

Final Project Report

Brush-Coated Nanoparticle Polymer Thin Films: structure-mechanical-optical properties (DE-FG02-07ER46412)

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Institution:

University of Michigan,
Office of Research and Sponsored Projects
3003 South State Street
Wolverine Tower, Room 1058
Ann Arbor, MI 48109-1274

Principal Investigator:

Peter F. Green,
Department of Materials Science and Engineering
2300 Hayward Street, 3062 Dow Building, University of
Michigan, Ann Arbor, MI 48108

PI Telephone: 734-764-8161

PI e-mail: PFGreen@umich.edu

Executive Summary

Our work was devoted to understanding the structure and properties of a class of thin film polymer nanocomposites (PNCs). PNCs are composed of polymer hosts into which nanoparticles (metallic nanoparticles, quantum dots, nanorods, C₆₀, nanotubes) are incorporated. PNCs exhibit a diverse range of functional properties (optical, electronic, mechanical, biomedical, structural), determined in part by the chemical composition of the polymer host and the type of nanoparticle. The properties PNCs rely not only on specific functional, size-dependent, behavior of the nanoparticles, but also on the dispersion, and organizational order in some cases, inter-nanoparticle separation distances, and on relative interactions between the nanoparticles and the host. Therefore the scientific challenges associated with understanding the interrelations between the structure and function/properties of PNCs are far more complex than may be understood based only on the knowledge of the compositions of the constituents. The challenges of understanding the structure-function behavior of PNCs are further compounded by the fact that control of the dispersion of the nanoparticles within the polymer hosts is difficult; one must learn how to disperse inorganic particles within an organic host.

The goal of this proposal was to develop an understanding of the connection between the structure and the thermal (glass transition), mechanical and optical properties of a specific class of PNCs. Specifically PNCs composed of polymer chain grafted gold nanoparticles within polymer hosts. A major objective was to understand how to develop basic principles that enable the fabrication of functional materials possessing optimized morphologies and combinations of materials properties.

Accomplishments:

We developed: (1) fundamental principles that enabled the creation of thin film PNCs possessing more complex morphologies of homopolymers and block copolymer micellar systems [1-6]; (2) a new understanding of physical phenomena associated with the structure of PNC systems and the glass transition and dynamics [7-11], including surface dynamics [12, 13]; designed PNCs to understand the connection between structure and specific optical responses of the material [14, 15]; electrorheological phenomena [16-18]; coarsening/aggregation phenomena [19, 20]; directed assembly [21] and elastic mechanical properties of thin supported films [22].

We established procedures to design and control the spatial distribution of gold nanoparticles (Au-NP), onto which polystyrene (PS) chains were end-grafted, within thin film PS hosts.[1-3] We explained how enthalpic and entropic interactions between the grafted layers and the polymer host chains, the nanoparticle (NP) sizes and shapes determine the spatial distribution of NPs within the host (i.e.: the morphology). In brief, the chemistries of the grafted chains and the polymer hosts, the degrees of polymerization of grafted and host chains (N and P, respectively), and the surface grafting densities S influence the thermodynamic interactions. Thin films are unique: the external interfaces (substrate and free surface) profoundly influence the spatial distribution of NPs within the PNC. For example, thin films are thermodynamically less stable than their bulk analogs due to the preferential attraction between the brush-coated nanoparticles and the external interfaces (i.e.: the free surface/polymer interface and the polymer/substrate interface).

We investigated the organization of the brush-coated nanoparticles within a host composed on block copolymer micelles in a homopolymer [4, 5]. Block copolymers, composed of a polymer of type A that is bonded covalently to another polymer of type B (A-b-B) are known to form micelles within homopolymers A or B. A micelle is composed of an inner core of the A component of the copolymer and an outer corona of the B-component, that resides within homopolymer B, which serves as the host. If the host is the A homopolymer then the core of the micelle is composed of the B component of the copolymer. One important objective in applications such as drug delivery is to incorporate nanoparticles into micelles. We developed phase diagrams and demonstrated how the nanoparticle could be located in different regions (micelle cores, interfaces, homopolymer hosts) of the system, based on manipulating the thermodynamic interactions [4, 5]. This work will enable the design of new PNC materials with specific functional properties.

In a separate series of experiments, we investigated the connection between structure and dynamics of polymer systems composed on mixtures of BCPs with homopolymer hosts. We investigated the dynamics of the individual polymeric constituents within pure copolymers and within micelles confined within different polymer hosts. Interestingly the dynamics manifested the structure of the local environment. In other words, the dynamics of chains of type-A within a copolymer, or in the pure homopolymer, or within a micelle were different. This has practical as well as technological implications. The latter is related to the potential design of polymer membranes.

In another series of experiments we investigated the dynamics of polymer chains at the free surface of a polymer/polymer blend of polystyrene and poly vinyl methyl ether (PS/PVME) and or a nanocomposite for which PS/PVME is the host [12, 13]. These measurements were performed using the sophisticated technique, X-ray photon correlation spectroscopy (XPCS). We showed for the first time how the surface dynamics of a single component could be orders of magnitude faster than the same component in the bulk of the sample. This has implications toward understanding the interrelations between the surface dynamics, the structure and other properties.

Having developed strategies to tailor the spatial distribution of gold nanoparticles (Au-NPs) of different sizes within polystyrene (PS) thin, supported, film hosts, we demonstrated the connection between the spatial distribution of Au-NPs within the polymer film and the optical properties (i.e.: surface plasmon response) [14, 15]. The optical spectra of samples (surface plasmon) manifest features associated with differences between the size and interparticle spacings as well as the proximity and organization of nanoparticles at the substrate and free surface.

We also investigated a well know phenomenon that occurs in physical systems that include condensation, phase separation and coarsening in liquid/liquid mixtures, metal alloys etc. Parenthetically, symmetric BCPs self organize to form lamellar morphologies. Such BCPs form thin films on substrates, with free surfaces characterized by topographic structures of thickness

equal to the interlamellar spacing. We showed that these surface structures coarsen in a manner reminiscent of 2-dimensional phase ordering systems of binary alloys, where the growth is self-similar, governed by classical capillarity driven Ostwald ripening and coalescence mechanisms. The coarsening dynamics in BCP/nanoparticle thin films, the dynamics are considerably slower, and the mechanism of coarsening occurs predominantly via coalescence.

Our studies also involved the discovery and scientific explanation of the electrorheological behavior (this program provided partial support) of a specific new polymer/nanoparticle system [16-18]. It shows how the application of an electric field to the system, results in a significant increase in the mechanical strength, due to an electric field-induced change in the polarization of the system.

References (these represent publications resulting from support)

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Graduate Students (GS) and Post Docs (PD) who worked on the project (percent effort-%)

Abraham Arceo (visiting scholar, GS)	(2007- 40%)	Anton Li (GS)	(2012-16%)
Xi (Chelsea) Chen (GS)	(2008-16%, 2009-33%)	Carl McIntyre (PD)	(2010-25%, 2012-35%)
Peter Chung (GS)	(2011-16%, 2012-16%, 2013-35%)	Luciana Meli (PD)	(2007-31%)
*Emmanouil Glynos (PD)	(2008-75%, 2009-75%, 2010-15%, 2013-33%)	Hyun Joon Oh (GS)	(2007-13%, 2008-50%, 2009-15%)
Jenny Kim (GS)	('08-15%, '09-25%, 2010-50%, 2011-30%, 2012-25%)	*Aaron Tan (PD)	(2013- 40%)
Junnan Zhao (GS)	(2011-13%, 2012-50%, 2013-50%)	Jolie Wu (GS)	(2013-13%)
		Hengxi Yang (GS)	('09-50%, '10- 37%, 2011-25%, 2012-13%, 2013-21%)

- *Emmanouil Glynos: established our Asylum atomic force microscopy (AFM); AFM technique development and nanoscale mechanical property measurements; trained students to do AFM. Aaron Tan: established local dynamics and thermal transition temperature measurement using AFM. AFM played a critical role in most publications.

Undergraduates who worked on the project:

Alexander Sholtz – 13% (2013 – 2014); Jesse Tzeng – 12% (2010 – 2011); Sotirios Malamis – 20% (2012 – 2013); Ga Ram Jun – 20% (2009 – 2013). %=percent of time per 40 hour week.