surface of a polymer matrix.\textsuperscript{26,27,28,29,30,31,32} The POSS/polymer nanocomposites exhibited reduced friction and melt viscosity, and improved nanomechanical properties, abrasion resistance and hydrophobicity. The level of property improvement was related to the extent of segregation and POSS molecular aggregation. Aggregation appears to be related to POSS concentration and solubility in the polymer matrix, and it has been suggested that melting temperatures and relative viscosities of the polymer and POSS molecules may play a role.\textsuperscript{33} However, these factors do not fully explain the observed behavior and the mechanism is not well understood.
Solubility parameters are often used to predict compatibility. A minimum in the enthalpy of mixing ($\Delta H_m$) is predicted when the difference in solubility parameters is minimized by the relation:

$$\Delta H_m = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2$$  \hspace{1cm} (V-1)$$
where $V$ is the volume of the system; $\phi$ is volume fraction; $\delta$ is the solubility parameter, and the subscripts 1 and 2 refer to components of the mixture. If the difference in solubility parameters is close to zero, then a low enthalpy of mixing is predicted, indicating potential compatibility.

The current study is an attempt to understand the relationship between POSS solubility in a thermoplastic polyphenylsulfone (PPSU) matrix and the resulting effects on composite rheology and material processing. Compatibility is predicted by calculation of solubility parameters using the method established by Hoy. PPSU and two different grades of POSS, a closed cage dodecaphenyl POSS (Dp-POSS) and an open cage trisilanophenyl POSS (Tsp-POSS), were identified as suitable for evaluation due to their thermal stability under the processing conditions of PPSU and possible compatibility with PPSU. Material processing is investigated by analyzing extruder torque during melt blending as well as the mold pressure during injection molding. Composite melt rheology is assessed using capillary rheometry. The molecular weight of PPSU and the POSS/PPSU nanocomposites is measured by gel permeation chromatography (GPC) to ensure that POSS does not induce degradation of the PPSU chains during material processing. Thermal behavior of the POSS/PPSU systems is examined using a combination of differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Optical microscopy is employed to investigate composite morphology, and the
tensile properties of molded test specimens are evaluated to determine the effects of POSS in relation to mechanical performance.

**Experimental**

**Materials**

PPSU resin (trade name Radel® R5100NT) was supplied by Solvay Advanced Polymers, L.L.C. (Alpharetta, GA). This grade of PPSU has a reported modulus of 2.3 GPa and a tensile strength of 70 MPa. It is a ductile polymer with reported percent elongation at yield of 7.2% and percent elongation at break that ranges from 60-120%.³⁸

(see Figure V-1) Dodecaphenyl-POSS® (Dp-POSS) (MS0802) and trisilanolphenyl-POSS® (Tsp-POSS) (SO1458) were supplied as dry white powders by Hybrid Plastics, Inc. (Hattiesburg, MS). The molecular structures of the two grades of POSS are shown in Figure V-2.

**Composite Blending and Sample Preparation**

POSS/PPSU nanocomposites were prepared using a B&P Process CT 25 twin screw extruder (screw diameter 25 mm; length:diameter ratio 40:1; three- hole die with diameters of 3/16 inches) equipped with high shear screws. Extrusion parameters were: feed rate 20 lb/hr, screw speed 950 rpm, barrel temperatures 205°C in feed section, 270 to 355 °C in compression zone, 355°C in the metering section and 316°C in the die. Melt temperatures were directly measured to be 375 to 400 °C using a temperature probe. The apparent shear rate \( \dot{\gamma}_{ap} \) in the extruder die is estimated to be 15 s⁻¹ by Equation 1.³⁹

\[
\dot{\gamma}_{ap} = \frac{4Q}{\pi R^3}
\]  

(V-2)

\( Q \) is the volumetric flow rate through a single die hole, and \( R \) is the radius of an individual die. The extruder torque was recorded to determine the effects of POSS
concentration on processing by monitoring the torque output of the extruder after each composite system had reached steady-state.

The PPSU resin was dried in a convection oven at 150°C overnight prior to blending. A master batch containing 10 wt% POSS was prepared by extrusion and further diluted by extruding with neat PPSU resin to create PPSU/POSS nanocomposites containing Dp-POSS and Tsp-POSS at 0.5, 1, 2.5, 5, 7.5 and 10 wt% POSS. Specimens for tensile testing were injection molded using a Mini-Jector model #55-1SOL by Miniature Plastic Molding (Solon, OH). Ten tensile bars for each sample were molded according to ASTM D638 specifications for type 1 tensile bars. During molding the temperatures of the barrel (366°C), die (368°C), and mold (104°C) were held constant, while the mold pressure was adjusted between 990 and 1500 psi to produce test specimens of appropriate dimensions. Once the correct mold pressure was determined for each POSS/PPSU composition, subsequent sample specimens had dimensions within the acceptable tolerance level.

**Gel Permeation Chromatography**

Gel permeation chromatography (GPC) was used to determine number-average molecular weight ($M_n$) and weight-average molecular weight ($M_w$) using a Waters GPC system (DMF eluent, Waters 2420 ELS detector and 1525 binary HPLC pump, Styragel HR 3 DMF and HR 4 columns). The system was calibrated using Shodex polystyrene standards from Waters (Milford, MA) having molecular weights of 1060, 13900, 55100 and 197000. Data was analyzed using Breeze version 3.3 software. Relative molecular weights based on polystyrene standards are reported.
**Thermal Characterization**

The glass transition ($T_g$) behavior was measured using a differential scanning calorimeter (DSC) model Q200 DSC by TA Instruments (New Castle, DE). Samples were heated in nitrogen at a flow rate of 50 mL/min to 350°C at 10°C/min to remove the thermal history of the samples. The samples were then cooled and heated to 350°C at a rate of 10°C/min, and the $T_g$ was recorded from the second heating scan as the temperature on the curve half way between the tangent lines drawn above and below the transition region.

The thermal degradation behavior in air at a flow rate of 40 mL/min was studied using a thermogravimetric analyzer (TGA) model Pyris 6 by Perkin Elmer (Waltham, MA). The samples were heated from room temperature to 850°C at a rate of 20°C/min. The thermal degradation behavior of the blends is defined by drawing a line tangent to the inflection point of the degradation curve obtained by TGA. The point where the tangent line crosses the line of 100% weight is the onset, and the point where the tangent line crosses the final steady (char) line is the end.

**Optical Microscopy**

The dispersion and aggregation behavior of POSS/PPSU composites was analyzed by optical microscopy using a Keyence VHX-600 Digital Microscope (Osaka, Japan) with an attached Keyence VH-Z100R polarized lens system (resolution 100-1000X). Imaging was performed at a magnification of 300X in a polarized light environment.

**Capillary Rheometry**

An LCR7000 capillary rheometer by Dynisco Instruments (Franklin, MA) was used to measure apparent viscosity ($\eta_{ap}$) as a function of shear rate at 380°C. The
capillary bore had a radius \( R \) of 0.020” and a length \( L \) of 0.800” with a 120° degree entry angle. Apparent viscosity is the ratio of the apparent shear stress \( \tau_{ap} \) to the apparent shear rate \( \dot{\gamma}_{ap} \). Using the dimensions of the capillary bore, the volumetric flow rate of material through the capillary \( Q \) and the pressure differential across the capillary \( \Delta P \), \( \eta_{ap} \) is calculated by Equation 1.

\[
\eta_{ap} = \frac{\tau_{ap}}{\dot{\gamma}_{ap}} = \frac{\pi \cdot \Delta P \cdot R^4}{8 \cdot Q \cdot L}
\]  

(V-3)

Specified shear rates of 25, 100, 500, 1500 and 3500 s\(^{-1}\) were used for viscosity measurements.

**Tensile Testing**

The tensile properties (modulus of elasticity, tensile strength, percent elongation at yield and percent elongation at break) were measured according to ASTM D638 using a universal testing machine by MTS (Eden Prairie, MN). PPSU is a hygroscopic material, and samples were conditioned prior to testing by placing them in a convection oven at 140°C for a minimum of 5 hours to remove any moisture and then cooling to room temperature in a desiccation chamber before testing. Testing took place in a temperature (27°C) and humidity (40-45%) controlled room. Ten specimens for each sample were tested, and the speed of testing was set at 2 in/min.

**Results and Discussion**

**Gel Permeation Chromatography**

The weight average molecular weight \( M_w \) and number average molecular weight \( M_n \) for the blends determined by gel permeation chromatography (GPC) are presented in Table V-1. The values in parenthesis and italics to the right of the measured molecular
weights represent the percent change of the POSS/PPSU composites’ molecular weights relative to PPSU. The measured molecular weights for the blends are generally within 5 to 10% of the measured molecular weight for the neat PPSU. The variations appear to be randomly distributed (higher or lower than neat PPSU), and are attributed to experimental variation rather than any significant degradation or crosslinking of the polymer matrix on addition of POSS.

**Thermal Characterization**

The $T_g$ and thermal degradation behavior of POSS/PPSU composites are shown in Table V-2. The $T_g$ of pure PPSU occurs at 222°C, and the $T_g$'s of all Tsp-POSS and Dp-POSS composites are within 1% of pure PPSU. The data in Table V-2 also indicates that addition Tsp-POSS or Dp-POSS at up to 10 wt% does not affect the $T_g$ behavior of PPSU. The thermal degradation behavior of composites containing Dp-POSS is similar to that of pure PPSU, but composites containing Tsp-POSS exhibit a gradual increase in temperatures associated with the degradation onset, inflection and end that is proportional to concentration of Tsp-POSS. At 10 wt% Tsp-POSS in PPSU the onset of degradation is increased by 18°C, the inflection point by 21°C, and the end by 18°C. Based on these results the thermal stability of PPSU can be increased by approximately 2-3% with 10 wt% addition of Tsp-POSS. The residual weight of the Dp-POSS nanocomposites at the end of the heating ramp remains constant relative to PPSU, but a small increase of 2 wt% is observed in the residual weight of the 10 wt% Tsp-POSS composite. The increase in the residual weight of the 10 wt% Tsp-POSS composite coincides with the observed increase in degradation temperatures associated with this composite. The thermal degradation behavior presented in Table V-2 agrees with measurements made by GPC
and further indicates that addition of POSS to PPSU will not induce degradation, cross-linking or unwanted chemical reactions. Analysis of the thermal behavior of Tsp-POSS composites suggests that addition of Tsp-POSS actually improves the thermal degradation behavior of PPSU. Two factors may be responsible for the observed increase in thermal stability of Tsp-POSS/PPSU composites. Hydrogen bonding can occur between the silanol groups present on the open Tsp-POSS cage and the ether and sulfone groups of PPSU, leading to increased thermal stability. In addition, POSS has been shown to improve flame retardancy in polymeric materials through formation of a char layer that serves as an oxygen barrier and inhibits degradation.\cite{11,40}

**Solubility Parameter Estimation**

The solubility parameter of PPSU is calculated to be 10.1 (cal/cm\(^3\))\(^{1/2}\) using the second virial coefficient (\(A_2\)) of PPSU in 1-methyl-2-pyrollidinone (NMP) measured by static light scattering\cite{41} and equations 4 and 5:

\[
\chi_0 = 0.5 - \rho_j^2 V_i A_2 
\]

where \(\chi_0\) is the Flory-Huggins (F-H) interaction parameter between PPSU and NMP as concentration approaches zero; \(\rho_j\) is the density of the polymer, and \(V_i\) is the solvent molar volume of the solvent. NMP is a “good” solvent for PPSU, and \(\chi_0\) is assumed to be independent of concentration.\cite{42} The entropic term of the F-H interaction parameter is neglected yielding the relation:

\[
\chi_0 = \left(\frac{V_i}{RT}\right)(\delta_i - \delta_j)^2 
\]

where \(R\) is the ideal gas constant; \(T\) is temperature; \(\delta_i\) is the solvent solubility parameter, and \(\delta_j\) is the solubility parameter of the polymer.\cite{35} Using the Hoy method\cite{36}
the solubility parameters of Dp-POSS and Tsp-POSS were calculated to be 10.2 and 8.8 (cal/cm$^3$)$^{1/2}$, respectively. Based on the difference between the calculated POSS solubility parameters and that of PPSU, Dp-POSS ($\Delta \delta = 0.1$) is expected to have a lower enthalpy of mixing with PPSU than Tsp-POSS ($\Delta \delta = 1.3$) and thus a higher solubility in the PPSU matrix. However, the potential for hydrogen bonding between the silanol groups present on the Tsp-POSS cage and the ether and sulfone groups of PPSU may increase the solubility of Tsp-POSS in the PPSU matrix and lead to a more homogeneous mixture.\textsuperscript{43}

Composite Processing and Rheology

The torque on the extruder screws is directly proportional to the viscosity of the material being processed. Monitoring extruder torque during compounding is an effective method for quantifying the effects of POSS on material processing and nanocomposite viscosity. Extruder torque is presented as a function of POSS concentration in Figure V-3. For both Dp-POSS and Tsp-POSS nanocomposite systems substantial torque reduction (and thus improvement in material processing) is observed. Tsp-POSS composites show a linear relationship between torque reduction and Tsp-POSS concentration. An approximate 3% reduction in torque is observed for every 1 wt% increase in Tsp-POSS concentration. Dp-POSS composites, on the other hand, exhibit a non-linear response, with strong initial reductions in extruder torque at low concentrations that reach a maximum at concentrations of around 5 wt% Dp-POSS.

This behavior is contrary to what is observed typically for rigid particulate filled systems, where viscosity increases with loading level, and appears to be related to POSS melt transitions. The observed melt temperatures during extrusion ranged from 375 to
400°C. The melting range for Dp-POSS is 313 to 386°C\(^{44}\), and Tsp-POSS undergoes a liquid-like transformation at 220°C.\(^{45}\) Therefore, it is safe to assume that Tsp-POSS is in the liquid state and Dp-POSS is largely in the melt state during extrusion. Under these conditions POSS acts as a viscosity modifier and effectively promotes flow.

Reductions in mold pressure, or hold pressure, provide a second indication of process enhancement. The mold pressure is increased to a maximum value to obtain optimum part densification without flashing the cavity. Less viscous polymer melts have a greater propensity to flash than those with higher viscosities. Therefore, observing the mold pressure during injection molding provides information about melt viscosity. The mold pressures required to produce tensile test specimens of appropriate dimensions without flash as a function of POSS concentration are shown in Figure V-4. A similar trend to that observed during extrusion is also observed during the injection molding process. For both types of POSS, the mold pressure is reduced as a function of increasing POSS concentration, indicating enhanced processability. A linear relationship between pressure and Tsp-POSS concentration is observed, while Dp-POSS exhibits greatest percent reductions at low concentrations that level off at higher concentrations.

The molded tensile bars of PPSU were highly transparent with an amber color. Upon addition of only 0.5 wt% Dp-POSS or Tsp-POSS the specimens became cloudy. Further addition of Dp-POSS or Tsp-POSS caused the specimens to become opaque, indicating agglomeration of the POSS nanostructured chemicals. Agglomeration and dispersion in molded test specimens was further investigated using optical microscopy. Representative optical micrographs of the molded POSS/PPSU test specimens are shown in Figure V-5. Tsp-POSS/PPSU composites show a relatively homogeneous surface at
loading levels of up to 10 wt% (see Figure V-5C). The 1 wt% Dp-POSS composite surface (see Figure V-5D) also exhibits a relatively homogeneous surface, but at 2.5 wt% Dp-POSS (see Figure V-5E) aggregates on the order of microns become apparent. These aggregates are isolated within a homogeneous matrix, and their dimensions range in size from approximately 10 to greater than 100 μm. As the loading level of Dp-POSS is further increased to 10 wt%, the agglomerates coalesce into larger phase separated domains as shown in Figure V-5F.

Capillary rheometry data for Tsp-POSS/PPSU and Dp-POSS/PPSU blends as a function of POSS concentration are shown in Figures V-6 and V-7. All blends and neat PPSU exhibit shear thinning behavior, and addition of POSS generally decreases the apparent viscosity of the blend. As observed in the extruder torque and mold pressure studies, the apparent viscosity decreases regularly with increasing Tsp-POSS concentration. Continuous reductions in apparent viscosity are observed over the entire shear regime for concentrations up to 10 wt% Tsp-POSS (Figure V-6). On the other hand, in Dp-POSS/PPSU composite systems apparent viscosity is strongly reduced at low POSS concentrations (Figure V-7). Nanocomposites containing 2.5 wt% Dp-POSS display the greatest viscosity reductions over the entire shear regime. At loadings higher than 2.5 wt% Dp-POSS, apparent viscosity increases, particularly at shear rates ranging from 25 to 1500 s⁻¹. At the highest shear rate, the greatest overall viscosity reductions are observed for 2.5, 5 and 10 wt% composites. This behavior is similar to the processing behavior observed in both material compounding and injection molding studies.

Substantial linear decreases in extruder torque, mold pressure and apparent viscosity were observed for Tsp-POSS systems. While the exact nature of Tsp-POSS in
the liquid state is unknown, it can be assumed that Tsp-POSS has a considerably lower viscosity than PPSU. Application of a mixing rule can be used to predict the viscosity ($\eta$) of a phase separated polymer mixture. For mixtures containing a high volume fraction of the more viscous component the additivity model is representative:

$$\eta_{\text{composite}} = \phi_1 \eta_1 + \phi_2 \eta_2$$

where $\phi$ is volume fraction, and the subscripts refer to the components of the mixture. However, when there is poor adhesion between the phases, interfacial slippage can occur. This results in negative deviation from the additivity model, and strong reductions in viscosity can occur at very low volume fractions of the less viscous component. The difference in solubility parameters between Tsp-POSS and PPSU ($\Delta\delta = 1.3$) suggests there may be poor adhesion between phases. If the data from capillary rheometry, extrusion and mold pressure are extrapolated to pure Tsp-POSS it becomes apparent that negative deviation from the additivity model occurs in this system, and Tsp-POSS has a strong internal lubricating effect on PPSU. In addition, evidence from tensile testing, which will be discussed later, implies that Tsp-POSS undergoes surface phase segregation, which further improves processing by reducing friction between the composite melt and the steel components in the extruder or mold cavity.

The rheological behavior of Dp-POSS/PPSU composites is significantly more complicated than that of Tsp-PPSU composites. Since Dp-POSS has melting range that encompasses the processing temperatures of PPSU, it is difficult to discern whether or not it has completely melted in the time frame of the experiments. Based on the observed agglomerates in optical micrographs, it is likely that a certain portion of the melted Dp-POSS enters the amorphous PPSU matrix, as would be expected by the similarity in their
solubility parameters \( (\Delta \delta = 0.1) \). However, the solid Dp-POSS resides in a separate phase and is not incorporated in the PPSU matrix. After the solubility limit of Dp-POSS in PPSU is reached, the remaining Dp-POSS domains will reside in the matrix as droplets containing a mixture of liquid and solid Dp-POSS. Three factors have been identified that possibly contribute to the observed behavior of Dp-POSS. The strong initial reductions in the viscosity of Dp-POSS composite systems at low concentrations may be due to the “nanoparticle effect” previously described. As the concentration of Dp-POSS is further increased partially melted Dp-POSS molecules act as a lubricant, which serves to improve processing and reduce viscosity. At higher concentrations, solid aggregates of Dp-POSS serve to increase viscosity as observed in capillary rheometry.

**Tensile Properties**

The tensile properties of the composite materials are presented in Figure V-8. The modulus of elasticity (Figure V-8A) and tensile strength (Figure V-8B) associated with Dp-POSS and Tsp-POSS composite systems lie within the standard deviation for the measured PPSU control at low concentrations. As the concentration of POSS is increased a slight increase in modulus accompanied by a small reduction in tensile strength is observed in both systems. While Dp-POSS and Tsp-POSS composite materials retain their high modulus and tensile strength, a loss in ductility is observed at higher loadings of Dp-POSS and Tsp-POSS (Figure V-8C and Figure V-8D). Percent elongation at yield is maintained at low additions, but a decrease is observed at loading levels of 5wt% and greater. While all samples exhibited a high degree of variation in the percent elongation at break measurement (PPSU standard exhibited variation of +/- 40%), a general decrease in the measured values was observed as a function of POSS
concentration. At higher concentrations (greater than 5 wt%) the composite materials exhibit behavior similar to those observed with traditional fillers, while at lower concentrations (less than 5 wt%) the tensile properties of the composite systems are relatively maintained. These tensile results parallel the observations made by Shiraldi et al. in their work with Tsp-POSS/polycarbonate systems.¹⁸

The complex fracture behavior that occurs during elongation provides valuable insight into the surface segregation behavior and interfacial adhesion in the POSS/PPSU systems investigated (Figure V-9). Dp-POSS composites exhibit necking until fracture for all compositions. However, in the 10.0 wt% Dp-POSS composite the surface crazes, and then the core region necks until fracture (Figure 9C). Tsp-POSS composites cease to display necking at concentrations of 7.5 and 10.0 wt% Tsp-POSS (Figure 9A). The skin of the test Tsp-POSS specimens fractures first, followed by a slight necking of the core region, and then complete fracture. Strong delamination is observed between the skin and the core region. The occurrence of a surface fracture or crazing before a core fracture implies the surfaces of the composite specimens are more brittle and enriched with either Dp-POSS or Tsp-POSS. The presence of delamination in the Tsp-POSS composite and absence of delamination in the Dp-POSS composite indicates Dp-POSS interacts more strongly with the PPSU matrix than Tsp-POSS, as predicted by the difference in solubility parameters between these two materials and PPSU. In fact, the delamination and homogeneous surface morphology of Tsp-POSS fracture surfaces together provide evidence that a film of Tsp-POSS may form on the surface of the articles produced during injection molding.
Conclusions

Substantial material processing enhancement was observed in POSS/PPSU composites without detrimental effects on thermal stability, glass transition temperature or molecular weight of the PPSU resin for both types of POSS additive. The consistent, monotonic process improvements observed in Tsp-POSS composite systems are attributed to internal lubrication resulting from weak interfacial interactions between phases as well as surface segregation of Tsp-POSS that lubricates the exterior of the composite melt and reduces friction during processing. The rheological behavior of Dp-POSS composites is significantly more complex, explained by the fact that Dp-POSS may exist as a mixture of liquid and solid during the melt experiments. At low concentrations of Dp-POSS, significant improvements in the material processing of PPSU occur. As Dp-POSS concentration is increased the process enhancements diminish, however typical behavior of micro-fillers is not observed. The exact mechanism for this behavior remains unknown, but it is speculated to be a combination of the “nanoparticle effect,” internal lubrication by melted Dp-POSS, surface segregation and the presence of large POSS aggregates.

Optical micrographs of nanocomposite morphology and observations of fracture mechanisms during tensile testing serve to explain the complex behavior of Dp-POSS and Tsp-POSS composite systems. Morphological images of Dp-POSS composites at low concentrations (1 wt% Dp-POSS and below) appear homogeneous, and the tensile properties of these systems are maintained. Large micron scale aggregates at higher concentrations cause the mechanical properties of this system to resemble a rigid particulate filled material. The homogeneous morphology observed in Tsp-POSS
fracture surfaces systems combined with their observed delamination during fracture suggest that Tsp-POSS is enriched at the composite surface during processing.

While solubility parameter matching can provide an indication of compatibility, it cannot be used as the sole predictor of rheology enhancement. Optical analysis of the composite systems showed them to be in a state of incompatibility, where only small quantities of either Dp-POSS or Tsp-POSS were dissolved in the PPSU matrix. The incompatibility observed in the Dp-POSS composites may arise due to incomplete melting of the Dp-POSS crystals during blending, while the incompatibility observed in Tsp-POSS composite systems is a result of differences in the melt viscosities of Tsp-POSS and PPSU as well as surface segregation attributed to poor solubility in the PPSU matrix.

The versatile and highly adaptable nature of the hybrid organic-inorganic POSS structure provides the opportunity for rheology enhancement in a range of polymer systems. Multiple factors, including melting temperature, polymer/POSS viscosity match, loading level and chemical structure must be considered in predicting rheological performance. In addition, the propensity of POSS to surface segregate provides a wide range of opportunities for surface modification when incorporated into a thermoplastic matrix.
Tables and Figures

Table V-1
*Molecular Weights of PPSU and POSS/PPSU Composites Measured by GPC.*

<table>
<thead>
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<th></th>
<th>$M_n\times 10^{-4}$</th>
<th>$M_n\times 10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPSU</td>
<td>9.21</td>
<td>2.29</td>
</tr>
<tr>
<td>0.5% Tsp-POSS</td>
<td>8.65 (-6.08)</td>
<td>2.21 (-3.49)</td>
</tr>
<tr>
<td>1.0% Tsp-POSS</td>
<td>9.12 (-0.98)</td>
<td>2.43 (6.11)</td>
</tr>
<tr>
<td>2.5% Tsp-POSS</td>
<td>9.72 (-5.54)</td>
<td>1.99 (-13.10)</td>
</tr>
<tr>
<td>5.0% Tsp-POSS</td>
<td>9.68 (-5.10)</td>
<td>2.54 (10.92)</td>
</tr>
<tr>
<td>7.5% Tsp-POSS</td>
<td>9.74 (5.75)</td>
<td>2.32 (1.31)</td>
</tr>
<tr>
<td>10.0% Tsp-POSS</td>
<td>9.42 (2.28)</td>
<td>2.14 (-6.55)</td>
</tr>
<tr>
<td>0.5% Dp-POSS</td>
<td>9.83 (6.73)</td>
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<td>9.81 (6.51)</td>
<td>2.10 (-8.30)</td>
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<tr>
<td>7.5% Dp-POSS</td>
<td>9.68 (-5.10)</td>
<td>2.06 (-10.04)</td>
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<tr>
<td>10.0% Dp-POSS</td>
<td>8.67 (-5.86)</td>
<td>1.92 (-16.16)</td>
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Table V-2
*Glass Transition and Thermal Degradation Behavior of PPSU and POSS/PPSU Composites.*

<table>
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<tr>
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<th>$T_g$ (°C)</th>
<th>Degradation Onset (°C)</th>
<th>Degradation Inflection (°C)</th>
<th>Degradation End (°C)</th>
<th>Residual Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPSU</td>
<td>222</td>
<td>564</td>
<td>594</td>
<td>623</td>
<td>48.0</td>
</tr>
<tr>
<td>2.5% Tsp-POSS</td>
<td>222</td>
<td>570</td>
<td>600</td>
<td>633</td>
<td>47.8</td>
</tr>
<tr>
<td>5.0% Tsp-POSS</td>
<td>221</td>
<td>574</td>
<td>609</td>
<td>636</td>
<td>47.8</td>
</tr>
<tr>
<td>7.5% Tsp-POSS</td>
<td>222</td>
<td>576</td>
<td>610</td>
<td>638</td>
<td>47.8</td>
</tr>
<tr>
<td>10.0% Tsp-POSS</td>
<td>222</td>
<td>582</td>
<td>615</td>
<td>641</td>
<td>49.9</td>
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<tr>
<td>2.5% Dp-POSS</td>
<td>222</td>
<td>562</td>
<td>596</td>
<td>632</td>
<td>47.1</td>
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<tr>
<td>5.0% Dp-POSS</td>
<td>220</td>
<td>571</td>
<td>607</td>
<td>636</td>
<td>48.0</td>
</tr>
<tr>
<td>7.5% Dp-POSS</td>
<td>221</td>
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<td>599</td>
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<td>10.0% Dp-POSS</td>
<td>221</td>
<td>566</td>
<td>600</td>
<td>631</td>
<td>47.5</td>
</tr>
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Figure V-1. Chemical structure of PPSU.

Figure V-2. Chemical structures POSS chemicals: (A) dodecaphenyl POSS (Dp-POSS) (B) trisilanolphenyl-POSS (Tsp-POSS).
Figure V-3. Reduction in extruder torque during melt blending of POSS and PPSU.

Figure V-4. Reduction in mold pressure during injection molding of test specimens.
Figure V-5. Optical micrographs of selected POSS/PPSU composites: (A) PPSU (B) 2.5 wt% Tsp-POSS (C) 10.0 wt% Tsp-POSS (D) 1.0 wt% Dp-POSS (E) 2.5 wt% Dp-POSS (F) 10.0 wt% Dp-POSS.
Figure V-6. Viscosity curve for Tsp-POSS composites.

Figure V-7. Viscosity curve for Dp-POSS composites.
Figure V-8. Tensile properties of POSS/PPSU composites: (A) normalized modulus of elasticity (B) normalized tensile strength (C) normalized percent elongation at yield (D) normalized percent elongation at break.
Figure V-9. Selected photographs of fractured tensile test specimens: (A) 10.0 wt% Tsp-POSS (B) 7.5 wt% Dp-POSS (C) 10.0 wt% Dp-POSS.
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45 Private communication with Hybrid Plastics.

CHAPTER VI
RECOMMENDATIONS FOR FUTURE RESEARCH

Investigations of the relationship of between SRP copolymer structure and its phase behavior in blends with PPSU revealed that polymer conformation and configurational entropy are the dominant factors in the formation of homogeneous blends, while enthalpic interactions only played a minor role. The conformation of the SRP in solution was able to be successfully adjusted by varying the ratio of substituted \textit{para} to unsubstituted \textit{meta} linkages in the polymer backbone. This indicates strong potential for the formation of molecular composites with other amorphous polymers that follow by conformational matching. Further analysis of this relationship in other systems could lead to development of molecular composites containing SRPs and an array of other amorphous polymers. For example, if an SRP with a modulus of 8 GPa is dispersed in an amorphous polymer matrix with a modulus of 1 GPa at a volume fraction of only 10\%, then the modulus of the composite following the rule of mixtures would be 1.7 GPa. Therefore, the modulus of the composite material has been increased by 70\% with only 10\% addition of SRP.

The calculated solubility parameters of Dp-POSS and Tsp-POSS provided an indication of the strength of interfacial interactions between POSS and PPSU. However, site-specific interactions such as hydrogen bonding can lead to deviations in the models used. The solubility parameter of PPSU was measured by light scattering and showed good agreement with other reported solubility parameters for PPSU. Measuring the solubility parameters of POSS molecules in solution using light scattering techniques
could strongly validate these calculated parameters or even account for site-specific interactions occurring in these systems.

The fracture behavior of POSS/PPSU nanocomposite specimens provided evidence for preferential surface segregation, and it is highly likely that the surface hardness and scratch resistance of these nanocomposite materials is significantly increased. Employing nanoindentation techniques to directly measure surface hardness and modulus would provide further evidence for surface segregation in these systems and quantify the enhancements in surface properties based on POSS composition and concentration.

The process enhancements observed in the POSS/PPSU nanocomposites were found to be strongly related to the phase transformations that POSS undergoes as a function of temperature. However, little is known about rheological behavior of pure POSS. Further investigations of the melt behavior of pure POSS would greatly help in the prediction of rheological properties of POSS/PPSU nanocomposites.
APPENDIX

MORPHOLOGICAL RESPONSE TO ELECTRICAL FIELDS OF PERFLUOROSULFONATE IONOMER MEMBRANES

Abstract

Perfluorosulfonate ionomer membranes (PFSIs) have received significant academic and commercial attention for use in electroactive ionic polymer-metal composites (IPMCs) due to their unique ability to change shape with an electrical stimulus. This study explores the mechanism of this behavior through the use of current sensing and intermittent contact atomic force microscopy to probe the morphological and hydraulic response of a hydrated PFSI to an applied electrical stimulus. Both current sensing atomic force microscopy (CSAFM) and applied potential atomic force microscopy (APAFM) suggest that when the bottom of the film is negatively charged, protons and water migrate to the negatively charged substrate forming isolated sulfonate rich domains, and dehydration occurs on the top surface of the PFSI membrane. Conversely, a positively charged substrate causes proton and water migration to the top surface of the membrane forming a cationic film on the top surface of the PFSI membrane.

Introduction

When the surface of a PFSI membrane is impregnated with a conductive metal the resulting IPMC responds to electrical stimulation by changing shape to neutralize or minimize the electrical potential developed at the PFSI/metal interface (see Figure A-1). Models explaining this behavior fall into two categories, hydraulic actuation and electrostatic actuation. In the hydraulic actuation model IMPC actuation is attributed to
ionic transport within the membrane in response to the applied electric field. In the electrostatic actuation model the motion is explained by a rearrangement of the ion aggregate structure in response to the electric field. The hydraulic model of IPMC actuation is based on the idea that, in the presence of an electric field, mobile ions within the membrane will migrate towards the cathode while dragging a polar solvent with it. This motion leads to a buildup of solvent at the cathode side of the membrane. The resultant hydrostatic pressure on this side of the membrane causes the IPMC to bend away from the cathode (see Figure A-2). This electrophoretic motion is a natural response to an applied electrical field.\textsuperscript{1,2,3}

In this study the IPMC actuation mechanism was characterized by atomic force microscopy (AFM). Various AFM studies on PFSIs have been performed previously with the goal of identifying the size and shape of hydrophilic domains distributed within the hydrophobic PTFE matrix.\textsuperscript{4,5,6} More recent efforts have involved the use of a platinum-coated conductive AFM tip to determine the distribution of electrochemically active ionic domains.\textsuperscript{7,8,9} However, there has been no detailed investigation regarding surface characteristics of PFSIs that are under the influence of electrical stimulation, which is clearly needed to understand the mechanistic details of IPMC actuation. This work describes the use of a combination of APAFM and CSAFM to capture surface morphological response and local conductivities, respectively, as a function of an applied electric field.

Experimental

Materials

The perfluorosulfonate ionomer, Nafion\textsuperscript{®} 117CS membranes (1100g/
equivalent, 7 mil thickness) were purchased from E.I. Dupont de Nemours & Co. and cleaned by refluxing in 8M aqueous nitric acid for 2 h, and then in deionized (DI) water for 1 h.

**Atomic Force Microscopy**

\( \text{H}^+ \)-form Nafion \( \text{®} \) was dissolved into a solvent system consisting of 50 vol % of ethanol and 50 vol % of DI water by heating the mixture to 250 °C in a pressure vessel for 2 h. Prior to film casting, the solution was filtered through a 200 μm inorganic membrane filter (Anotop 25, Whatman, Maidstone, UK) and cast onto a steel AFM stage puck. The solvent was removed in a vacuum oven at a vacuum pressure of 10 inches Hg and 50 °C. A copper wire was adhered to the steel disc using colloidal silver to form the working electrode.

AFM measurements were made in an environmental chamber at room temperature where the relative humidity (RH) was controlled by a nitrogen purge and kept between 60 % and 70 %. The morphology and response to an applied electrical field were studied using an Agilent 5500 AFM (Agilent Technologies, Santa Clara, CA) in both tapping mode atomic force microscopy with an applied potential (APAFM) and current sensing atomic force microscopy (CSAFM) modes. The AFM has a variable voltage source attached to the copper wire (Figure A-3) that is capable of applying a potential of –10 V to +10 V to the stage. APAFM was used to image both topography (height image) and domain behavior (phase image) of the cast films using a non-conductive silicon cantilever (RTESP, Veeco, Santa Barbara, CA) with a nominal resonant frequency of 300 kHz and a nominal force constant of 40 N/m. A bias ranging from 0 V to +3 V was applied to the metal stage puck through the attached copper wire.
and the topography and phase images were taken as a function of applied voltage using the same type of non-conductive cantilever (Figure A-3a, applied potential). In APAFM a static electrical field is generated and there is no counter electrode. The changes in phase response of the cantilever are monitored with respect to voltage applied to the PFSI membrane. During APAFM, the ratio of the setpoint amplitude to the free amplitude (A/A₀) was maintained at a constant value.

CSAFM was used to probe the topography and local conductivity of the film with a bias ranging from –2 V to +2 V. A conductive platinum-coated silicon nitride cantilever (N9540-60002, Agilent Technologies, Santa Clara, CA) with a nominal force constant of 0.35 N/m was used for imaging (Figure A-3b). In CSAFM the conductive tip serves as the counter electrode. Current flows perpendicular to the PFSI membrane surface in the same direction and at similar voltages as the planar actuator. Topography and current images (detection of localized current) were obtained in contact mode. The voltage of the applied bias was verified by measuring the voltage between the metal stage puck and a ground on the AFM using a multimeter. During CSAFM the setpoint was maintained at a constant value. Data was processed using Gwyddion 2.10 software to improve image quality and remove artifacts. Images were leveled by mean plane subtraction, and scan lines were removed by matching the height median.

Results and Discussion

Ion and water redistribution under electrical stimulation was probed by measuring the local mechanical energy dissipation on the surface of a PFSI membrane subjected to an applied bias voltage using APAFM (Figure A-4). In APAFM the cantilever was operated in the intermittent contact regime to minimize destructive
lateral forces on the sample surface while both topographical and phase images were obtained. By measuring the phase shift with constant excitation force, differences in probe-tip sample interactions produce compositional contrast in a heterogeneous sample.\(^\text{10}\) Contrast arises from differences in mechanical energy dissipation between the tip and the sample.\(^\text{11,12}\) In the intermittent contact regime, softer, more viscous, energy dissipative components appear as darker features in the phase image, while harder, more elastic, components appear brighter.\(^\text{13}\) In Figure A-4 topographical images are presented on the left, and the corresponding phase images are on the right. In Figures A-4a and A-4b, there is no applied bias voltage. In Figures A-1c and A-1d, a 1 V bias was applied to the stage puck producing a negative charge on the puck surface in contact with the PFSI membrane. No significant change in surface roughness is observed when a 1 V bias is applied, but the average phase shift of the cantilever’s response to the surface increases from 14.3° to 23.3°, indicating an overall decrease in energy dissipation. The same trend is observed in Figures A-4f and 4h as the bias is increased from 1 to 3 V. At 3 V, the average phase shift of the cantilever increases to 30.1. Surface roughness and average phase shift data are summarized in Table 1 below. Table A-1 shows that the surface roughness remains relatively constant, while the phase shift increases with applied voltage. The disappearance of the darker, more energy dissipative features as the applied bias is increased indicates that the total surface has become more energy conservative. Since the presence of water on the surface of a membrane will increase the energy dissipative characteristics of the surface, the observed increase in energy conservation of the PFSI membrane surface suggests that the surface is becoming dehydrated. This
observation is in complete agreement with the neutron imaging results obtained by the Moore Research Group and further supports the mechanism of proton and water migration to the negatively charged substrate as shown in the schematic presented in Figure A-6.

Further examination of the electrically-stimulated gradients was conducted using the CSAFM method (operating in the contact regime) and presented in Figure A-5 with topographical images on the left, and the corresponding current images on the right (note that the scan size is larger than that in Figure A-4). In Figure A-5a (topography) and Figure A-5b (current), a +2V bias was applied to the metal stage puck giving the substrate surface of the PFSI membrane a negative charge. The conductive domains (brighter areas, see scale bar) in Figure A-5b correspond to the high regions of the topographical image in Figure A-5a. Current flow is isolated to the bright areas that indicate measurable current. The average current over the entire surface (512 × 512 data points) of Figure A-5b is 2.8 pA. In Figure A-5c (topography) and Figure A-5d (current), the polarity is now reversed and –2V bias is applied to the substrate, yielding a positive charge at the substrate surface of the sample. The average current of Figure A-5d is –90.6 pA, which suggests that conduction occurs over the entire surface. The regions of high current flow in this image are the dark features, and correspond to the dark, lower regions of the topography image (see scale bar). Average diameter of the conductive domains determined by image analysis is 41 nm with a standard deviation of 8nm. The insert in Figure A-5d shows a step change in voltage from -2V (bottom of inserted image) to +2V (top of inserted image) during a single scan. While little quantitative
information can be obtained from the insert due to the time dependant dynamic processes that occur from a sudden change in applied bias, it qualitatively shows the shift in surface conductivity of the PFSI membrane as the substrate bias is changed. The insert shows that a negative charge applied to the substate produces a negative charge on the top surface of the PFSI membrane, and a positive charge applied to the substrate produces a positive charge on the PFSI membrane surface. This further illustrates the change in PFSI membrane response as a function of applied voltage.

The PFSI investigated in this study is known to form a phase-separated morphology where the ionic domains, termed ionic clusters, are distributed throughout the non-polar polytetrafluoroethylene (PTFE) matrix, and continuous ionic channel formation in a hydrated condition provides the percolation pathway for ionic conduction.\(^3,14\) When no charge is applied to the membrane, the sulfonate groups residing in the interfacial region between the PTFE matrix and the ionic channel are in equilibrium with protons in solution, and the sulfonate groups residing on the top surface of the PFSI membrane are in equilibrium with protons residing in the thin liquid layer present on the top surface of the PFSI membrane. This is illustrated schematically in Figure A-6b.

The light features in Figure A-5b correspond to the dark features in Figure A-5a and indicate that these are actively conductive channels. The direction of positive current flow in Figure A-5b suggests that the light features represent the immobile, negatively charged sulfonate groups producing positive current flow to the grounded, platinum coated cantilever. The dark, continuous region of Figure A-5b corresponds to the light continuous region of Figure A-5a, suggesting that this is the
nonconductive PTFE matrix. The direction of current flow indicates that the surface is absent of positively charged cations and suggests that these species have migrated to the negatively charged substrate as shown in the schematic presented in Figure A-6a.

In Figure A-5d the darker features correspond to the dark features in Figure A-5c, providing further evidence that these domains represent the actively conductive channels. The direction of negative current flow in Figure A-5d suggests that the mobile protons and water have migrated to the surface giving it a positive charge. The magnitude of the negative current flow and the presence of current flow over the entire surface suggest that the cationic fluid has not only migrated to the surface of the actively conducting domains but have actually formed a cationic film on the top surface of the PFSI membrane, which is illustrated schematically in Figure A-6c.

Conclusions

AFM allowed surface characterization of the nanoscale morphology and local surface properties due to migration of water/counterion under electrical stimulation. Water/counterion migration in response to various voltages was characterized using APAFM. The increase in energy conservation of the PFSI membrane surface suggested that the surface was being dehydrated due to migration of protons and water to the negatively charged substrate, which correlates very well with the neutron imaging results. Water/counterion migration was further supported by CSAFM. Under a +2 V bias, only a low 2.8 pA of average current was detected over the PFSI surface. This indicated that positively-charged cations were essentially absent on the surface. On the contrary, application of −2 V bias to the substrate/sample interface
led to a high average current of –90.6 pA on the opposing surface, which suggests that the protons and water have migrated to the surface away from the positively-charged substrate.
Tables and Figures

Table A-1
Summary of Average Height and Phase Variations as a Function of Applied Voltage.

<table>
<thead>
<tr>
<th>Height (nm)</th>
<th>Phase (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
</tr>
<tr>
<td>0 V</td>
<td>2.13</td>
</tr>
<tr>
<td>1 V</td>
<td>1.80</td>
</tr>
<tr>
<td>2 V</td>
<td>1.93</td>
</tr>
<tr>
<td>3 V</td>
<td>4.17</td>
</tr>
</tbody>
</table>

* The root mean square deviation associated with each value is presented in italics.

Figure A-1. Actuation of IMPC under an applied DC bias.
Figure A-2. Theoretical model for hydraulic actuation of IMPC under an applied DC bias.
Figure A-3. Schematic drawings of (a) APAFM and (b) CSAFM. AFM voltage supply verified externally using multimeter. Non-conductive silicon cantilever in 3(a) acts as open switch. Conductive cantilever in 3(b) acts as closed switch.
Figure A-4. APFM topographical (left) and corresponding phase (right) images of PFSI film as a function of applied bias voltage: (a and b) 0 V, (c and d) 1 V, (e and f) 2 V, (g and h) 3 V.
Figure A-5. CSAFM topographical (left) and current (right) images of PFSI film: (a and b) +2 V, (c and d) –2 V. Each current image is composed of 512 × 512 individual data points. The insert in 9d shows the response of the surface of the PFSI membrane as a step change in voltage is applied to the substrate from -2V (bottom of image) to +2V (top of image).
Figure A-6. Description of electrophoretic motion (a) illustration of proton and water migration to the negatively charged substrate and formation of isolated sulfonate-rich domains and dehydration on the top surface of the PFSI membrane, (b) Illustration of the equilibrium state between sulfonate groups and protons in the PFSI membrane with no applied bias, and (c) illustration of proton and water migration away from the positively-charged substrate forming a cationic film on the top surface of the PFSI membrane and neutralization of the positively charged substrate by non-mobile sulfonate ions.
References


9 Takimoto, N; Ohira, A; Takeoka, Y; Rikukawa, M. Chemistry Letters 2008, 37, 164.


