

## Hybrid Polymer Nanolayers for Surface Modification of Fibers

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Surface structure and behavior of fibers are of the utmost importance to textile properties during processing and use, since friction, abrasion, wetting, adhesion, adsorption and penetration phenomena are involved. To obtain a textile material with the desired performance, the fiber surface is often modified with polymer layers before use. In the future, however, many textiles will be required to change their characteristics during use, depending on their environment. The textile material may have to be hydrophobic at one point and hydrophilic at another, acidic or basic, conductive or nonconductive, deliver or adsorb some species, change color etc.

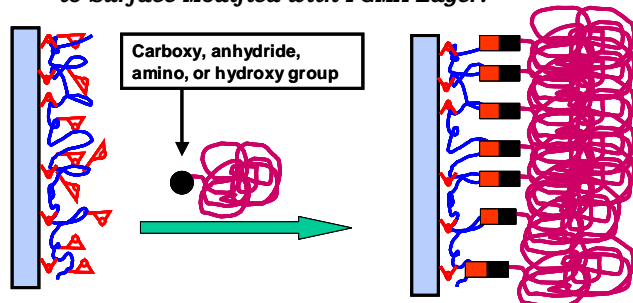
**We are developing ways to create multi-functional responsive/adaptive "smart" fibers by modifying their surface with hybrid polymer nanolayers.**

Our idea is to create "intelligent" hybrid polymeric coatings for fibers and textiles, which would demonstrate a number of specific functions. An effective means to build the covering is to combine in one coating several "intelligent" polymer systems. Then, every component of the nanostructured hybrid layer will play its specific role and support versatile behavior of the textile material.

### PGMA as a Universal Anchoring Interlayer

Poly(glycidylmethacrylate) [PGMA] could serve as a universal anchoring interlayer to attach functional polymers and initiators of polymerization to the substrate surface, thus ensuring a strong interaction between the grafted layer and substrate polymer. Initially we permanently grafted polymer layers onto the PGMA substrate surface in two steps (See Figure below). We chose PGMA with epoxy functionality, since epoxy groups can react with different functional groups (carboxy, hydroxy, amino and anhydride) that are often present or can be created on the surface of various fiber and textile materials. PGMA's epoxy groups of the polymer chemically anchor it to the fiber surface. PGMA's glycidylmethacrylate units located in the "loops" and "tails" sections of the attached macromolecules are not

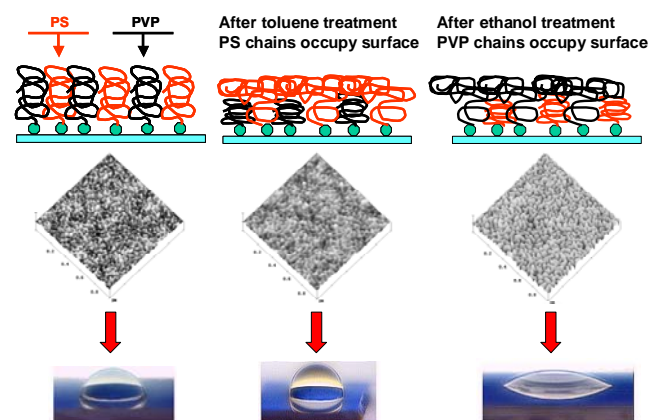
#### Grafting of Functionalized Polymers to Surface Modified with PGMA Layer.



connected to the fiber surface. Instead, these free groups serve as reactive sites for the subsequent attachment of polymerization initiators and/or polymer with functional groups, which exhibit an affinity for the epoxy modified surface. We found that an epoxy containing PGMA polymer layer could be permanently deposited on polymeric (PET, polyethylene, silicon resin, nylon) and inorganic (silicon, glass, titanium, alumina, gold, silver) surfaces by adsorption or dip-coating. Then, hydrophilic and/or hydrophobic polymers could be attached to the polymer (e.g. PET or polyethylene). Scanning probe microscopy images revealed a polymeric surface completely covered with grafted layers; the polymer that was grafted dictated the surface properties of the polymer film.

### Hybrid Polymer Nanolayers

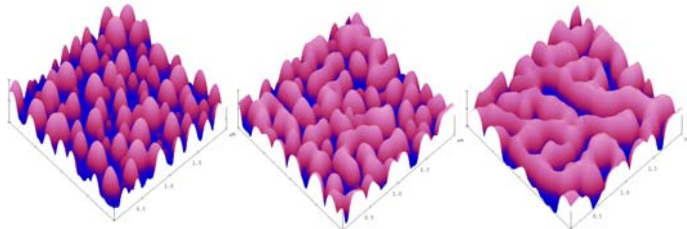
The key characteristic of the "smart" materials is the ability to switch and/or tune their properties in response to external stimuli. An example of this type of smart material is a binary (hybrid) polymer grafted layer composed of two immiscible polymers, grafted to a substrate. Due to the phase segregation, 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, polystyrene (PS) and poly(2-vinylpyridine) (PVP) polymer layers were grafted to the epoxy modified PMGA surface in collaboration with the Institute of Polymer Research (Dresden, Germany). The wettability measurements clearly showed that a top layer of the binary brush switched from hydrophobic to a hydrophilic energetic state, upon exposure to the solvents toluene and ethanol, respectively. When exposed to toluene, PS preferentially occupied the top layer; while after ethanol exposure, PVP dominated the surface (See Figure below).



Scanning Probe Microscopy Topographical Images and Wettability Measurements for Hybrid Polymer Layers of Polystyrene and Poly(2-vinylpyridine)

Using PGMA as an anchoring interlayer we also synthesized a switchable polymer nanolayer on the surface of a PET fabric which was hydrophobic after exposed to toluene, and hydrophilic after exposure to methyl ethyl ketone. The wettability changes were reversible.

We also used the PGMA layer to attach an initiator for Atom Transfer Radical Polymerization (ATRP) to the surface and conducted grafting of polymers initiated from the surface to synthesize the layers possessing high grafting density (See Figure below). We utilized the developed process for the synthesis of the hybrid nanolayers with phase segregation at different levels.



**Scanning Probe Microscopy Topographical Images of Nanolayers Precursors Possessing Different Morphologies. Samples Synthesized by ATRP. Image size = 1x1  $\mu$ m.**

**For Further Information:**

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4. I. Luzinov, V. V. Tsukruk, *Ultrathin Triblock Copolymer Films on Tailored Polymer Brushes*, *Macromolecules* **35**:5963 (2002).
5. D. Julthongpipit, Hyo-Sok Ahn, Doo-In Kim, V. V. Tsukruk, *Tribological Behavior of Grafted Polymer Gel Layer*, *Tribology Letters*, **13**(1):35 (2002).
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7. A. Sidorenko; D. Julthongpipit; I. Luzinov; V. V. Tsukruk *Oily Nanocoatings*, *Tribology Letters*, **12**:101 (2002).
8. I. Luzinov, V. V. Tsukruk, *AFM Study of Ultrathin Tri-block Copolymer Film on Tailored Grafted Polymer Layer*, *Proceedings of Annual Technical Conference - Society of Plastics Engineers* **60**( 2):1982, San Francisco (May 2002).
9. B. Zdyrko, V. Klep, I. Luzinov, *Surface Morphology of High Density Poly(ethylene Glycol) Brushes Grafted to Poly(glycidyl methacrylate) monolayers*, *Abstracts of Papers of The American Chemical Society* 224, 430-POLY, AUG 2002; *Polymer Preprints: ACS, Div Polym Chem*, **43**(2):785 (2002).

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