In-Situ formation of nanoparticles in polymers

1. No hazardous nanoparticle synthesis
2. Eliminates difficult polymer-nanoparticle mixing
3. Capable of fabricating hundreds of various nanoparticle polymer composites
4. Capable of producing large volumes of nanoparticle/polymer materials
5. Relatively inexpensive to other nanotechnologies

New Technology Platform
Nano Infusion Process

Is Independent of Initial Polymer Matrix
(Films and Resins)

Virgin Polymer

Evacuate
Vapor Infuse Precursor

Intermediate Polymer

Reagent-filled Nano-pores

Polymer Nano-Composite

Metal, Ceramic or Polymer Nanocomposite

Example: FEP + Cd(CH₃)₂ → FEP/Cd(CH₃)₂ → FEP/CdS

(Dimethyl Cadmium Precursor)

CdS Nanoparticle Composites

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Selected Examples: Can form Metal quantum dots using almost any metal precursor in the periodic table

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Conditions</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-chelate + MFA-Teflon</td>
<td>24 hrs. @ ~ 80°C</td>
<td>Pd in MFA</td>
</tr>
<tr>
<td>VOCl₃ + ECTFE-Halar</td>
<td>24 hrs. in air</td>
<td>V₂O₅/ECTFE</td>
</tr>
<tr>
<td>VOCl₃ + FEP-Teflon</td>
<td>24 hrs. in air</td>
<td>V₂O₅/FEP</td>
</tr>
<tr>
<td>TiCl₄ + FEP-Teflon</td>
<td>24 hrs. in air</td>
<td>TiO₂/FEP</td>
</tr>
<tr>
<td>TiCl₄ + PFA-Teflon</td>
<td>24 hrs. in air</td>
<td>TiO₂/PFA</td>
</tr>
<tr>
<td>W(CO)₆ + FEP-Teflon</td>
<td>2 hrs. UV in air</td>
<td>WO₃ &amp; WOₓFᵧ/FEP</td>
</tr>
<tr>
<td>Pyrrole + FEP-Teflon</td>
<td>24 hrs. in HNO₃</td>
<td>Polypyrrole/FEP</td>
</tr>
<tr>
<td>Chelate + Polypropylene</td>
<td>Hydrolyze &amp; Ag⁺</td>
<td>Ag-chelate/PP</td>
</tr>
</tbody>
</table>

A Wide Variety of Nano-scale Reinforcements can be Dispersed Throughout Polymer Matrices.
<table>
<thead>
<tr>
<th><strong>Synthesis</strong></th>
<th><strong>Structure-Property Relationships</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>▪ Non-Oxide Ceramics (e.g., Phosphides, Sulfides, Selenides)</td>
<td>▪ Size and Shape Effects</td>
</tr>
<tr>
<td>▪ Shape Control (e.g., platelets &amp; whiskers)</td>
<td>▪ Particle Loading Effects</td>
</tr>
<tr>
<td>▪ Magnetic Particles (carbonyl iron, maghemite (γ-Fe₂O₃ &amp; ferrites)</td>
<td>▪ Matrix Effects (Fluoropolymers, Hi-Temp Thermoplastics &amp; elastomers)</td>
</tr>
<tr>
<td></td>
<td>▪ Matrix Re-melt Effects</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Processing Aspects</strong></th>
<th><strong>Polymer/Nano Composite Effects</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>▪ Macromolecular Structure Processing</td>
<td>▪ Multifunctional Materials</td>
</tr>
<tr>
<td>▪ Combined Plasma/Infusion Processing</td>
<td>▪ Enhanced Thermal and Mechanical Prop.</td>
</tr>
<tr>
<td>▪ Post Processing</td>
<td>▪ Sensors</td>
</tr>
<tr>
<td>▪ High Loading Processing (&gt; 10%)</td>
<td>▪ Optical Band Gap Engineering</td>
</tr>
<tr>
<td></td>
<td>▪ Composites Having Catalytic Properties</td>
</tr>
</tbody>
</table>

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Polymer Matrix Flexibility

10nm Pd Nanoparticles in FEP Fluoropolymer

10nm Pd Nanoparticles in PEEK

TiO₂ whiskers form Interpenetrating network in FEP
Infusion, Plasma, Polymer Film Treatment
Deposition Capabilities

1. Polymer films (60 inch reel to reel)
2. Polymer Resins (50 lbs per infusion)
3. Plasma and Infusion of Ceramic and Polymer Components
4. AGL 6400 advanced adhesive lamination and sublimation
Nano Infusion Technology Platform

Advanced Polymer Composites
1. Enhanced Thermal and Mechanical Properties
2. Inexpensive POSS alternative
3. Self-Healing
4. Advanced Interface Control
   - Adhesion
   - Foul Release

Photonics and Spintronics Based Sensors
1. Environmental
2. Biomedical
3. Chem-Bio
4. Catalytic Materials

Optical Band Gap Engineering
1. Controlled Optical Wavelength filters
2. Electromagnetic Radiation Absorbers and Converters
   - Protection and Optimization of Algae growth
   - Solar Cell Protection
   - Outer Space protective coatings

Novel Coating Systems
1. Corrosion control coatings
   - Nanoparticles with enhanced redox properties
2. Non-Toxic Marine Bioactive coatings
   - Nano Infusion and Sol-Gels

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Advanced Polymer Composites

Infused Nano-TiO₂ Enhances Mechanical and Thermal Strength of Polymers

Polyimide Tg (Glass Transition Temperature) (With and Without Nanoinfusion)

Polyimide Wear Performance at 700F (With and Without Nanoinfusion)

TiCl₄-infused film in air  →  TiO₂ nano PMC in bulk + TiO₂-rich surface

Analysis of Polyimide after infusion of TiO₂ demonstrated a Tg increase of 15°C and a Mechanical Wear Performance Increase of 70%
Nano Infusion Can Utilize Self-Assembly Design Concepts to Control Interface and Bulk Polymer Reactivity Via 3-D Interconnected Quantum Dot and Siloxane Networks.

Surface and Bulk sites comprised of organo-siloxane functionalized (e.g., amines, epoxides, isocyanates, vinyls) networks for advanced control of adhesion and release characteristics.

**Demonstrated Applications**
- Enhanced Interfacial Adhesion
- Water/Stain Repellence
- Dyeing of Polymers
- Anti-Microbial Properties
- UV Shielding
- Gas Permeation Properties

**Selected Previous Programs:**
1. Synthetic Multifunctional Materials
   - MDA972-02-C-0006
   - Electro-optical
   - Mechanical
2. Phonon Transport in Polymer Nano-composites
   - MDA972-02-C-0039

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Advanced Polymer Composites

Molecular Grafting of Materials
via
Nano-Infusion Technology

Chelation of Dyes, Sensor Molecules, Polymers, Coatings, etc. to Polymers Via Interpenetrating Networks of Infused Organosilanes

Graft or co-polymerizations to introduce reactive groups suffer from surface energetic problem (ie: reactive groups are buried in the bulk)

Infusion introduces reactive groups into the free volume

Eg. 1. Infusion of EDA: Acid dyeable – electrostatic
2. Infusion of SiCl₄ or TEOS: Base dyeable – electrostatic
3. Infusion of GOPS: Acid or base dyeable - covalent

Anti-Microbial Polymers

Infusion of Ethylenediamine, Diethylenetriamine or Ligand-bearing Organosilanes

Exposure to Metal Ion Solution (Ag, Zn or Cu)

Ligated Metal POLYMER

Top 2 -10 Microns

\[ M^+ + L \rightleftharpoons ML^+ \quad K_f = 10^7 - 10^{28} \]

Controlled Release of M⁺ Regulated by \( K_f \)

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# Synthesis of Nano-metallic Quantum Dot Polymer Films for Sensors and Catalysts

**Infusion Agent**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd^{2+} (C_5H_7O_2)_2</td>
<td>Pd^0 + Organic Residue</td>
</tr>
<tr>
<td>Ag^{+1} (CF_3COCHCOCF_3)(C_8H_18Si)</td>
<td>Ag^0 + Organic Residue</td>
</tr>
<tr>
<td>(CH_3)_2Au^{+3} (CF_3COCHCOCH_3)</td>
<td>Au^0 + Organic Residue</td>
</tr>
<tr>
<td>Fe (CO)_5</td>
<td>Fe^0 + 5CO</td>
</tr>
<tr>
<td>Ni (CO)_5</td>
<td>Ni^0 + 5CO</td>
</tr>
</tbody>
</table>

*A Wide Range of Inorganic and Organo-Metallic Compounds are Now Readily Available for Infusion Synthesis*

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Reversible Nano Au based Ozone Sensor

Infusion fabricated Nano-Au fluoropolymer film demonstrates
1. Red shift in Ozone environment
2. Blue shift back to original spectral character after removal from ozone

Super-Ionic Nano Composites

Infusion fabricated Nano Ag/I fluoropolymer films demonstrate
1. Ion Conductivity
2. Reversible Color change control

Super-Ionic Nano Polymer Film Composites

Percolated Metallic Nano-Composites layers can be converted in-situ into Percolated Superionic Nano-Crystal Layers
Nanoparticles change the absorption characteristics and are easily broken down to yield a surface plasma when exposed to energetic laser pulses.

Pd mp = 1,550°C; ΔHf = 38.6 cal/g  
Ag mp = 961°C; ΔHf = 25 cal/g  
Au mp = 1,063°C; ΔHf = 15.3 cal/g

In all cases the laser pulse duration was ~10 ns. For the Pd and Ag infused films, the pulse fluence was ~100 mJ/cm². The frequency doubled wavelength was used for the Au infused film to provide absorption.

EXAMPLES

1. $V_2O_5$ in FEP 1mm resin beads
   - Effectively Converts $SO_2$ to $SO_3$ ($H_2SO_4$) @ RT

2. Pd (.84% by weight in 10 mil FEP and PP film)
   - Decreases $O_2$ transport by 2 orders of magnitude due to conversion of $O_2$ to $H_2O$ in the presence of $H_2$ concentration in air

3. TiO$_2$ in Polymer + UV or
   - Converts Styrene monomer into polystyrene within free volume of the FEP with subsequent increase by 1 order of magnitude in $O_2$ transport.
   - (Self-Healing??)

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Optical Band Gap Engineering


Note: Projected Spectra Based on Experimental Results to Date

CdS nanoparticle infused Fluoropolymer films and resins exposed to Ultraviolet radiation (Emission ~ 550nm)
Optical Band Gap Engineering

(Radiation Protective Films)

Technology Platform allows us to protect Substrates from selected radiation by conversion to radiation that can be harvested for:

1. Algae Ponds
2. Solar Cells
3. Outer Space Protective Coatings

Al oxide nano dots
Convert UV energy
To 520-580nm visible

< 400nm

520-580nm

PbS nano dots
Convert IR energy
to broadband visible

3-5um

> 500nm
Enhanced Barrier Properties
Novel Membranes

Infused IPN of V₂O₅ or TiO₂ can be used to catalyze the polymerization of Polymer monomers within the free volume of the polymer.

This can result in unique ion or gas selective membranes.

Infused Pd-ETFE Powder
Optically Absorbing - Electrically Conductive Resin

The high surface area and low bulk density of commercial electrostatic grade fluoropolymer powders make them ideally suited for infusion processing.

Percolated Nano Dots for Ionic, Electronic, or Thermal Conduction

Tungsten Oxide (Iionically Conductive)

Percolated Pd Nano dots Electrically Conductive

Pd nanostructure is preserved through industrial-scale (melt) processing - uniformly dispersed, un-agglomerated and nano.
Nano-Infusion into CNT’s and CNF’s

A: SEM

Applications include the ability to form polymer/carbon composites

1. Crosslinkers for enhancing polymer composite strength
2. Crosslinkers for achieving bondability to other materials
3. Catalysts for enhancing corrosion resistance
4. Catalysts for active surfaces that resist fouling

B: Backscattered image

Au nanoparticle coated CNT’s

SEM of CNT’s With Nanoinfused Fe coating

Backscattered Electron Image of CNT’s With Nanoinfused Fe coating

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CeO CNT’s for anti-corrosion

Figure 1.2: MIL-PRF-23377 Polyurethane Topcoat with ca 1% CNT loading

Figure 1.3: Acrylic Pressure Sensitive Adhesive w/ 3% CNT loading
Surface resistance = $10^4$ ohms cm$^{-2}$

Figure 1.4: MIL-PRF-23377 Polyurethane Topcoat with ca 1% CNT loading
Spray coated onto Aluminum Plate

Conventional Carbon Nanofiber Dispersion

Boyce Components Carbon Nanofiber Dispersion
Standard Epoxy Primer, MIL-PRF-85582D TY 1 CL 2 mixed with 1% and 2% Ce oxide nanoparticle coated CNT’s

EDX analysis of Carbon Nanofibers with CeO Nanoparticle Coating

1% scribed no corrosion 5000hrs Salt Fog

2% scribed no corrosion 5000hrs Salt Fog

2% CeO loading
Bio-active Marine Anti-fouling Coatings via Nanoinfusion and Sol Gel Technology

Reagents in Seawater Can Be Used to Generate an Anti-Fouling Surface

\[ 0.5 \text{ M } \text{Cl}^- + 0.2-50 \mu\text{M} \text{ H}_2\text{O}_2 \text{ (in marine organisms)} \rightarrow \text{HOCl, HOBr, HOI} \]

Up to 50 \mu M produced by biofilm


Hybrid Xerogel Structure

- Bulk Crosslinked Porous Structure
- Inexpensive
- Optically transparent
- Physically entrap a dopant
- Improve dopant long-term stability
- Mechanically stable with tailored surface energies

Goal: “Active” coating with “ideal” critical surface tension. “Active” components provide anti-fouling characteristics; critical surface tension, foul release
TECHNICAL APPROACH

1) Xerogel coatings derived from Sol-gel Process

**Hydrolysis**

\[ \equiv \text{Si-OR} + \text{H}_2\text{O} \rightleftharpoons \equiv \text{Si-OH} + \text{HOR} \]

**Alcohol Condensation**

\[ \equiv \text{Si-OR} + \text{HO-Si} \rightleftharpoons \equiv \text{Si-O-Si} \equiv + \text{ROH} \]

**Water Condensation**

\[ \equiv \text{Si-OH} + \text{HO-Si} \rightleftharpoons \equiv \text{Si-O-Si} \equiv + \text{H}_2\text{O} \]

2) organochalcogen catalyst

0.5 M Cl\(^-\) + 0.2-50 µM Te- or Se-enzyme

1 mM Br\(^-\) + H\(_2\)O\(_2\)

\[ \text{Te- or Se-enzyme} \rightarrow \text{HOCI} \]

\[ \text{HOBr} \]
Mechanistically, the CeO$_2$ nanoparticles behave similarly to Te and Se catalysts previously shown to work for this application:

1. Peroxide adds to a vacant site

2. Halide attack generates the hypohalous acid (the formal oxidative step)

3. Loss of hydroxide reestablishes the ceria crystal lattice, which can then reenter the catalytic cycle.
New Platform Technology for Fabricating Advanced Multi-functional Materials

**Infusion Technology**
- Nano-Scale
- Novel Nano Effects
- Low Loadings (<10% vol)
- 3D Microstructures
- Evolving Technique
- Optical, Thermal, Mechanical
- Ionic Transport Effects

**Resin Compounding**
- Micro-Scale
- Classical Blending Effects
- High Loadings (up to ~30%)
- Blended Microstructures
- Time-Tested Approach
- Optical, IR & RAM

Infusion and Compounding are Complementary Approaches to Property Modification

Today, there is no Existing Database for Fluoropolymer-Based Composites.

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