

National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No.

M01-CL03

Competency: Materials

Hybrid Polymer Nanolayers for Surface Modification of Fibers

Project Team:

Leader: Igor Luzinov/Clemson University/Synthesis and Characterization of Thin Polymer Layers

Email: luzinov@clemson.edu Phone: 864-656-5958

Members: Richard V. Gregory/Clemson University/richar6@clemson.edu /Synthesis of Responsive Polymers

Stephen H. Foulger/Clemson University/foulger@clemson.edu/Polymer Responsive Systems

Vladimir V. Tsukruk/Iowa State University/vladimir@iastate.edu/Materials and Surface Science

Objective:

The ultimate goal of the proposed study is to develop fundamental and practical approaches that will enable us to create multifunctional responsive/adaptive fibers and textiles, which can change a number of specific properties in response to variation of environment or to application of some physical/chemical incentives.

It is necessary to emphasize that surface structure and behavior of fibers are of the utmost importance for the properties of fibers and textiles in processing and use, since friction, abrasion, wetting, adhesion, adsorption, and penetration phenomena are involved. In order to obtain textile materials with the desired performance, the fiber surface is often modified with polymer layers before use. However, further advances in industrial textiles impose requirements for the modification that are frequently in conflict: a given textile material, depending on the conditions under which it is utilized, has to be either hydrophobic or hydrophilic, acidic or basic, conductive or nonconductive, deliver or adsorb some species, etc. We believe that a tailored hybrid nanolayer consisting of polymers having diverse natures will allow the combination of several antipodal properties in one thin polymer film. Therefore, the project focuses on the *fabrication of hybrid polymer nanolayers on the surface of fibers and textiles, their characterization and understanding*. Attention also will be paid to the *relationships between the structure and properties of the layer and the performance* of the fibers and textiles.

Progress Statement:

It is clear that fine tuning of the properties of a particular fiber or textile material to its anticipated use requires the ability to regulate the morphology of the hybrid nanolayer. Indeed, several immiscible polymers constituting the sub-micron heterogeneous film can be organized in different manner on the fiber surface, and, consequently, the structure and properties of the hybrid coating made of the same components may be altered in a wide range. It is an important task to stabilize the morphology once the required properties of the hybrid nanolayer are reached. Thus, the elements of the coating have to be firmly attached to the surface; and the layer has to have only some definite degree of freedom to perform the required tasks. A number of commonly used methods of thin film preparation on substrates are created. It is necessary to highlight that grafting techniques have advantages over others in several ways [Y. Uyama, K. Kato and Y. Ikada, Surface Modification of Polymers by Grafting, Advances in Polymer Science, vol. 137, 1998, p.1.]. They include easy and controllable introduction of new polymer chains with a high surface density, precise localization of the chains at the surface, and long stability of the grafted layers, since covalent attachment of the macromolecules onto a polymer surface can avoid their delamination in liquid media. Thus, for successful building of the hybrid polymer layers, at least part of the coating is to be grafted to the fiber surface, namely a primary grafted layer is to be created.

It is necessary to stress that a primary grafted polymer layer consisting of several polymers can itself serve as a hybrid responsive/adaptive coating. In other strategies, it can be a decisive part of the heterogeneous nanolayer. Basically, this ultrathin grafted film will direct the formation of the very first monolayer of coating, which is in contact with the surface and be a guide for further coating organization. Therefore, the initial stage of the investigation was devoted to synthesis of the primary grafted polymer layer on the surface of the fibers. We have concentrated on the permanent grafting of thin polymer layers onto a substrate surface from the melt. It was found that poly(glycidylmethacrylate) (PGMA) could serve as an universal anchoring interlayer for attachment of

functional polymers and initiators of polymerization to the surface and ensured strong interaction between the grafted layer and substrate. We studied attachment of PGMA to various surfaces and found that the epoxy containing polymer layer could be deposited on polymeric (PET, polyethylene, silicon resin, nylon) and inorganic (silicon, glass, titanium, alumina, gold, silver) surfaces by adsorption or dip-coating (See Annual Report for details). We utilized the PGMA layer for the grafting of functionalized polymers to various substrates. For example, hydrophilic (poly(ethylene glycol, PEG)) and hydrophobic (polystyrene, PS) polymers were attached to PET, polyethylene and polysiloxane surfaces. Figures 1a and 1b show morphology and wettability of the PET surface modified with PS and PEG grafted layers. The scanning probe microscopy images revealed that the polymeric surface completely covered with the grafted layers and the polymer grafted dictated the surface properties of the polymer film. The obtained results suggested that polymers possessing functional groups could be indeed grafted to polymeric surfaces modified with the PGMA anchoring layer. PEG and PS were also successfully grafted to PET fiber and textile materials utilizing the proposed approach (Figure 2).

Hydrophobic PET surface. Polystyrene was grafted. Hydrophilic PET surface. Poly(ethylene glycol) was grafted.

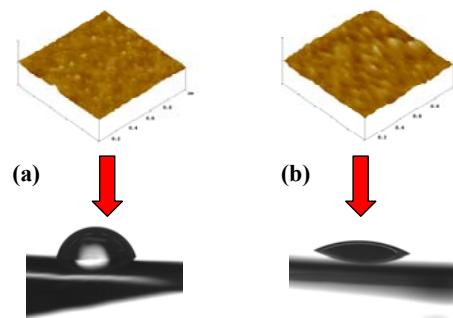


Figure 1. Scanning Probe Microscopy topography images (1x1 μm) and wettability measurements for PET surface modified with grafted layers.

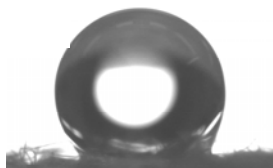


Figure 2. Droplet of water on the surface of PET fabric with grafted polystyrene layer.

We also used the PGMA layer to attach an initiator for Atom Transfer Radical Polymerization (ATRP) to the PET surface and conducted grafting of polymers initiated from the surface to synthesize the layers possessing high grafting density (See Annual Report for details).

The key characteristic of the “smart” materials is the ability to switch and/or tune the properties by applying external stimuli. An example of this type of smart material is a binary (hybrid) polymer grafted layer composed of two immiscible polymers, grafted to a substrate. Due to the phase segregation the morphology of the mixed polymer nanolayers is sensitive to the surrounding medium. Hybrid layers can be switched between different surface energetic states upon exposure to different temperatures, selective solvents, or other physical stimuli. For instance, the interaction of the binary polymer layer with a selective solvent will cause a change of the surface properties of the polymer film, since one of the two polymers preferentially occupies the surface layer. We report here on the surface morphologies and wettability of polymer coatings prepared from hybrid polymer layers of varying composition of grafted chains of polystyrene (PS) and poly(2-vinylpyridine) (PVP). This work was done in collaboration with Institute of Polymer Research Dresden, Germany (Dr. S. Minko and Dr. M. Stamm). The layers were synthesized by grafting of the polymers to epoxy modified surface. The wettability measurements clearly showed that a top layer of the binary brush switched from hydrophobic to a hydrophilic energetic state, upon exposure to selective solvents toluene and ethanol, respectively. When we exposed the sample to toluene, PS preferentially occupied the top of the layer, while after ethanol treatment the surface properties were dominated by PVP (Figure 3). The switching effect was also confirmed by Scanning Probe Microscopy. The morphology of the surface differs upon exposure to different solvents. Using PGMA as an anchoring interlayer we have synthesized a switchable polymer nanolayer on the surface of PET textile material. The

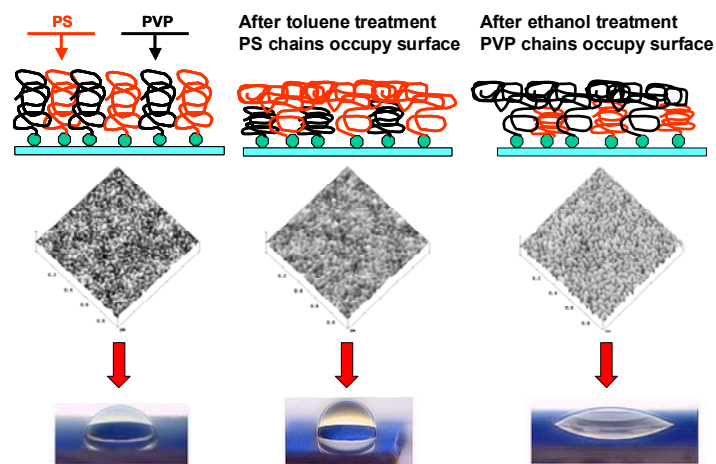


Figure 3. Scanning Probe Microscopy topography images (1x1 μm) and wettability measurements for hybrid polymer layers consisted of polystyrene and poly(2-vinylpyridine).

PET fabric changed the surface properties after being treated with different solvents (Figure 4). When the fabric was exposed to toluene, it became hydrophobic and water did not penetrate through the material. Conversely, water penetrated throughout the textile materials, if it was exposed to MEK. The wettability changes were reversible.

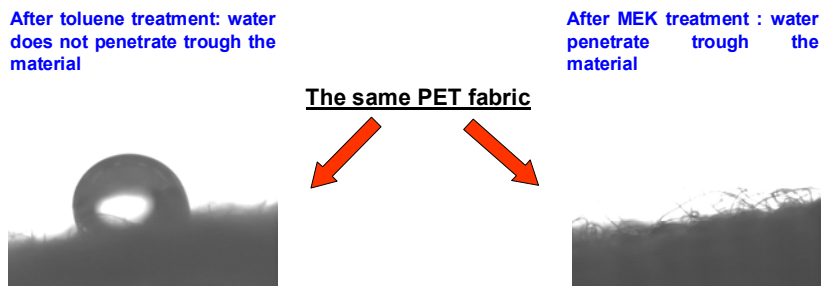


Figure 4. Wettability of PET fabrics covered with switchable polymer nanolayer after treatment with different solvents.

Next Year's Goals:

(1) Maintain development of the stimuli-sensitive grafted nanolayers. (2) Study deposition and self-organization of the polymer hybrid nanolayer on the surface of model substrates modified with the primary grafted layer. (3) Synthesize different binary and ternary hybrid nanolayers of various morphologies and compositions on fiber surface. (4) Conduct comprehensive characterization of the nanolayers produced. (5) Compare the nanolayer behavior on the model and fibrous substrates. (6) Establish structure-properties relationships for the hybrid nanolayers.

Approach:

At the third year of the present study we will focus on the generation and characterization of the responsive/adaptive hybrid nanolayers possessing different morphology and composition. The layers will be deposited on model and fiber surfaces. Recently we found that a primary grafted polymer layer consisting of several polymers can itself serve as a hybrid stimuli-sensitive coating. We will continue our efforts in this direction. The binary and ternary layers consisting of polymers of different nature will be grafted on the surface through PGMA monolayer. Color-tunable diacetylene based copolymers, conductive polythiophenes, thermoreversible polymer gels, stiff and rubbery polymers, hydrophobic and hydrophilic polymers with different functional groups will be considered as components of the grafted layers. In other strategies, we will first synthesize primary grafted layers that will be a template for the attachment of the stimuli-sensitive components of the heterogeneous coating. In this part of our investigation the focus will be on the self-organization of the hybrid layer on the surface of the model and fibrous substrates covered with the primary layer. During the third year of the study we will conduct a comprehensive study of microstructure, interfacial ordering and properties of the hybrid nanolayers produced from the stimuli-sensitive polymer systems. The morphology and level of heterogeneity of the covering will be correlated with the ability of the different components to perform their functions. Special attention will be paid to comparison of the nanolayer structure and performance on the model and fibrous substrates. The following questions will be addressed: What is the most effective way to generate the responsive/adaptive nanolayers? What are relationships between fabrication methods used and morphology/performance of the layers? How precisely may one regulate the morphology and switching properties of the hybrid coatings? What structural parameters of the layers are important to obtain well performing surface attached assemblies?

AFM, TEM, SEM, DSC, DMA, FTIR, XPS, Ellipsometry, and Contact Angle will be used to analyze the structure and functions of the primary grafted layer, hybrid nanolayer, and modified fiber and fabric. All of the necessary analysis and characterization equipment is readily available in laboratories at Clemson and Iowa State.

Outreach to Industry:

We had contacts with representatives of several companies (namely BMW, DuPont, Teijin, Contec, Andreas Co., and Milliken) regarding the new fibrous materials being developed. We will continue to survey fiber and industrial textile producers and users in order to develop a priority list of the needs and potential applications. The methods of surface modification of fibers and textile materials have been designed to be compatible with the equipment and technology that are used in modern textile industry for dyeing, finishing and coating.

New Resources Required:

No major equipment purchases are anticipated in Year 3 funding. It is planned to invite Dr. S. S. Minko (specialist in stimuli-sensitive polymeric systems) from Institute of Polymer Research Dresden, Germany to be a consultant for this project.