Nanotechnology Applications for Green Manufacturing

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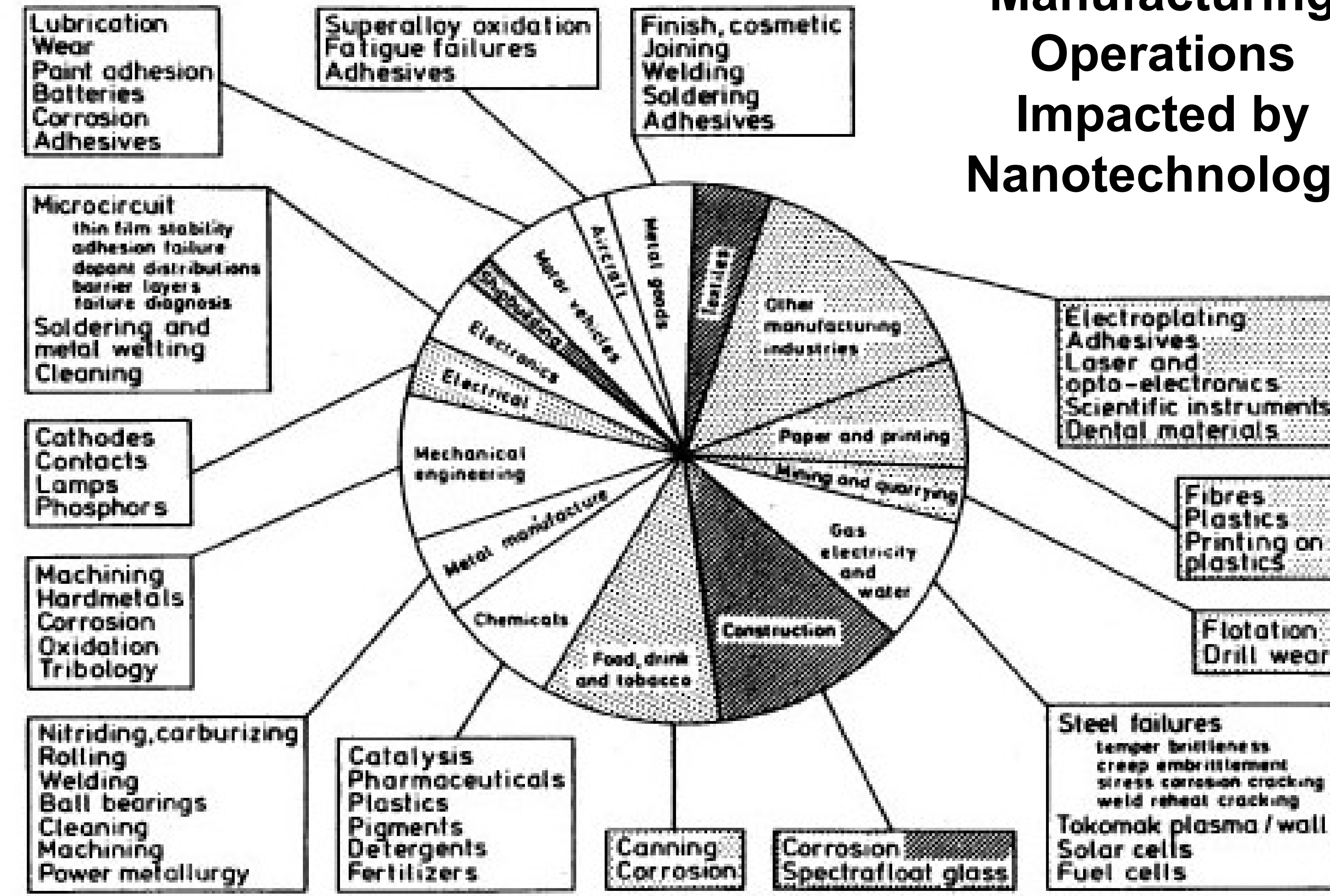
Manufacturing (def.)

- **The conversion of materials and energy into useful products through a designed process utilizing a combination of chemical, biological and mechanical processes…**
- **…(green manufacturing) at the same time reducing waste, minimizing pollution, protecting human health and the environment.**
- **Nanotechnology can enable the transition.**

Nanotechnology Elements

- Morphologies
  - Nanoparticles (amorphous or crystalline)
  - Nanotubes
  - Nanoplatelets
  - Nanolayers (monolayers)
- Physical and Chemical Properties
  - Small number of atoms
  - High surface area
  - Surface activity and reactivity
  - Size dependent optical, electronic and chemical properties
- Self-Assemble
  - Respond to electrostatic, hydrogen bond, polar, hydrophilic, hydrophobic forces

Manufacturing Operations Impacted by Nanotechnology



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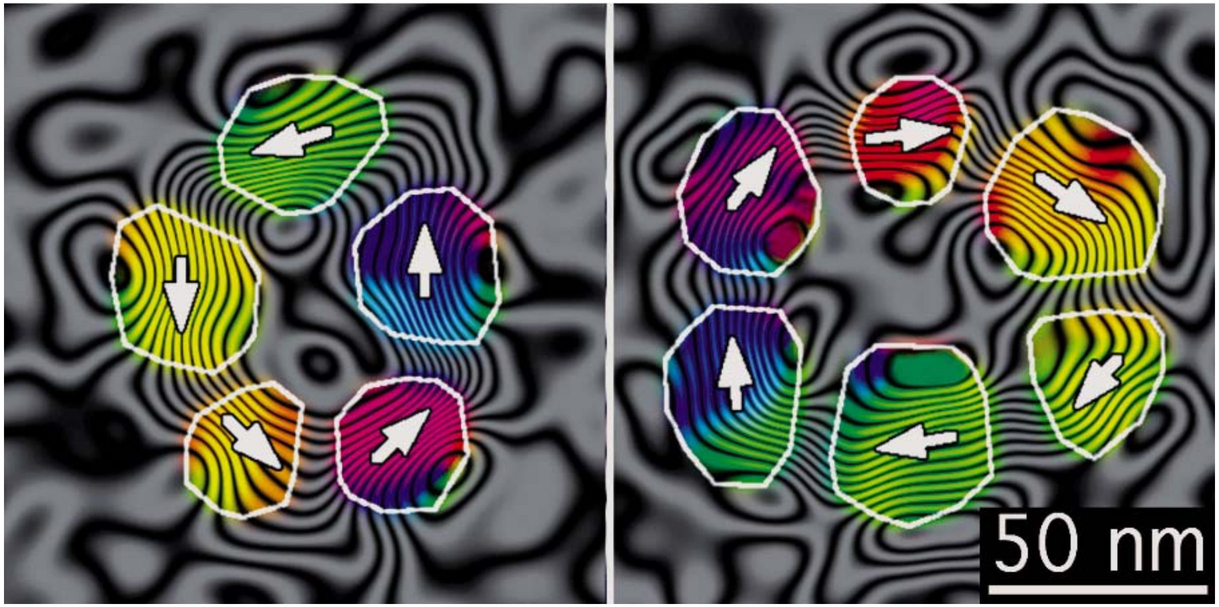
e.g. Microelectronics

- **Currently a ‘top-down’ lithographic approach**
- **Large amounts of hazardous materials and resources**
- **Part Integration and toxic components prevent recycling**
  - **32 MB microchip**
    - **Requires 1.7kg of fossil fuel and 32 kg of water***
- **‘Bottom-up’ nanotechnology approaches can replace current chip production methods**
  - **Lithography**
  - **Nanoparticle**
  - **Self-assembly**

**Environ.Sci.Tech.,36, 55-4-5510 (2004)*

Nonvolatile Computer Memory Through Self Assembly



Cobalt nanoparticles form rings from nanoparticles which link up and self-assemble into rings. The magnetic dipoles responsible for nanoring formation also produce a collective magnetic flux within the rings themselves, stemming from the magnetic poles each particle possesses. But after the particles form rings, the net magnetic effect is zero outside. The researchers developed conditions leading to the self-assembly of the cobalt nanorings and were able to observe directly the flux-closure states, which are stable at room temperature.

---Wei , Tripp and Dunin-Borkowski (Purdue-Cambridge) November 2003 Angewandte Chemie.

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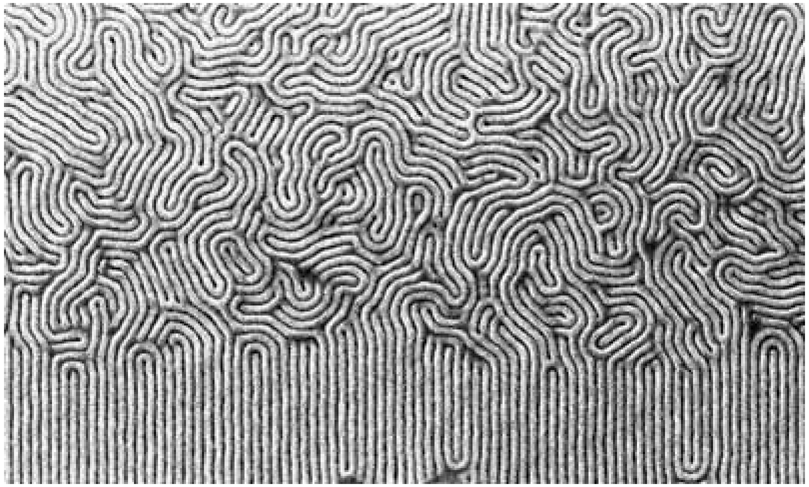
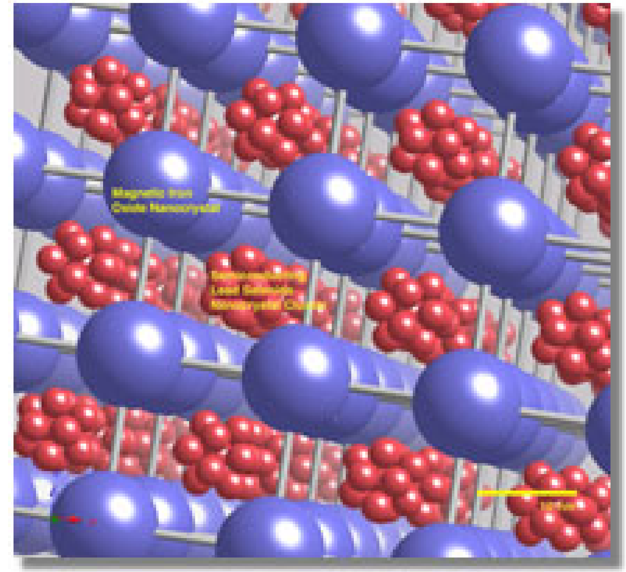
Epitaxial self-assembly of block copolymers on lithographically defined nanopatterned substrates



- **Manufacturing microelectronics through manipulating block copolymers to form into desirable patterns – e.g. parallel lines.**
- **Lithography used to create patterns in the surface chemistry of a polymer.**
- **The block copolymers on the surface arranged themselves into the underlying pattern without imperfections.**

---Neeley, dePablo and Stoykovich, Nature, July 24, 2003

Self-assembled 3D Designer Material



- **Precision chemistry methods developed to alter nanoparticles sizes in increments of less than one nanometer and varying in size by less than 5%**
- **Tailor the experimental conditions so the particles would self-assemble themselves into repeating 3-D crystal strctures.**
- **To produce multiconstituent structures**
  - **iron oxide particles 11 nanometers in diameter**
  - **lead selenide particles 6 nanometers in diameter**
  - **~60,000 atoms in one of the iron oxide nanoparticles and ~3,000 atoms in the lead selenide particles.**

- **---*Redl, Cho et al., Nature, June 26, 2004 (Columbia, IBM and U NewOrleans)***

Enzyme "Ink" For Nanomanufacturing

- **An enzyme ‘DNase I’ was the ‘ink’ in a process called dip-pen nanolithography -- a technique for etching or writing at the nanoscale level.**
- **The dip-pen allowed them to inscribe precise stripes of DNase I ink on a gold plate, which they had previously coated with a thick forest of short DNA strands. The stripes of the enzyme were 100 nanometers wide**
- **The enzyme was activated with a magnesium-containing solution to allow it to efficiently breaks down DNA in its path.**
- **The stripes of activated enzyme carved out 400 nm-wide "troughs" in the DNA coating.**
- ***---Chilkoti, J. Amer. Chem. Soc., May 2004, (Duke U)***

e.g. Structural Polymer Composites

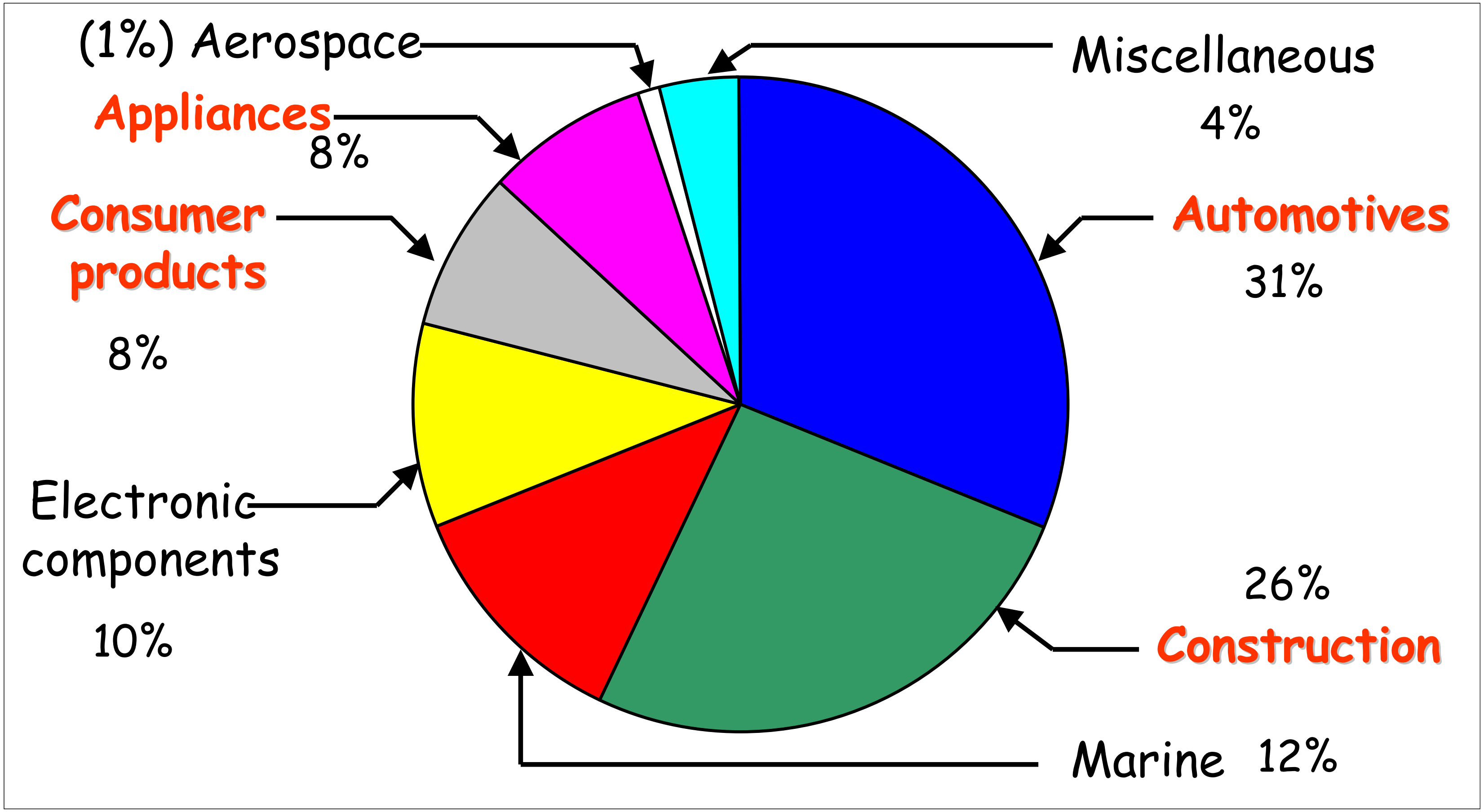
- **Currently utilizes petroleum based materials**
- **Energy intensive processing methods**
- **Significant VOCs**
- **Large amounts of hazardous materials and resources for fabrication and surface preparation**
- **Limited recycle, reuse capacity**

- **Biobased polymers have less than useful mechanical properties that can be improved by the addition of nanoparticles (nanoreinforcements)**
- **Nanoreinforcements can add multifunctionality to polymers through small additions of these nanoparticles.**

**Environ.Sci.Tech.,36, 55-4-5510 (2004)*

Fiber Reinforced Plastic Composites Usage in 2003 - 2.5 x 10^9 lb

(Plast. News Aug. 2003)



Glass used in 95% of cases to reinforce thermoplastics/thermosetting composite

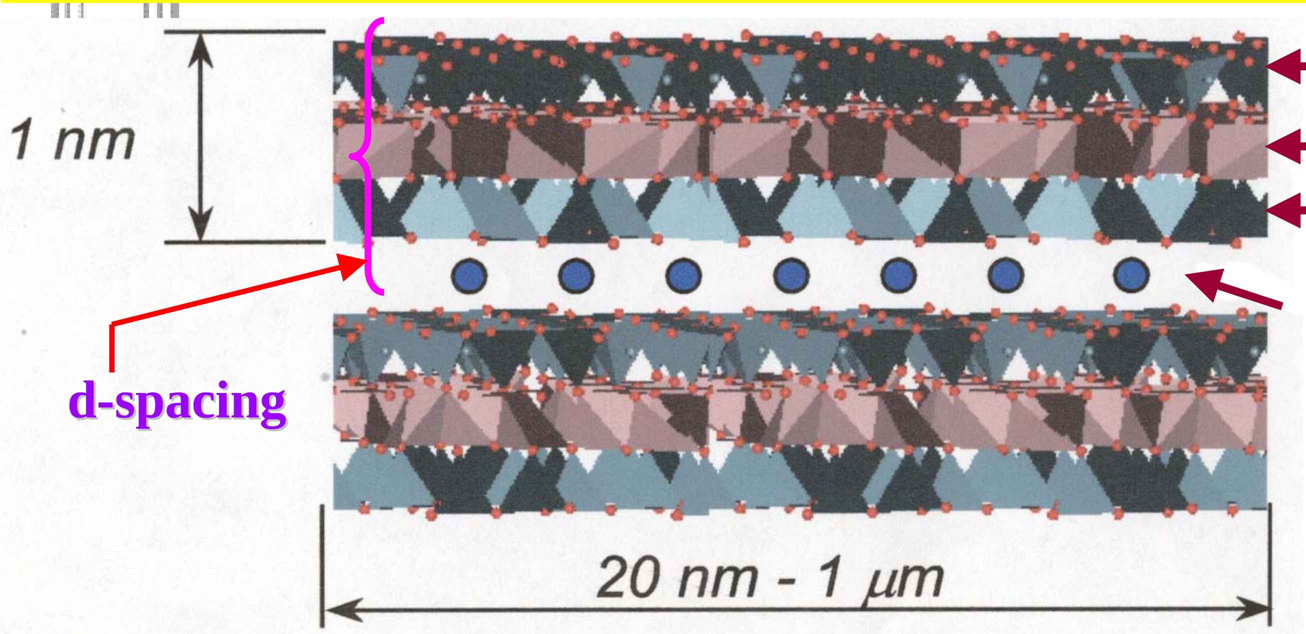
Potential Polymer and Composite Property Modifications resulting from Use of Nanoreinforcements

- Mechanical-Structural
  - High Stiffness, High Strength, Toughness, Low Density
- Electrical
  - Conductor, Semi-conductor, Insulator
    - ES charge dissipation, ES painting, EMI shielding, sensors, smart materials, antenna
- Thermal
  - Conductor, Insulator
    - CTE, Thermal Conductivity
- Barrier
  - Chemical, Biological, Flammability

Nanoreinforcement Multifunctionality

	Exfoliated Clay	*Carbon Nanotube VGCF*	*Exfoliated h-BN BN Nanotubes*	*Cellulose Nanowhisker*	*Graphite NanoPlatelets*
PHYSICAL STRUCTURE	Platelet ~1nm x 100nm	Cylinder NT ~1nm X 100nm VGCF ~20nm X 100um	Layer	Needle-Whisker	Platelet ~1nm X 100nm
CHEMICAL STRUCTURE	SiO_2, Al_2O_3, MgO, K_2O, Fe_2O_3	Graphene (chair, zigzag, chiral)	Boron Nitride	Cellulose	Graphene
INTERACTIONS	Hydrogen bond Dipole-Dipole	π - π	Hydrogen bond	Hydrogen Bond	π - π
TENSILE MODULUS	0.17 TPa	NT 1.0-1.7 TPa VGCF 0.25-0.5 TPa	~1 TPa	~ 130 GPa	~1.0 TPa
TENSILE STRENGTH	~1 GPa	(NT 180 GPa) VGCF 3-7 GPa	?	10 GPa	~(10-20 GPa)
ELECTRICAL RESISTIVITY	$10^{10} – 10^{16}$ Ω cm	NT ~ 50 x 10^{-6} Ω cm VGCF 5-100 x 10^{-3} Ω cm	insulator	$10^{10} – 10^{16}$ Ω cm	~ 50 x 10^{-6} Ω cm ‖ ~ 1 Ω cm ⊥
THERMAL CONDUCTIVITY	6.7 x 10^{-1} W/m K	3000 W/m K (NT) 20-2000 W/m K (VGCF)	conductor	insulator	3000 W/m K) ‖ 6 W/m K ⊥
COEF. THERMAL EXP.	8 – 16 x 10^{-6}	-1 x 10^{-6}	~1 x 10^{-6}	8 – 16 x 10^{-6}	-1 x 10^{-6} ‖ 29 x 10^{-6} ⊥
DENSITY	2.8 – 3.0 g/cm^3	NT 1.2 – 1.4 g/cm^3 VGCF 1.8-2.1 g/cm^3	~2.0 g/cm^3	1.2 g/cm^3	~2.0 g/cm^3

Clay and Organically Modified NanoClay

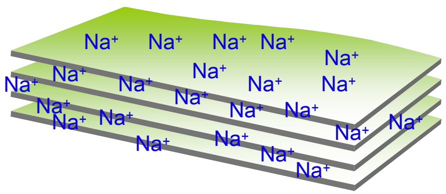


Tetrahedra SiO_4

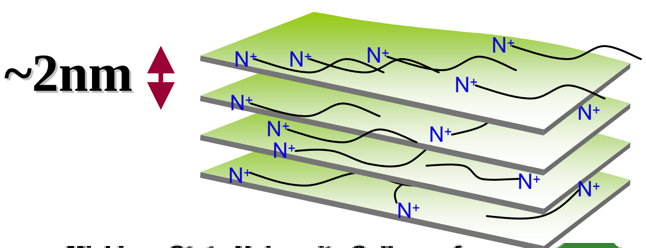
Octahedra AlO_6

Tetrahedra SiO_4

Solvated counter-ions: Na^+, Li^+, Ca^{2+}



Na^+-Montmorillonite + Organic modifier



Modified organophilic clay ⇦ Modification by 4^0 ammonium

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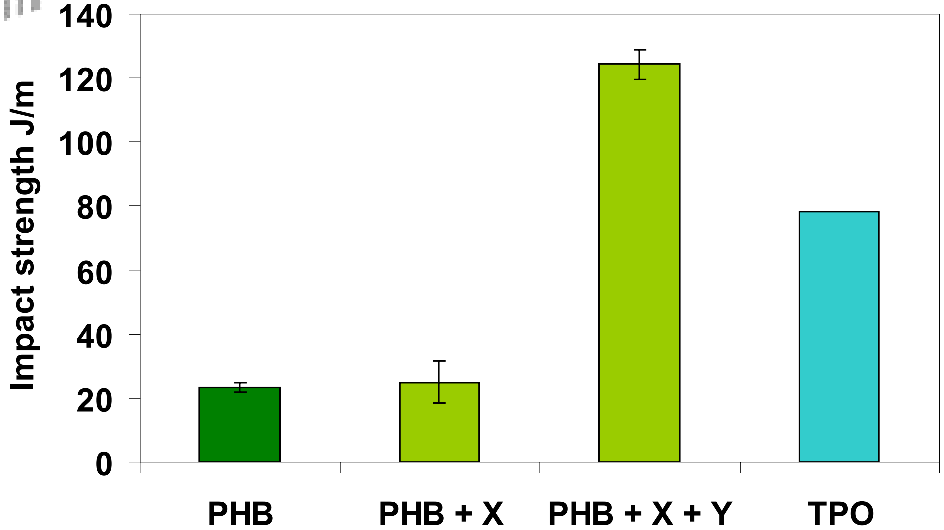
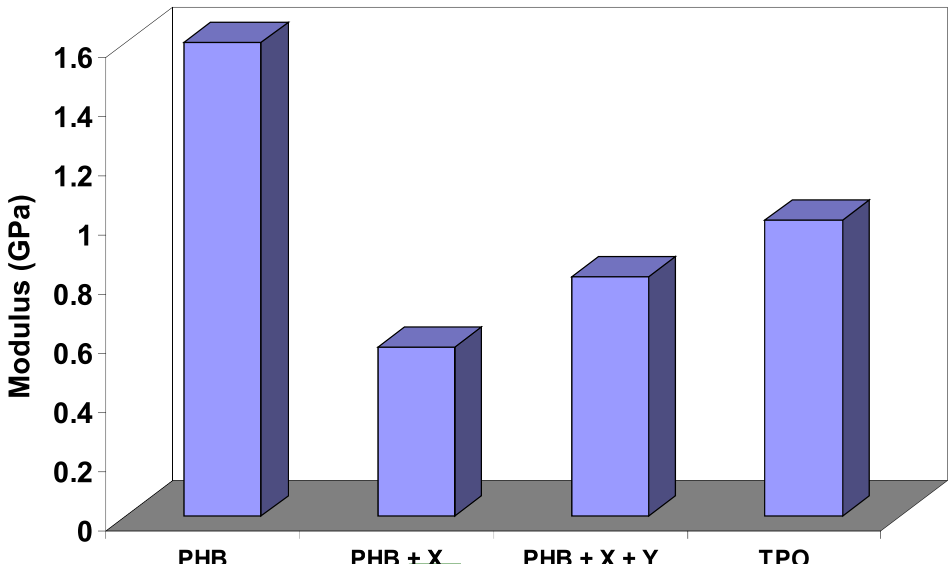
Nanoclay Improves Properties of PHB to be competitive with TPO



Addition on nanoclay improves the impact strength by 440% (even more than TPO)



The modulus of PHB modified (~TPO) by addition of nanoclay

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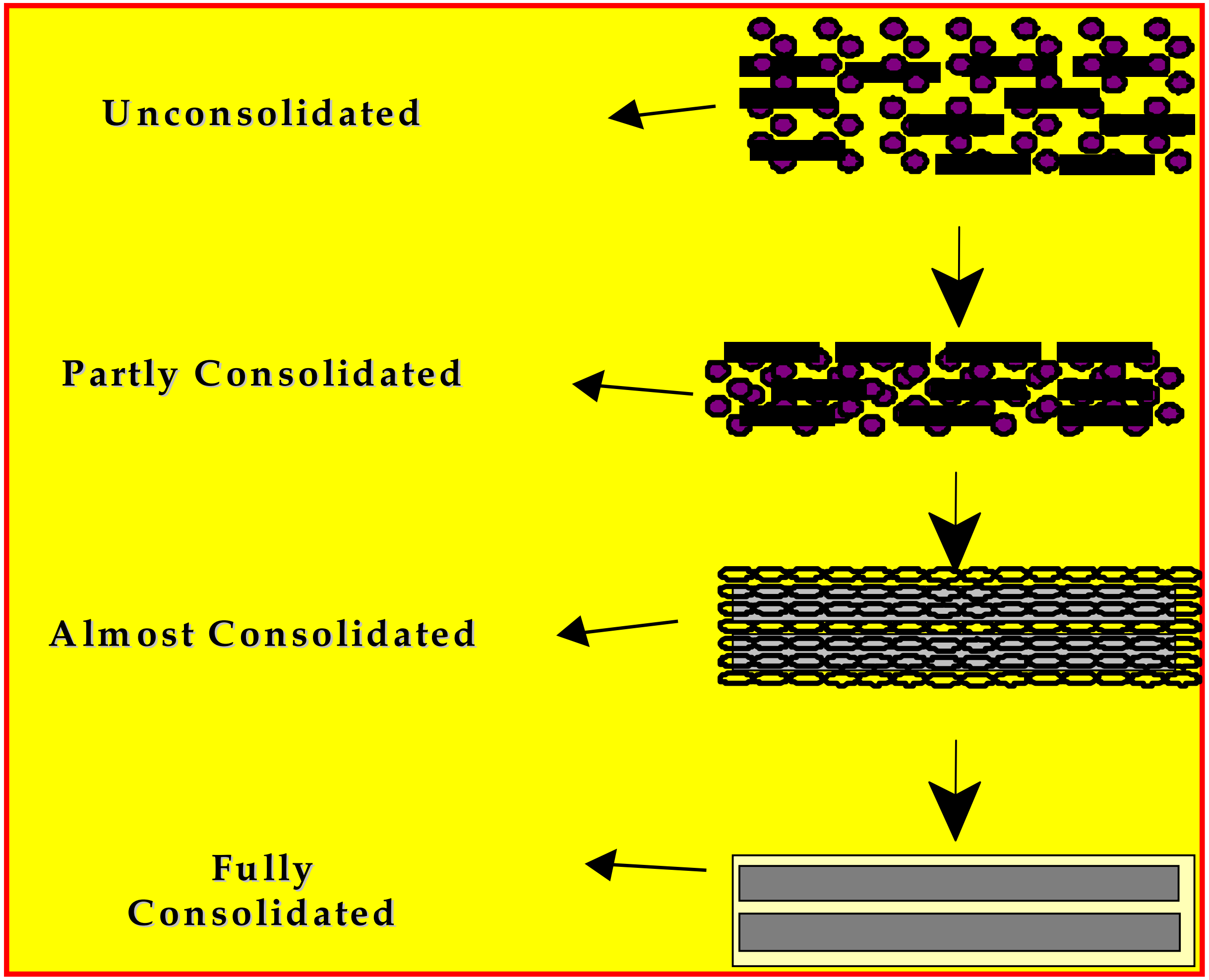
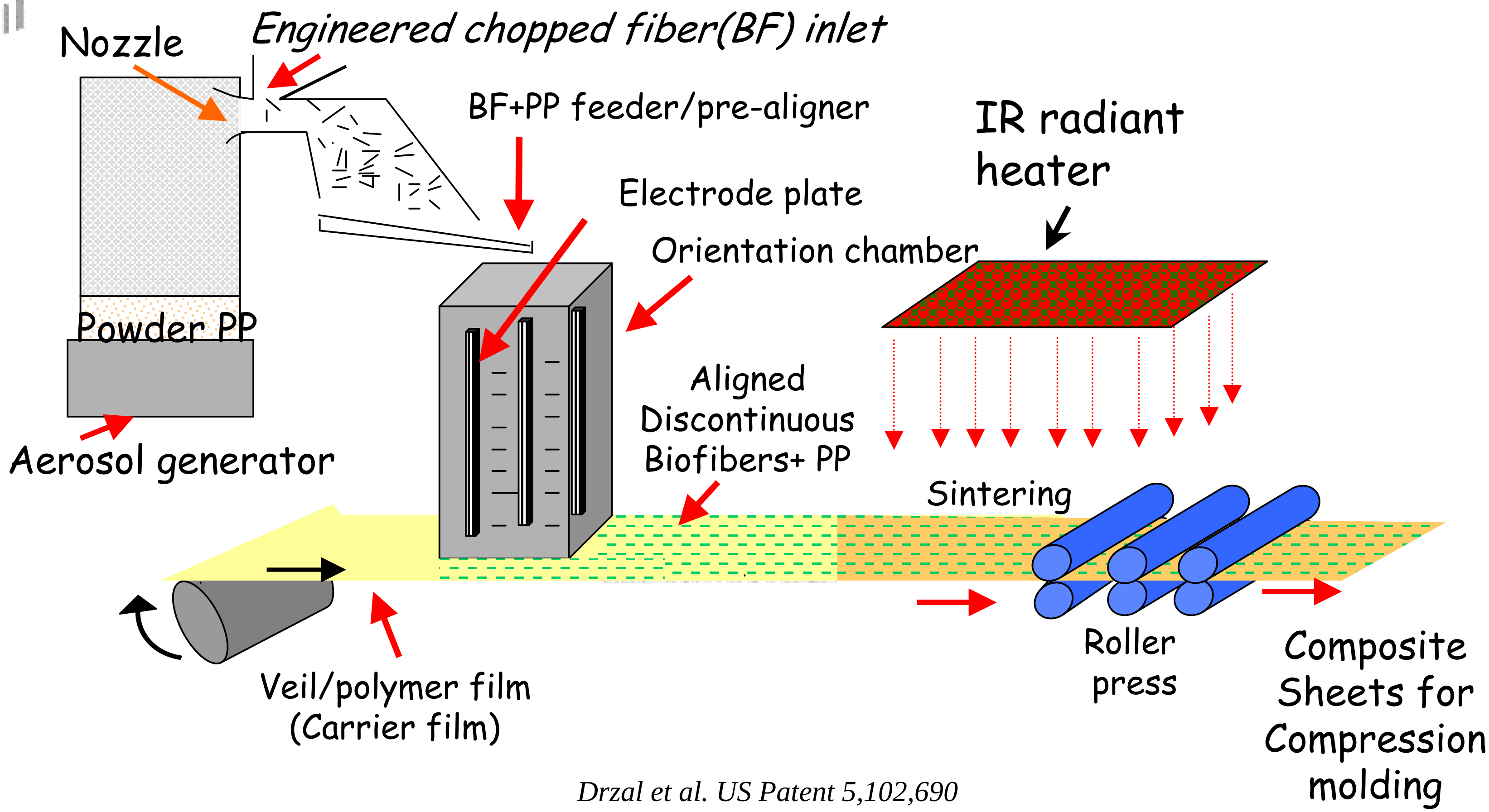
Various Stages of Consolidation



Drzal et al. US Patent, 5,102,690 (1992); 5,123,373 (1992); 5,128,199 (1992)



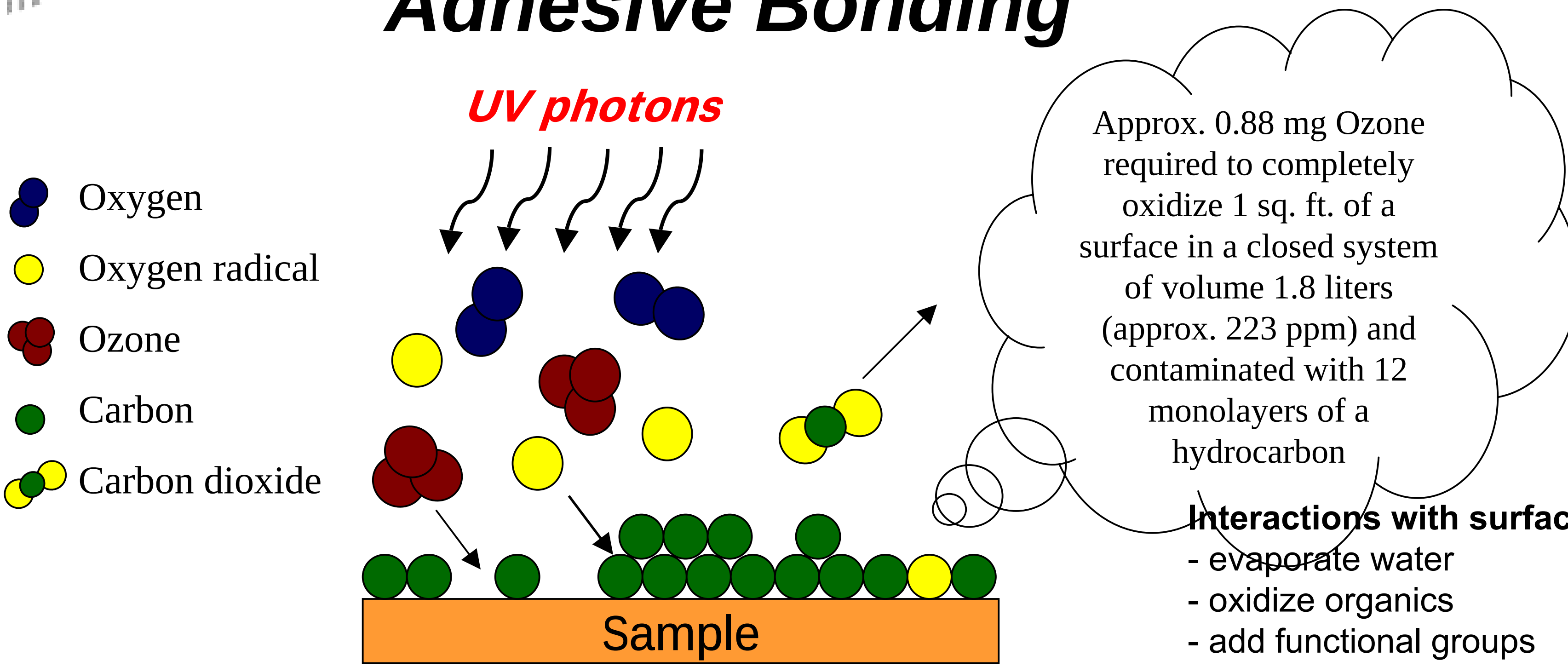
Drzal et al. US Patent 5,102,690

Process to make stampable formable biofiber reinforced thermoplastic sheet by the use of fine polymer particles to coat plant fibers directly at ambient temperature without solvents.

Nanolayer Lubricants

- NIST researchers are working to develop surface protecting and lubricating films that will shield super-small machines and their even tinier components from friction and wear.
- Nanolayer films will be needed for the minuscule nanomachines to come.
- The lubricating potential of a mixed-molecule, nanolayer films consisting of combinations of up to four different molecules, each one chosen to achieve desired capabilities, from wear resistance to self-repair.
- E.g., a particular group of molecules is selected to adhere tightly to the surface, anchoring the film and protecting against high-shear collisions. Other molecules flow among the anchors to prevent friction.

NanoSurface Cleaning for Painting and Adhesive Bonding



Interactions with surface

- evaporate water
- oxidize organics
- add functional groups
- increase surface energy
- change morphology
- degrade surface
- evolve CO_2, water

Step 1 $O_2 + h\nu\ (184.9\ nm) \longrightarrow O_2^* \longrightarrow 2O$

Step 2 $O + O_2 \longrightarrow O_3$ and $O_3 + h\nu\ (253.7\ nm) \longrightarrow O_2 + O$

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Comparison of various surface treatments

Technologies	Performance	Ability to treat complex geometries	Controlled Environments	Treatment Times	Stability of treatment	Cost	Environmental Impact	Suitability for Production Environments	Overall Rating	Ranking
Chemical Wash	3	1	4	2	1	1	5	1	18	4
Flame	2	5	2	1	1	2	2	1	16	3
Corona	1	2	1	1	1	2	1	1	10	1
Plasma	1	1	5	3	1	3	2	4	20	5
UV	1	1	2	**2**	1	**2**	1	1	11	2

1 = Best 5 = Worst

UV Treatment ~ $.01/ft^2 for polymeric surfaces.

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Other Examples of Nanotechnology Applications for Green Manufacturing

- **Manufacturing of nanoparticles using SCO_2**
- **Incorporation of metal or metal oxides nanoparticles to produce coatings with anti-corrosion properties (replace chromates)**
- **Self-assembled monolayers in mesoporous supports for improved selectivity in separations, reactions and sensing**
- **Reversible self-assembly for end-of-life and recyclability and reuse**
- **'Dematerialization' through increased use of nanoscale materials to replace macroscale elements.**

McKenzie and Hutchinson, Chemistry Today, 2004 (in press)

Future of Nanotechnology and Green Manufacturing?

- 'Motivating Factors'
  - Increasing environmental concern
    - Carbon dioxide and VOC emissions
    - Depletion of natural resources
    - Limited solid waste disposal capacity
  - Legislative actions
    - Incentive vs Regulation
  - Economic Situation
    - Energy Costs

$$$ Nanotechnology

- Worldwide research and development spending in the emerging field of nanotechnology should rise about 10 percent this year to $8.6 billion.
- Corporations are projected to spend ~$3.8 billion on nanotechnology
- Venture capital spending on nanotechnology ~$200 million.
- Government spending ~$4.6 billion in research and development this year.
- New legislation will inject $3.7 billion into nanotechnology research over four years.
- In 2005, the private sector should outspend the public sector.

Lux Research Inc. (2004)

Principles of Green Engineering (and Manufacturing)*

1. Material and energy inputs and outputs are inherently nonhazardous as possible
2. Prevent waste rather than remediate it
3. Design Separation and Purification processes to minimize energy and materials
4. Maximize mass, energy, space and time efficiency
5. ‘Output-pull rather than ‘input-push’
6. Conserve complexity
7. Design for durability not immortality
8. Meet need, minimize excess
9. Minimize material diversity
10. Integrate local material and energy flows
11. Design for ‘commercial afterlife’
12. Use renewables rather than depletable resources

**Green Engineering, Anastas, P.T., ACS (2000)*

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