Surface Functionalization Techniques and Applications

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1. Fritzen, P, “The Role of Particle Functionalization in Coatings”, American Coatings Conference 2012, Indianapolis, IN


7. EP 2571943 A1, Functionalized Particles and Use Thereof”, Sachtleben Chemie GmbH


1. References


17. Jonschker, G., Et al, “Matched to the Medium”, *European Coatings Journal, 10/2008*


1. References

20. Thin Films: Polymer Composites Laboratory, 
   [http://nanocomposites.tamu.edu/LayerbyLayerAssembly/Index.php](http://nanocomposites.tamu.edu/LayerbyLayerAssembly/Index.php) (Jun. 2010)


26. Antifungal coating by biofunctionalized polyelectrolyte multilayered films, 


29. Wacker Chemie A.G., Product Brochure, Geniosil Organofunctional Silanes: “For Powerful Connections”
“God made the bulk; surfaces were invented by the devil”

--Wolfgang Pauli, 1945, Nobel Laureate in Physics
2.1 Applications: Particles

1. Energy efficient dispersibility of pigments and fillers

2. Enhanced stability (shelf life) of paints/coatings: Improve colloidal stability (Flocculation resistance) of particles w.r.t. Sedimentation, Diffusion and Viscous drag: Both in aqueous & non-aqueous systems

3. Enhanced cohesive strength of the coating film

4. Introduce cross-linking ability on the particles in the film → Improve mechanical/anticorrosive/resistance properties

5. Enhanced transparency of pigments in industrial/automotive and wood coatings
2.2 Applications: Substrates

1. Improve adhesion

2. Cross-linkability to the substrate

3. Enable Thin film coatings (Antireflective, Photochromic)

4. Super hydrophobicity / Super hydrophilicity

5. Antimicrobial properties

6. Anticorrosive properties

7. Special function coatings
3. Introduction: Surface Functionalization

**Definition**

- Technique of physico-chemical modification of a surface or interface at molecular level
- To bring about a change in the nature of its interaction with the surrounding matrix
- To enhance end use properties synergistically
3.1 Introduction: Surface Functionalization

Classical Examples

1. Phosphate/Chromate conversion pretreatment of metals

2. Plasma/Flame treatment of plastics to improve adhesion

3. Surface treatment of pigments/fillers: Silica/ alumina/ fatty acid/ Organic polyols/waxes

So, “What is new about Surface Functionalization?”
There is a overlapping region!!
3.2 Introduction: Surface Functionalization

Characteristics

1. Shift from Physical/Chemical Adsorption → Chemical Coupling

2. Use of specific reactive sites on the surface for chemical coupling

3. Thicker layers → Monomolecular Layers

4. Microparticles → Nanoparticles

5. Use of surface groups to initiate chemical reactions: Surface Initiated Polymerization (SIP)

6. Polymer Grafting: ‘To’, ‘Through’ and ‘From’ the surface → Polymer Brushes
3. 3 Introduction: Surface Functionalization

1. Polymer Brushes
2. Layer by Layer Deposition
3. Silane Coupling
4. Anti-Microbial Surfaces
Polymer Brushes on Particles & Flat Surfaces

Spherical Particles

Flat Surfaces

Source: http://www.cmu.edu/maty/images/4h-surfaces-1.jpg
## Polymer Brushes
### Comparison to Self Assembled Monolayers (SAM)

<table>
<thead>
<tr>
<th>SAM</th>
<th>Polymer Brushes</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Long chain organic molecules adsorbed on the surface</td>
<td>• Self assembled chemically tethered macro-monolayers</td>
</tr>
<tr>
<td>• Mechanically, chemically &amp; solvent fragile</td>
<td>• Mechanically &amp; solvent robust</td>
</tr>
<tr>
<td>• Tightly packed due to van der Waals forces</td>
<td>• Loss of entropy is overcome by high excluded volume</td>
</tr>
<tr>
<td>• Functional groups only on the surface (2D)</td>
<td>• Functionality is carried along the backbone (3D)</td>
</tr>
<tr>
<td>• Switchchability is difficult</td>
<td>• Switchable surfaces: Hydrophobic /- philic with pH</td>
</tr>
</tbody>
</table>

Source: Ref 5
Techniques of Grafting Brushes to Surfaces

Pre-formed polymer is coupled

Initiator is anchored to the surface

Macromonomer is reacted with unsaturation site

http://pubs.rsc.org/en/content/articlelanding/2014/py/c4py00007b#!divAbstract
Grafting Density vs. Brush Height

Higher the grafting density, the higher is the stretched brush height.

Silica filter modified with polymer brushes. Oil is unable to pass; while water passes through smoothly. Also for anti-fog applications.

https://engineering.purdue.edu/MSE/People/Faculty/jpyoungb/research3.html
4.5 Surface Initiated Polymerization (SIP-CRP) → “Click” Reaction

1. “Grafting From” the surface is the preferred technique providing high brush density

2. CRP technique like RAFT or ATRP is used: Control of chain length, block co-polymers

3. Initiator is anchored to the active sites on the surface

4. Sequential polymerization is carried out in the hetero-phase to grow the brushes

5. Post intra-brush modification by “Click Chemistry” is possible with UV or Sunlight
Surface Initiated Polymerization

Azo-Initiators

Aromatic Ketone Photoinitiators

Controlled Radical Initiators

RAFT

4.7 Applications of Polymer Brushes

1. Cross-linking sites on nanoparticles, fillers and pigments: TiO₂, BaSO₄, Silica, Clay

2. Improvement of adhesion of the substrates

3. Improvement of pigment wettability and dispersibility: Fillers for powder coatings

4. Long lasting deposition of biocides or enzyme inhibitors; Non bio-fouling surfaces

5. Switchable: Hydrophobicity ← → Hydrophobicity
5.1 Layer by Layer Film (LbL) Deposition: Principle (Ref: 18~24)

- **Definition:**
  - Sequential deposition of monolayers of macromolecules or nanoparticles on a substrate by alternating the charge on the incoming layer such that there is an adsorptive force for its spontaneous deposition.

- Typically, polyelectrolyte solutions have been used for this purpose.
- Positively charged substrate upon dipping attracts monolayer of the negatively charged macromolecules.
- The substrate is then rinsed to remove excess solution.
5.2 Layer by Layer Film (LbL) Deposition: Principle  
(Ref: 18~24)
5.3 Layer by Layer Film (LbL) Deposition: Principle
(Ref: 18~24)

• This is followed by dipping in the solution of positively charged macromolecules which is adsorbed due to the electrostatic attraction to the previous layer and a double polymeric layer is formed.

• In this manner, a number of bilayers can be deposited.

• The degree of order in such films is lower in comparison to the LB and SA films.

• However, the films are stronger and can be cast upon the substrate of any size and shape.

• Such films can be cast with thickness of 5 ~1000 nm with the precision of 1nm.
5.4 Layer by Layer Film (LbL) Deposition: Principle
(Ref: 18~24)

- Thick films $\rightarrow$ Thin films i.e Disorder $\rightarrow$ Order (At molecular level)
- Ordered structure at molecular level $\rightarrow$ Novel properties
- Langmuir-Blodgett Films (LB)
- The next major development happened in the 1980s: SA (Self assembled) coatings.
- Example of SA technique: octadecyltrichlorosilane molecule (its derivatives) used to coat silicon or gold surfaces. Different chemistries to tailor the end groups to provide good anchorage to the substrate.
- The van der Waals interaction among the side chains provides cohesion to the film.
- These SA layers are specific to silicon and gold surfaces and have short life due to oxidation.
### 5.6 Building Blocks for LbL Thin Films
(Ref: 18~24)

<table>
<thead>
<tr>
<th>No</th>
<th>Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polycations</td>
<td>Poly dimethyl diallyl ammonium chloride (PDDA)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Poly aniline (PANI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyvinyl pyridine (PVP)</td>
</tr>
<tr>
<td>2</td>
<td>Polyanions</td>
<td>Polystyrene sulfonate (PSS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyacrylic acid (PAA)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polyvinyl sulfonic acid (PVS)</td>
</tr>
<tr>
<td>3</td>
<td>Nanopolymers</td>
<td>Dendrimers (PAMAM)</td>
</tr>
<tr>
<td>4</td>
<td>Nanoparticles</td>
<td>TiO2, SiO2, CdS, CdSe, Exfoliated anionic and cationic clay platelets</td>
</tr>
<tr>
<td>5</td>
<td>Nanopores</td>
<td>Ceramic nanoparticles layers that form interstitial voids</td>
</tr>
<tr>
<td>6</td>
<td>Biomolecules</td>
<td>Proteins, lipids, gelatin</td>
</tr>
</tbody>
</table>
5.7 Layer by Layer Film (LbL) Deposition: Characterization (Ref: 18~24)

- QCM: Since the principal mechanism in formation of LbL films is adsorption, Quartz Crystal Microbalance is an indispensable tool in studying the kinetics of deposition.

- UV visible absorption spectroscopy is used to monitor the build-up of multilayers.

- FTIR is used to investigate hydrogen bonding between the layers.
5.8 Applications: LbL Deposition

(Ref: 18~24)

1. Super gas barrier coatings for packaging

2. Anti-flammable coatings for PU Foam

3. Electrochromic thin films on glass with High Contrast Ratio & High Switching Frequencies

4. Electrically conductive layers with Conductivity of the order of >2 S/cm.

5. Multifunctional Nanostructured Coatings: conformal, broad band antireflective, antifog, self cleaning and structured colour coatings.
5.8 Applications: (Ref: 18~24) 

LBL

1. Anti-flammable coatings for PU Foam
Silane Coupling

\[ R-(\text{CH}_2)_n \quad \text{Si} \quad X_3 \]

- **Organofunctional Group**
- **Linker**
- **Silicon atom**
- **Hydrolyzable Groups**

- **Monoalkoxysilane**
  \[ R \quad (\text{CH}_2)_n \quad \text{H}_3\text{C} \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{CH}_3 \quad X \quad X \quad X \]

- **Trialkoxysilane**
  \[ R \quad (\text{CH}_2)_n \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad X \quad X \quad X \quad X \]

- **Dipodal Silane**
  \[ R \quad (\text{CH}_2)_n \quad \text{Si} \quad (\text{CH}_2)_n \quad \text{Si} \quad X \quad X \quad X \quad X \]

Ref: 8, 9
Silane Coupling Reaction

Ref: 8,9
6.3 Features of Silane Coupling

1. Reaction takes place through hydrolysis and condensation

2. Reaction with inorganic hydroxyl groups very facile even at room temperature

3. Methoxy/ Ethoxy silanes are most commonly used

4. Functionalized density depends upon the OH group density, particle geometry, type of hydroxyl groups, hydrolytic stability of the silyl ethers

5. Can be used in non-aqueous as well as aqueous media

6. Silyl ether bonds are very stable to heat and chemicals
6.4 Applications of Silane Coupling

Improvement in

1. Adhesion
2. Mechanical properties
3. Dispersion
4. Cross-linking
5. Hydrophobicity

Silane Effectiveness on Inorganics

<table>
<thead>
<tr>
<th>SUBSTRATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXCELLENT</td>
</tr>
<tr>
<td>Silica</td>
</tr>
<tr>
<td>Quartz</td>
</tr>
<tr>
<td>Glass</td>
</tr>
<tr>
<td>Aluminum (AlO(OH))</td>
</tr>
<tr>
<td>Alumino-silicates (e.g. clays)</td>
</tr>
<tr>
<td>Silicon</td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>Tin (SnO)</td>
</tr>
<tr>
<td>Talc</td>
</tr>
<tr>
<td>Inorganic Oxides (e.g. Fe₂O₃, TiO₂, Cr₂O₃)</td>
</tr>
<tr>
<td>Steel, Iron</td>
</tr>
<tr>
<td>Asbestos</td>
</tr>
<tr>
<td>Nickel</td>
</tr>
<tr>
<td>Zinc</td>
</tr>
<tr>
<td>Lead</td>
</tr>
<tr>
<td>Marble, Chalk (CaCO₃)</td>
</tr>
<tr>
<td>Gypsum (CaSO₄)</td>
</tr>
<tr>
<td>Barytes (BaSO₄)</td>
</tr>
<tr>
<td>Graphite</td>
</tr>
<tr>
<td>Carbon Black</td>
</tr>
</tbody>
</table>

Ref: 8,9
6.5 “Alpha Effect” Silane Coupling

1. Conventionally propylene group as bridge between Si & -NH2 or -NCO
2. Replaced with “Methylene Bridge”
3. Electronic interaction between Si & N
4. High reactivity of alkoxy groups by 10X
5. Commercially available

Ref: 29
6.6 Applications: Functionalized Silica Particles

- Fait Accompli Technology
- Useful in 2-K Clear Coats: Auto & Wood
- 2~3 % addition enhances scratch hardness
- Easily dispersible

Gloss of 2-K Auto Clear: Crockmeter & hot reflow

Ref: 17
7. 1 Antimicrobial Surface Functionalization

- Surfaces support colonies and transmit bacteria, fungi, virus; thereby spreading diseases
- Frequently touched surfaces like door handles, railings, seats need to be sterile
- These can be molecularly modified to provide biocidal functionality
- These molecular layers are robust, long lasting and non-leaching
- Variety of chemistries are available towards this end
7.2 Antimicrobial Functionalization Techniques

Organosilanes

- These are silane couplers with long hydrophobic chains projecting outwards (~C8)
- These chains acts as swords and penetrate the cell membrane killing the microbes
- This piercing effect along with hydrophobization provides antimicrobial surface
7.3 Antimicrobial Functionalization

Quaternary Amino Silanes

- E.g. 3-Trimethoxy silyl propyl dimethyl octadecyl ammonium chloride
- Consist of three segments: Coupler group, N+ center, Hydrophobic Chain
- Coupler group enables permanent covalent bonding to the surface rich in OH Groups
- N+ Center attracts microbes as cell wall is negatively charged
- Hydrophobic group penetrates the cell wall
- Mechanism of kill: Piercing and electrocution
- Long lasting effect
7.4 Antimicrobial Functionalization

Antimicrobial Polypeptides (AMP)

- E.g. CGA 47-66: Chromofungin (Antifungal Peptide)
- Enzyme / Amino acid based biocides
- Completely non-toxic to mammals; eco friendly
- Can be deposited onto the surface by Ionic Sheath Deposition Technique
- Non-leaching
- Also function as degreasing agent: Anti-finger oil
- Can be added to the paints
- Long lasting efficacy
Antibacterial plastic surfaces: Bacterio-phages
Visit [www.coatingsys.com](http://www.coatingsys.com) to view this presentation

Thank you!