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Exploiting Polymer Nanomaterials Technology for the U.S. Army's Objective Force

by Sandra K. Young, Frederick L. Beyer,
and Matthew S. Bratcher

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Abstract

Many polymeric nanomaterials are being investigated for use in advanced clothing, sensor, actuators, medical technologies, and fuel-efficient energy systems among other Army needs. The U.S. Army Research Laboratory's Weapons and Materials Research Directorate Polymers Research Branch has many programs directed toward advancing materials for these and other technologies. A few of these specific programs will be discussed in more detail in this report. Polymer-layered silicate nanocomposites are materials of compelling interest for Army applications. These materials offer the possibility of significantly improved physical properties with the addition of a small amount of inexpensive filler, but are not a mature technology because of critical gaps in the current understanding of their equilibrium behavior. One project, which attempts to address these gaps, is described. Carbon nanotubes have high potential payoffs in nanotechnology and are being investigated. Early efforts include quantification and functionalization of defect sights with polymers. Nafion perfluorosulfonate ionomers have shown usefulness in many areas including fuel cells, sensors, and actuators. Understanding the nature of the polymer structure, under what conditions the polymer structure can be changed, and whether the polymer structure can be controlled through modification are many of the important issues needing answers in order to have success in making nanoscopic structures within polymers. A variety of experiments have been done in order to unravel the complicated structure of the material.

Acknowledgments

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1. Introduction

For the past 5 years, the U.S. Army has been investigating nanomaterials—from dendritic nanomolecules to nanoparticulates to nanotubes—for applications in next-generation Army systems. However, many other nanomaterials will need to be developed for future Army applications (Figure 1). Targeted applications range from electronics and sensing to chemical agent protection to armor and armaments. Numerous programs are ongoing in the U.S. Army Research Laboratory (ARL) Weapons and Materials Research Directorate (WMRD) Polymers Research Branch (PRB) (Figure 2). Some recent successes have included ultralightweight ceramic armors based on nanoparticulate ceramics, durable flame-resistant coatings for ballistic protective eyepieces, and novel permselective polymer membranes for breathable clothing and compact power sources. An overview of technologies will be presented, followed by highlights of material designs and characterization activities from the perm-selective membranes program. Many of these projects were discussed at the National American Chemical Society 2001 spring meeting held in San Diego, CA in the Symposium on Defense Applications of Nanomaterials. Abstracts should be available from the meeting, and a book on Defense Applications of Nanomaterials is in the process of being edited and published as a result of the session at the meeting. Here, a few of these topics will be discussed in more detail.

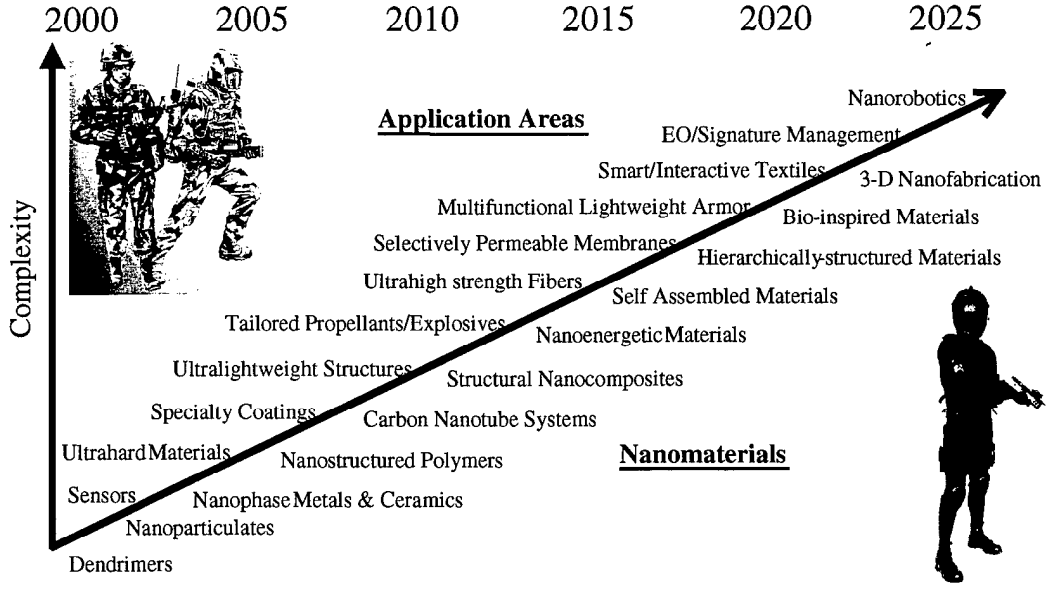

Figure 1. Nanomaterials directions for the Army's Objective Force.

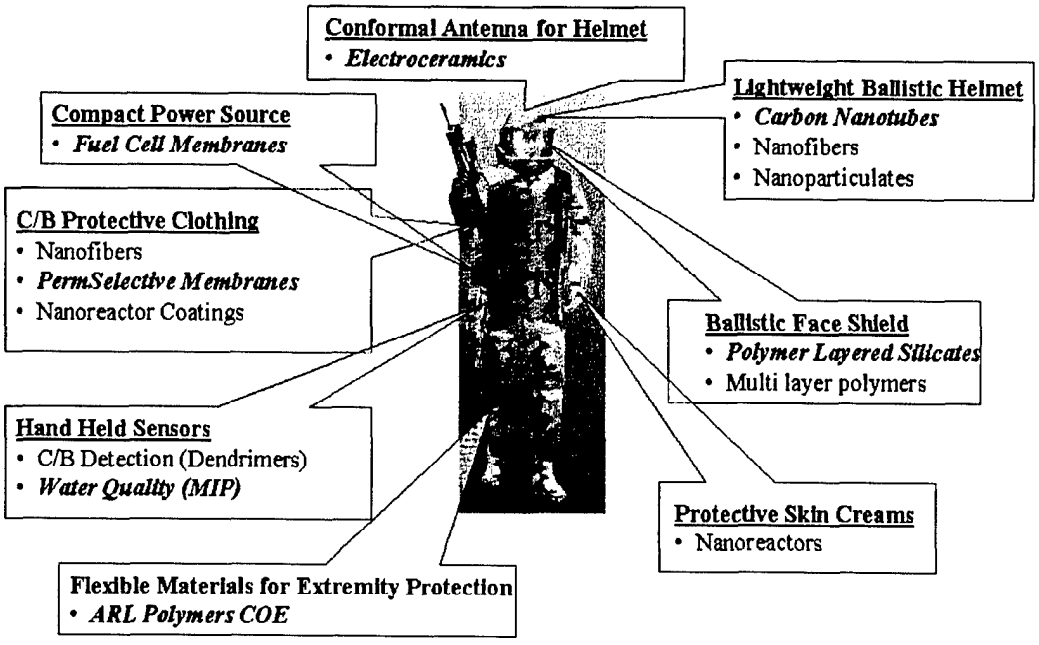

Figure 2. Some of the current polymer nanomaterials programs applicable to the Objective Force Warrior effort.

2. Studies of a Model System for Polymer-Layered Silicate (PLS) Nanocomposites

PLS nanocomposites have been a focus of great interest over the last decade as a result of the significant improvements in mechanical and thermal properties reported by researchers at Toyota for nylon-6-based materials [1, 2]. PLS nanocomposites are composed of a polymeric matrix with a small amount of a layered silicate clay mineral filler, usually on the order between 2 and 5 weight-percent. The most commonly used filler in research has been montmorillonite, which has a net negative charge in the crystal structure of the layers as a result of isomorphous substitutions in the crystal structure [3]. The negative charge is compensated by the presence of naturally occurring cations found in the galleries between individual clay sheets, and these cations are commonly replaced with amine-terminated alkyl chains to help compatibilize the clay with the organic matrix.

During this timeframe, a significant research effort has been focused on the fabrication of nanocomposites having the morphology giving the most benefit in properties, which is an exfoliated morphology. Exfoliation has occurred when the individual silicate sheets are dispersed within the matrix. Three processing

methods are predominant currently for fabricating nanocomposites with the preferred morphology. These methods include in situ polymerization of monomer, solution processing of clay and polymer in a cosolvent, and melt mixing by mechanical processing techniques such as twin screw extrusion. Unfortunately, these techniques place restrictions on candidate materials for nanocomposites. Solution processing requires that the polymer and clay be soluble in the same solvent. In situ polymerization affects the molecular characteristics of the polymer. Melt processing relies on overwhelming kinetic energy to break up the clay tactoids. Finally and most notably, little work has been directed at a methodical understanding of the basic underlying thermodynamic driving forces between the components in PLS nanocomposites, which ultimately govern equilibrium behavior [4].

Recent research at ARL, with colleagues at the University of Delaware (UD), has sought to define these basic relationships between layered silicate, surfactant modifier, and homopolymer matrix. The experimental work has been developed based on the theoretical predictions of Balazs et al. [5]. The general predictions of the model are that the addition of a modified surfactant encourages intercalation and exfoliation by reducing the entropic penalty incurred by a homopolymer when it is confined in the silicate gallery. The model also indicates, accordingly, that longer surfactants are more capable of that task, and that increasing the coverage of the surfactant on the silicate surfaces reduces the effectiveness of the surfactant. It is inferred that this result is due to the silicate modifier, at high coverages, behaving as a dense polymer brush.

In our work, we have attempted to follow, as closely as possible, the molecular details of the Balazs model. To reduce the number of variables in our system, polystyrene was chosen as the model system in that synthesis of polystyrene is well understood and allows much flexibility and control. While the Balazs model examines the effect of enthalpic interactions, given by a Flory-Huggins-type parameter, χ, between different components, here we wanted to eliminate those interactions as a variable. Therefore, we have considered a system in which the surfactant and homopolymer matrix are chemically identical, both being polystyrene. Custom synthesis of the surfactant allowed precise control of molecular weight, narrow molecular weight distributions, and quantitative end-functionalization with trimethylamine moieties.

Using the custom surfactants, the morphological behavior of a model system based on polystyrene (PS) and montmorillonite has been examined roughly according to the specified conditions in the Balazs model. The amine-terminated PS surfactants were exchanged with the naturally occurring cations in the montmorillonite by a solution cation exchange reaction. After standardizing the modification procedure, cleaned montmorillonite was modified to high levels of coverage with each of three surfactants. The modified clays were then mixed with PS homopolymer 95 repeat units long and annealed for one week at 125 °C.

Based on self-diffusion of PS homopolymer, 1 week was felt to be sufficient at this temperature to allow intercalation. It was hoped that this process would allow an equilibrium morphology to be formed. It was also hoped that without the addition of any sheer forces, based on the predictions of the Balazs model, intercalated or exfoliated morphologies would be formed. The modified clays and the nanocomposites were then characterized by thermal gravimetric analysis (TGA) and small-angle x-ray scattering (SAXS).

The SAXS data, such as those shown in Figure 3, have repeatedly and conclusively shown that, while modification with surfactant was successful, no intercalation of the PS homopolymer occurs during annealing. This result is somewhat contrary to other published results indicating that PS will, by melt annealing, intercalate commercially available clays [6]. Our results are attributed to autophobic dewetting of the homopolymer from the surfactant modified clay surfaces, which is a result of forming a dense polymer brush on the clay surfaces.

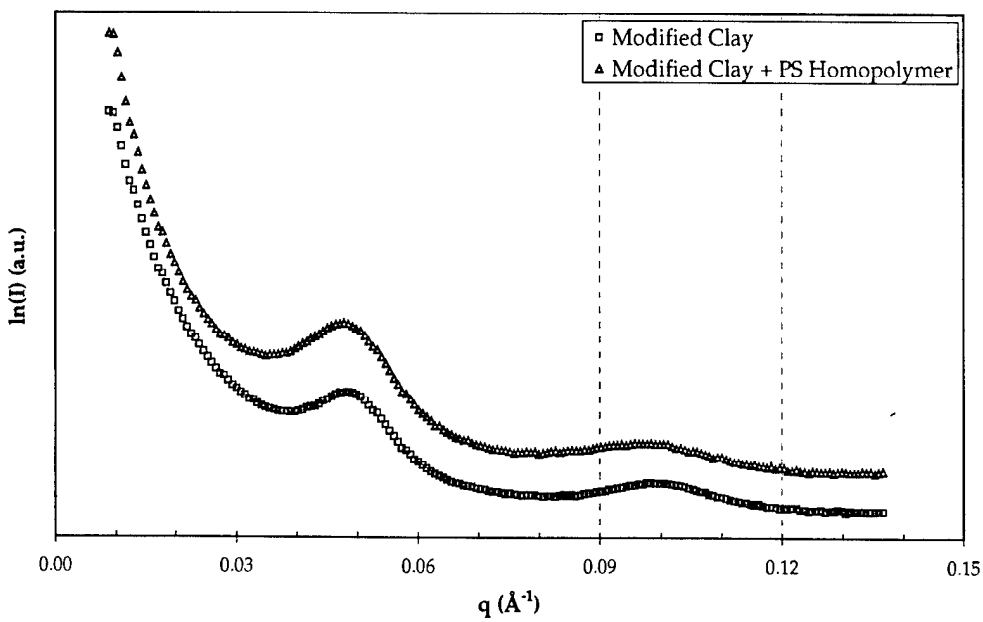

Figure 3. SAXS data for a modified layered silicate clay and the same clay after annealing with PS homopolymer.

This work has focused attention on several aspects of the Balazs model. First, although most commercially available modified clays are modified to a high level, usually approaching 100%, the model uses a low coverage of 0.04 cations/lattice unit. For a PS-based system such as used here, this measure corresponds roughly to the very low coverage of 1 cation/12 nm^2. A future consideration will also be the effect of the repulsive interactions between the silicate surface, which is hydrophilic, and the intercalating homopolymer, which is typically hydrophobic. In the model, these interactions seem to be set to zero,

which is not often the case in reality. Additionally, while the model predicts that longer surfactants should aid the intercalation process by returning conformational entropy to the confined homopolymer, at high coverages, it was found that simply using a longer surfactant did not reduce the autophobic dewetting behavior observed, even at lower coverages as low as 50%.

Work currently underway on this system seeks to address the issues raised by these results. First, lower surfactant coverages are being examined, targeting the specific level of coverage used in the Balazs model. To address the repulsive forces acting between the homopolymer matrix and silicate surface, work is also underway to examine a surfactant mixture which would completely cover the silicate surface, but use both long and short chains, thereby allowing both reduction of the homopolymer entropy penalty and shielding of the interactions between surface and polymer.

In conclusion, it is hoped that this basic research effort will provide valuable insight into the equilibrium behavior of polymer-layered silicate nanocomposite materials. Whereas currently, empirical efforts based on limiting fabrication techniques such as in situ polymerization dominate the research into new nanocomposite materials, the goal of this work is to allow the fabrication of PLS nanocomposites from existing polymers with specific, well-defined properties.

3. Carbon Nanotubes for Army Applications

3.1 Background

The discovery of carbon nanotubes (CNTs) in 1991 by Ijima [7] has spurred a tremendous amount of carbon-based nanotechnology research throughout the world. CNTs were synthesized under similar conditions to fullerenes such as arc discharge of graphite and chemical vapor deposition methods; however, it was soon found that in addition to a carbon-based fuel, a metallic catalyst was required for an effective synthesis. The search for ideal synthetic approach is still underway, but many advances have been made since the initial discovery. The desire to synthesize CNTs was undoubtedly motivated by their unique properties. The pairing of a high Young's modulus with high electrical conductivity certainly attracted much attention as well as chemical resilience of CNTs and the thermal conductivity, which rivals that of diamond.

The unique structure and properties of CNTs make them ideal candidates for many applications in both the military and commercial sectors. Although these developmental areas have yet to bear fruit, many scientists are eager to exploit this new material. The applications listed here are not all-inclusive, but they address some key issues for the soldier of the future.

3.1.1 Power Sources

The soldier of the future is envisioned to have a power system that is lightweight and very efficient. CNTs can be utilized in this system as a component of a battery. Lithium is known to intercalate in CNTs and with their semiconductor/metallic properties may offer unforeseen advantages in this application. Furthermore, the low density of the CNTs (1.3 g/cm^3) makes the CNTs ideal candidates for lightweight battery materials.

3.1.2 Electromagnetic (EM) Shielding

EM shielding is a critical element for protection in soldier systems. Not only do electronics require shielding, but the soldiers themselves will also need to be shielded from their "on-board" systems. The high electrical conductivity of CNTs makes them a new alternative for EM shielding, and their large aspect ratios inspires one to think about conductive CNT-doped fibers that could be embedded in the soldier uniform itself.

3.1.3 Armor

CNTs are expected to have an impact in the area of textile fibers used for ballistic protection. The high tensile strength of the CNTs may improve protection properties by a factor of 10. One can imagine a CNT-polymer composite with low density that could be layered with ceramics materials to make a new hybrid system with high strength and stiffness for armor protection.

3.1.4 Thermal Regulation

The need for thermal regulation is key for future military systems. Technology will be required to warm and cool the soldier wearing a chemical/biological agent protective suit. The high thermal conductivity of CNTs may solve some of these issues by fabricating efficient heat sinks with CNT materials. Thoughts have also turned towards CNT-doped fluids that would dramatically increase efficiency in radiant heating/cooling systems for both soldier needs as well as for vehicles.

3.1.5 Flat Panel Displays

The vision of the soldier of the future indicates that volumes of information will be communicated through a heads-up display in the helmet. Researchers have been tackling the challenge of fabricating CNT-based displays. The molecular and electronic features of CNTs are well suited for light emission applications.

3.1.6 Filtration

CNTs like activated carbon have potential uses in both liquid and gas filtration. CNT materials have already shown promise to be equally if not more effective

than reverse osmosis in water filtration. CNTs offer the soldier increased chemical agent protection as a new filtration media in both the uniform fabric as well as breathing.

3.1.7 Actuators

Baughman et al. have successfully demonstrated that CNT-coated substrates can act as actuators under modest fields [8]. Although much of the interest in actuators lies in creating artificial muscles capable of doing work, there are certainly other aspects that can be considered. For example, actuators incorporated into membranes could become active filtration materials. These membranes could then be electronically tuned to optimize performance for a given situation.

Some of the technical barriers associated with CNTs have proven difficult to overcome, but are certainly being addressed in order to fully exploit their properties. Certainly, the problems associated with the high-purity large-volume production of CNTs have been addressed extensively in the literature. It is worth noting that several different approaches that have been developed lend themselves to different applications. For example, plasma-enhanced chemical vapor deposition developed by Huang et al. [9] could be used for flat panel displays, while single tube syntheses developed by Franklin and Dai [10] are more suitable as sensors. Furthermore, synthetic strategies for bulk CNT production may be selected on whether electronic or structural properties are critical for the final product. A final consideration in the synthetic aspects is the catalyst. A myriad of catalysts has been studied, but it is evident that a fundamental understanding of the catalyst role in the growth mechanism is still incomplete at best. Cassell et al. [11] take a practical approach to catalyst discovery by using combinatorial methods for building catalyst libraries and testing and evaluating performance.

One of the other technical hurdles associated with CNTs is processing. While a large knowledge base exists for incorporating micron-sized carbon-based fibers, by comparison, very little has been done for CNT incorporation. Certainly, in the past few years as CNT supplies have become more plentiful, more efforts to successfully process CNTs using extrusion, ultrasonic radiation, high shear mixing, and melt spinning have been developed to overcome this problem. Dispersion of the tubes is particularly important. Failure to disperse leads to a phase separation due to the strong surface interactions between the tubes. It is likely that chemical functionalization would not only serve to facilitate dispersion but could stabilize the CNTs and prevent agglomerations, which could lead to defects, from forming.

Here we describe our approach to overcoming some of the technical barriers involved with developing nanotubes materials. We are studying the density of defect sites, chemically modifying the sites with polymers using two approaches

and then re-examining the properties to understand the impact of the polymer modification. To further understand the significance of the polymer modification we have explored two approaches: coupling a preformed polymer to chemically treated nanotubes and chemically modifying a tube such that a polymerization can be initiated from the defect site on the tube (Figure 4).

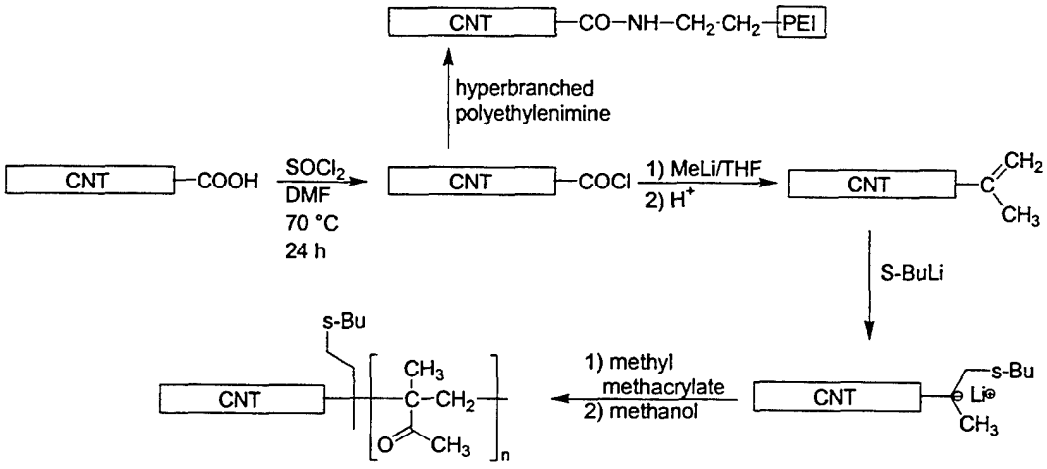

Figure 4. Synthetic strategies for new nanotubes materials.

3.2 Experimental

Below are typical conditions for the synthesis of nanotubes-polymer hybrid materials.

A sample of nanotubes (obtained from NanoLab*) was placed in a flask and mixed with thionyl chloride. The mixture was refluxed, the thionyl chloride was removed by vacuum distillation, and the residue was dried under vacuum. Then polyethylenimine was added to the flask with methylene chloride. The reaction was stirred under nitrogen for 24 hr. The reaction was quenched by adding the mixture to water and vacuum filtration. The solids were washed with copious amounts of water to remove unreacted polymer. The treated nanotubes were then dried under vacuum.

A sample of nanotubes was immersed in thionyl chloride with 1 mL of dimethylformamide as a catalyst. This mixture was refluxed for 24 hr, and then most of the thionyl chloride was decanted while the residual thionyl chloride and dimethylformamide removed under vacuum. When the sample was dried, tetrahydrofuran was distilled into this flask. Then methyl lithium was added into this flask by injection. The reaction was stirred and then quenched using dilute hydrochloric acid solution.

* Nanolab, 164 Market St., Brighton, MA 02135.

The sample of modified nanotubes from the thionyl chloride/methyl lithium treatment was placed in a home-built all-glass reactor. This reactor is equipped with five ampules containing sec-butyllithium (s-BuLi), lithium chloride (LiCl), 1,1-diphenyl ethylene (DPE), methyl methacrylate, and methanol. When high vacuum is reached in the reactor, tetrahydrofuran is distilled into it. The reactor is kept at -78 °C from this point forward. Then, s-BuLi is introduced into the reactor. The nanotubes were mixed with s-BuLi for 1 hr. Then the break-seal of LiCl and DPE were fractured. After 15 min, the break-seal of methyl methacrylate was fractured. After all the methyl methacrylate is transferred into the reactor, the reaction was kept at -78 °C for 2 hr. Then, the polymerization was terminated by addition of methanol. Before precipitation, the reaction mixture is concentrated using a rotary evaporator. The CNT-poly(methyl methacrylate) (PMMA) is collected by precipitation in tenfold excess of methanol. The precipitate can then be dried under vacuum.

3.3 Results and Discussion

In order to exploit the defect sites as a chemical handle for the CNTs, it is clear that quantification of these sites in a given material is highly desirable. Using procedures published by Hu et al. [12], we followed acid/base titration descriptions to determine the density of defect sites in our CNT materials. While more detailed studies are required to examine this material, our results indicate that less than 1% of the carbon atoms are chemically reactive toward bases. Further investigation is planned and includes x-ray photoelectron spectroscopy as well as infrared spectroscopy to quantify the acidic defects sites spectroscopically.

To determine how the polymer functionalization compares with surfactant treatment samples of raw nanotubes, nanotubes treated with 5% surfactant, and polyethylenimine-CNTs were analyzed to determine the average aggregate size when suspended in distilled water. Results from the particle-size analyses indicate that the CNTs tend to be smaller aggregates after functionalization. The polyamine functionality undoubtedly increases the hydrophilicity of the CNTs thereby stabilizing the suspension. This result validates our initial hypothesis that the modification of the polymer defect sites would reduce the surface interactions between tubes and facilitate dispersion even in poor solvents like water. CNTs that were treated with nitric acid also appeared to have a slightly smaller aggregate sizes relative to the as-produced material. While the data indicate treatment with a surfactant seems to reduce the size of aggregates marginally, it is unclear if this marginal change is significant. The surfactant was chosen based on the favorable amine-carboxylic acid interaction, but the propylsiloxane is probably not ideal for the aqueous conditions. Also, it should be noted that this data does not account for the large aspect ratio of the CNT materials and should therefore not be considered to be very precise data. The trends observed in the data, however, certainly give insight into how these materials behave.

3.4 Conclusions

We performed initial characterization nanotube materials to evaluate defect site densities, and then exploited these defects to attach polymers to the nanotubes using two approaches. We coupled a preformed polymer to the nanotubes and initiated polymerizations from the defect sites. Preliminary results indicate that the new hybrid materials have desirable properties that should facilitate dispersion while maintaining the unique properties of the nanotubes.

4. Nafion Perfluorosulfonate Ionomer Membranes

Membrane research is a continually evolving area of materials science and engineering. Many of these continual changes are due to the increasing demand for technologies such as fuel cells, permselective materials for chemical and biological defense, and filtration membranes for water. Part of the challenge in developing these membranes is the broad range of materials available for use. To date, Nafion has been the industry standard for fuel cells. Due to its excellent properties, many researchers have tried to develop other materials that perform similarly to Nafion for many different applications.

Nafion is a perfluorosulfonate ionomer, consisting of a tetrafluoroethylene main-chain and a perfluoroether sulfuric acid side chain [13] (Figure 5). Coulombic interactions between the ions in Nafion result in aggregation of the sulfonate groups into tightly packed ionic regions referred to as clusters. Ionic clustering in Nafion improves the materials' mechanical, thermal and transport properties. The relationship between these properties and the membrane's structure have made Nafion the focus of many structural studies [13–20].

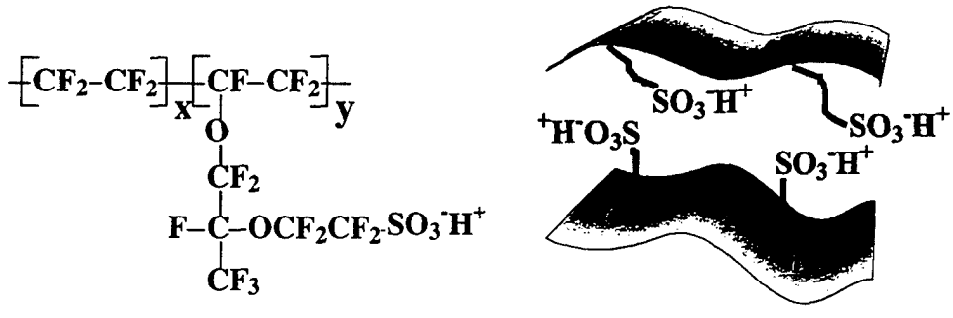

Figure 5. Chemical structure and aggregate structure of the Nafion ionomer.

4.1 Chemical Identification

There have been a variety of methods used in the characterization of Nafion—Fourier transform infrared (FTIR) [21–23], nuclear magnetic resonance (NMR) [24–28], dynamic mechanical analysis (DMA) [29–32], x-ray diffraction (XRD) [33–35], and small-angle scattering (SAS) [13–17, 36–41]. Of these, chemical knowledge of the counterion associated with the perfluorosulfonic acid group and the quantity of water within the membrane is critical before any applications evaluation of Nafion membranes. The sulfonic group ($-SO_3-$) is the sole site for chemical variation in the membrane through simple chemical manipulations. The counterion, whether a proton, alkali metal, or other metal cation, has an effect on the interactions of the sulfonic acid or sulfonic acid salt groups, which in turn affects the strength of the ionic aggregates. The presence of small amounts of ion exchange, while altering the chemical structure, can also change the interaction of the aggregates. Therefore, a method for identifying the ion(s) at the exchange site is needed to fully characterize the membranes.

Cold neutron capture prompt gamma activation analysis (PGAA) is an ideal method for the evaluation of composition on Nafion membranes due to its nondestructive nature and sensitivity to trace ions, especially hydrogen. Through experimentation, PGAA has been found to yield rapid, accurate, and reproducible results on the chemical composition of Nafion membranes and can be used to confirm ion exchange reactions and determine contamination by water (through detection of hydrogen) or other counterions. In our experiments, we applied PGAA to the characterization of ion and water content in Nafion membranes that were subjected to a variety of drying, pretreatment, and counterion exchange conditions. These measurements are used to evaluate the effectiveness of various treatments for removing water and contaminants in the membranes and confirm the efficiency of ion-exchange reactions.

Prompt gamma data were collected for H+-form Nafion membranes, in addition to several other counterion forms (K^+, Cs^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}), and prepared. The acid-form membrane, because of pretreatment, only showed the presence of H, K, and S. The counterion experiments show that the exchange procedures used successfully, result in replacement of 94–100% of acid protons. Conversions are slightly lower for monovalent cations than for di- and trivalent cations. Monovalent K+ and Cs+ ions exhibited the most difficulty in achieving maximum conversion. These ions are the largest in size and it is a possibility that in the membrane aggregates there is a limit to the accessibility of the ion for exchange. The accessibility limitation in the aggregates seems to be supported by solubility and diffusion measurements. Monovalent cations reduce the solubility and diffusion coefficients for water and simple alcohols much more than di- and trivalent ions [41].

4.2 Small-Angle Neutron Scattering (SANS) Experiments

SANS experiments were performed on Nafion swollen in a variety of solvents. The scattering curves showed the features that are known to be characteristic of Nafion membranes—a low-angle intensity upturn, a broad peak around 0.04 $Å^{-1}$ that has been associated with crystalline regions of the structure [13, 16, 42], and a peak around 0.1 $Å^{-1}$ -0.2 $Å^{-1}$ that has been associated with the ionic regions [13, 16, 42]. These features are observed regardless of the swelling solvent and for membranes in the acid form and ion-exchanged forms. Though the structural features are consistent regardless of counterion or solvent type at a given volume fraction of absorbed solvent, the total solvent uptake reached is strongly dependent on the chemistry of the swelling solvent and the counterion of the sulfonic acid group. Similar results have been reported previously [41].

Both the mid-q peak (or crystalline peak) and the ionic peak shift in position as a function of the volume fraction of solvent absorbed by the membrane. The positions of the ionic and crystalline peaks have been determined by fitting using a normalized Gaussian for the peak description and a power function of q to represent the background. The physical dimension or spacing, d, associated with the peak position was calculated using the Bragg relationship, $d = 2\pi/q$. The ionic peak shifts to lower q values (higher d spacing) as the volume fraction of solvent in the membrane increases, in agreement with the results of other researchers [2, 4, 10]. This shift is consistent across the entire range of solvents studied; however, the magnitude of the shift at a given volume fraction of solvent is solvent dependent. Two interesting observations may be made from Figure 6. First, the Bragg spacing corresponding to the ionic peak position increases linearly with the volume fraction of solvent absorbed by the membrane, regardless of solvent type, at solvent concentrations between ~2% and ~50%. Second, the slope of the spacing vs. volume fraction curve is different for different solvents. Each observation has implications with regard to the various structural models proposed for Nafion membranes.

Research continues in this area, with further investigation of acid samples (DMA and XRD of dry and swollen samples) and acid-form stretched samples and counterions (swollen samples, swollen to different volume fractions, DMA and XRD of samples). In addition, we are in the process of correlating data from these specific membrane morphologies to the methanol diffusion and conductivity. More information on the Nafion systems can be found in other ARL tech reports and refereed journal articles by S. Young [43–46].

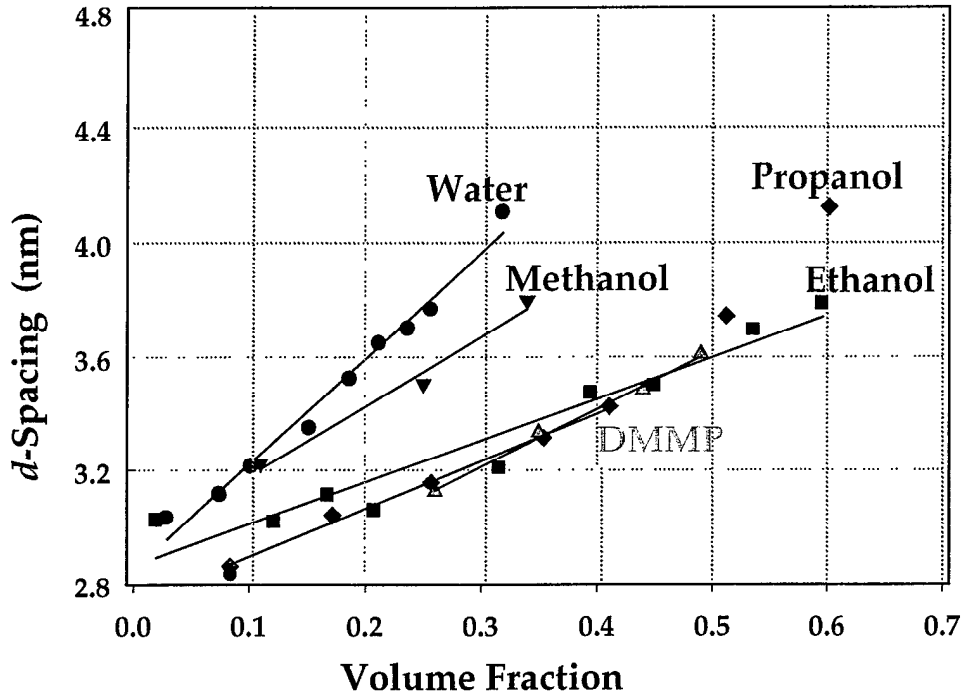

Figure 6. Bragg spacing corresponding to the ionic cluster peak vs. volume fraction solvent for Nafion membranes swollen with various solvents.

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13. ABSTRACT *(Maximum 200 words)*

Many polymeric nanomaterials are being investigated for use in advanced clothing, sensor, actuators, medical technologies, and fuel-efficient energy systems among other Army needs. The U.S. Army Research Laboratory's Weapons and Materials Research Directorate Polymers Research Branch has many programs directed toward advancing materials for these and other technologies. A few of these specific programs will be discussed in more detail in this report. Polymer-layered silicate nanocomposites are materials of compelling interest for Army applications. These materials offer the possibility of significantly improved physical properties with the addition of a small amount of inexpensive filler, but are not a mature technology because of critical gaps in the current understanding of their equilibrium behavior. One project, which attempts to address these gaps, is described. Carbon nanotubes have high potential payoffs in nanotechnology and are being investigated. Early efforts include quantification and functionalization of defect sights with polymers. Nafion perfluorosulfonate ionomers have shown usefulness in many areas including fuel cells, sensors, and actuators. Understanding the nature of the polymer structure, under what conditions the polymer structure can be changed, and whether the polymer structure can be controlled through modification are many of the important issues needing answers in order to have success in making nanoscopic structures within polymers. A variety of experiments have been done in order to unravel the complicated structure of the material.

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