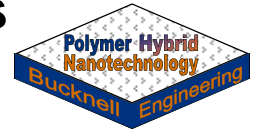




# Polymer Blends and Nanocomposites for Real-World Applications



Polymer Processing Laboratory, College of Engineering, Bucknell University

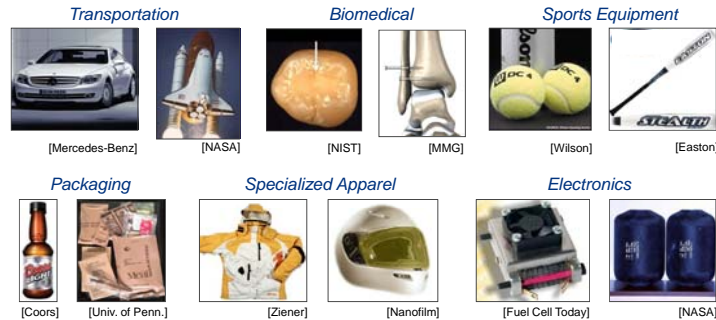
Katsuyuki Wakabayashi (Chemical Engineering) & Michael A. Malusis (Civil & Environmental Engineering)

## Polymer Hybrids on the Nanoscale



- Mechanical robustness (tensile strength, stiffness, toughness, hardness)
- Thermal stability (melting, degradation, expansion)
- Chemical resistance and gas barrier improvements
- Electrical and thermal conductivity
- Flame retardance
- ... and many others!

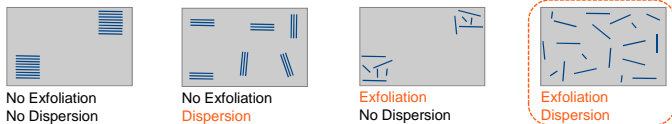
## Applications



## Challenges

### Ideal Morphology of Blends and Nanocomposites

- Well-separated ("exfoliated", "intercalated") from each other
- Well-dispersed throughout the polymer matrix
- The above morphology must be stable at molding conditions (i.e. high temperature)



### Previous Fabrication Techniques:

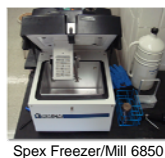
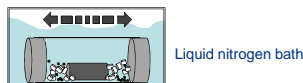
Technique	Method	Limitations
In situ polymerization 	Nanofiller is swollen with monomer, then polymerized	<ul style="list-style-type: none"> <li>Few selection of filler-monomer pairs</li> <li>Small-scale production</li> <li>Not environmentally benign</li> </ul>
Solution intercalation 	Polymer and filler are co-dissolved in solution, sonicated, then solvent is removed	<ul style="list-style-type: none"> <li>Small-scale production</li> <li>Use of solvent</li> <li>Filler dispersion not stable</li> <li>Not environmentally benign</li> </ul>
Melt processing 	Polymer and filler are melt mixed above T <sub>m</sub> and/or T <sub>g</sub>	<ul style="list-style-type: none"> <li>Few selection of filler-monomer pairs</li> <li>Prone to thermal degradation</li> <li>Filler dispersion not stable</li> </ul>

## Solid State Processing Methods

- Mechanochemistry in the solid state (below T<sub>melt</sub> or T<sub>glass</sub>)
- No solvents, monomers, additives, compatibilizers, heat
- Chain scission, intimate mixing, ultimate dispersion

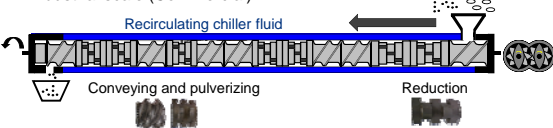
### Cryogenic Mill (Cryo-mill)

- Impaction of milling medium against material (at -196°C)
- Laboratory scale (scientific)



### Solid-State Shear Pulverization (SSSP)

- High compressive & shear forces in the solid state (at -12°C)
- Industrial scale (Commercial)



## Materials

### Polymer Matrix

- Polyethylene (PE)**: CC1=CC=CC=C1
- Polystyrene (PS)**: C1=CC=C(C=C1)C2=CC=CC=C2
- Poly(lactic acid) (PLA)**: C1=CC=CC=C1
- Polypropylene (PP)**: CC1=CC=CC=C1
- Polyethylene terephthalate (PET)**: C1=CC=CC=C1
- Polycaprolactone (PCL)**: C1=CC=CC=C1

### Nanofiller

- Nanosilica**: [LCE, Finland], [Furukawa]
- Graphite**: [Wikimedia], [Asbury]
- Diamondoids**: [Chevron]
- Gold nanoparticles**: [NRL], [Toyota]
- Carbon nanotubes**: [Wikimedia], [Theodore Gray]
- Montmorillonite (clay)**: [Southern Clay], [Triganic]

## Characterization Methods

### Structural Characterization

- Gel permeation chromatography (molecular weight)
- Optical microscope (macro-scale)
- Scanning electron microscope (micron-scale)
- X-ray diffraction (nano- and Angstrom-scale)

### Thermal Behavior Probing

- Differential scanning calorimetry (T<sub>melt</sub>, T<sub>glass</sub>, T<sub>crystallization</sub>)
- Thermogravimetric analysis (T<sub>degradation</sub>, filler content)

### Mechanical Property Measurement

- Uniaxial tensile and compression test (modulus)
- Impact test (impact strength)
- Hardness test (hardness)
- Dynamic mechanical analysis (rubbery/glassy)

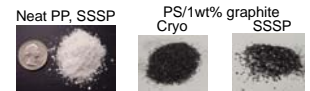
### Barrier Properties

- Oxygen permeation (O<sub>2</sub> Permeability)
- Water vapor transmission (WV Permeability)

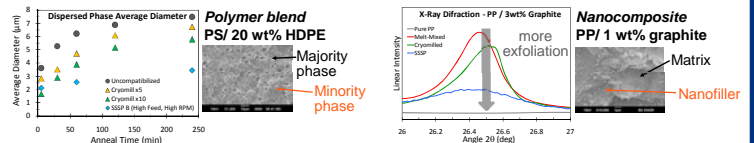
## Results

### Solid-State Processing Output

- Flake, powder, particulate
- Depends on process parameter and materials

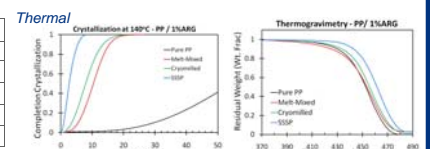


### Morphology



### Performance

Molecular weight	M <sub>n</sub> (kg/mol)	M <sub>w</sub> (kg/mol)
Neat PS	150	188
Cryo 5	125 (-18%)	188 (0%)
Cryo 10	114 (-24%)	178 (-6%)
SSSP High RPM	95 (-37%)	125 (-32%)
SSSP Low RPM	78 (-48%)	109 (-42%)



### Mechanical & barrier

	Modulus	Strength	Strain at Break	O <sub>2</sub> Permeability
Pure PP (Total PP 3276)	900 MPa	27 MPa	800 %	3090 cc.mil/m <sup>2</sup> .day
PP 3wt% Clay (Nanocor PGW)	980 MPa	25 MPa	800 %	2350 cc.mil/m <sup>2</sup> .day
PP 3wt% Graphite (Asbury 4827)	1070 MPa	28 MPa	650 %	2820 cc.mil/m <sup>2</sup> .day
PP 3wt% Cellulose (Aldrich 20µm)	960 MPa	26 MPa	730 %	2780 cc.mil/m <sup>2</sup> .day

## Acknowledgements

- Poster by Stephen R. Norton, (Bucknell Chemical Engineering 2010)
- Northwestern University (Professor John M. Torkelson)
- National Science Foundation Major Research Instrumentation Grant (CMMI #0820993)
- Krauss Maffei Berstorff Corporation