Thermoset and Thermoplastics Clay Nanocomposites

Presented by:
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CP Polymer
Topics

• Nanoclay Technology and Preparation
• Thermoset: Epoxy Nanocomposite
• Thermoplastics:Nylon Nanocomposite
• Applications
Nanoclay

Selective Mining

Purification & Surface Modification

Bentonite
Nanoclay

US Patents, Amcol, 6,050,509 and 6,235,533
Clay as mined

Clay after purification
Making a Nanoclay

High Aspect Ratio

1st Step: Surface Treatment

\[ \text{Si}^4+ = \text{Al}^3+ + \text{Na}^+ \]
\[ \text{Al}^3+ = \text{Mg}^2+ + \text{Na}^+ \]

Hydrophilic → Hydrophobic

1st Step
The Goal: To Exfoliate the Individual Layer!

Nanomeric® (Nanoclay)

2nd Step
Monomer

Hydrophobic

3rd Step
Polymerization

Alternative Process
a) Direct Melt Compounding
b) Pre-swollen Master Batch

Polymer Melt

Making Nanocomposite

Nanocomposite
Nylon 6 Nanocomposite: TEM

TEM-2% Nanoclay

Exfoliated Clay Platelets

TEM-8% Nanoclay
Why Exfoliation is Important?

To get 50% Barrier enhancement

- Melt-compounding: Need 5% Nanoclay
- Polymerization Route: Need 2-2.5% Nanoclay

50% Better Oxygen Barrier
Topics

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• **Thermoplastics: Nylon Nanocomposite**
• Applications
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*Sigma-Aldrich offer lab size quantities*
Thermoset Nanocomposites

• Nanoclay Incorporation into Monomer and Curing.
  
  Epoxy, Urethane, UPE, Silicones...
Dispersion Guide

- Nanoclay has good compatibility with most of thermoset resins
- Low viscosity resin will allow nanoclay wetting or swelling
- Common defoamer may be needed to reduce foaming
- Degas to eliminate entrapped air bubbles.
Epoxy Nanocomposites

- Amine, Anhydride and DICY Cured
- Nanomer Incorporation into Resins, or Resin/Curing Agent Mixtures
- Improved Modulus, Tg, and Solvent Resistance
- Synergistic effect with fumed silica
Amine Cured
Nanomer® I.30E (Heat Cured)

Major Surface Treatment:

\[ \text{Acidity of the Primary Onium Ion} \]
\[ \text{Promotes Epoxy-Amine Intragallery Polymerization.} \]
Epoxy Nanocomposites

- Increase Modulus and Tg
- Increase Chemical Resistance
- Increase Compression Strength
- Reduce Shrinkage, and Lower CLTE
PROPERTIES

Amine-Cured Epoxy Nanocomposites

I.30E, 10 phr

Epon828-D230
**Epoxy Nanocomposites**

Anhydride Cured

Nanomer® I.28E, and I.22E

Major Surface Treatment:

\[ N(CH_3)_3^+ \]

Quaternary Onium Ion Promotes Epoxy-Anhydride Intragallery Polymerization.
PROPERTIES
Anhydride-Cured Epoxy Nanocomposites

- Increased Modulus and Tg
- Enhanced High Voltage Resistance
- Elimination of Curing Accelerators
Epoxy Nanocomposites

DICY Cured

Nanomer® I.28E

Major Surface Treatment:

Quaternary Onium Ion Promotes Epoxy-DICY Intragallery Polymerization.
PROPERTIES

DICY-Cured Epoxy Nanocomposites

• Lowered Curing Temperature
• Curable without Polyamine Accelerators
• Increased Modulus, and Tg
• Increased DICY-Epoxy Dispersion Stability
Summary: PROPERTIES
Thermoset Nanocomposites

- Increased Mechanical Properties
- Increased Tg in Epoxy systems
- Reduced Flammability
- Improved Chemical and Solvent Resistance
- Reduced Shrinkage
APPLICATION
THERMOSET NANOCOMPOSITES

- Structural Application, Composites
- Paint and Coating Application, Chemical Resistance, Thixotrope and Crater Control
- Adhesives
- Potting and Encapsulation
- Flooring
- Tank Lining
- Tooling
Topics

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• **Thermoplastics: Nylon Nanocomposite**
• Applications
Nylon 6 Nanocomposite: *in-situ* Polymerization

- Two Commercial Nanoclay products
- Both Nanoclay tether to the polymer chain after polymerization
- Patent coverage
- FDA/EU approval status

![Monomer Structure](image1.png)

Nylon 6 Nanocomposite

Mechanism: Barrier Properties

Polymer Film

Tortuous Path

Dispersed Nanoclay
Barrier of Nylon 6 Nanocomposite

Cast Film

Oxygen

Water Vapor

Nanoclay L loading (%)

WVTR (g mil/m² day)

OTR (cc-mil/100in²/day-atm)

0%RH
65% RH
90% RH

0% 2% 4% 6%
Film: Mechanical Properties

- **Tensile Modulus**
  - Increase 80% to 160% on machine direction and transverse direction

- **Elongation at Break**
  - Slight decrease of elongation at break from 280% for pure PA6 to 220% for PA6 nanocomposite on both machine and transverse directions

- **Heat Deflection Temperature**
  - Increase from pure Nylon 6’s 60°C to PA6 nanocomposite’s 140°C with 4% Nanoclay @264 psi (1.80 MPa) ASTM D 648
Nylon 6 Nanocomposite

• Optimized Exfoliation
• Enhanced Moisture, Oxygen Barrier Properties
• Higher Stiffness
• Higher Heat Distortion Temperature
• Better Clarity

• What you get is a total package: barrier improvement along with high stiffness and high heat resistance
Film Appearance

- Haze reduced by \(~50\%\) at 2\% nanoclay loading
- Nylon 6 Nanocomposite film has better clarity than standard nylon 6.

Nucleating effect!

Standard PA (TEM, cross section)  
Nylon Nanocomposite (TEM, cross section)  

Dr. Marcus Schäfer, Lanxess Deutschland GmbH, Nanocomposite 2006, Brussels, Belgium, Feb. 2006
Nylon MXD6 Nanocomposite (MXD6-NC)  
Ultra Barrier System

- Patented technology
- MXD6-NC is fully cleared for use as non-food contact layers.
  - All food group and Condition-of-Use A
- Easy processing
- Excellent O$_2$ barrier
- Superb CO$_2$ barrier
- Higher HDT than EVOH

Consideration for Packaging Applications

• **Package Design**
  – FDA and any regulatory issues
  – Cost vs. performance
  – Monolayer vs. multilayer
  – Appearance

• **Packaging Manufacture**
  – Process parameter

• **Package performance**
  – Barrier of the total package
  – Strength
Nanocomposite: Packaging Applications

- Flexible Packaging: Multi-layer Polyolefin/nano PA films
- Extrusion Coating of Paperboard: Juice Packaging, Milk Cartons
- Single Layer Film: Down Gauging to Save Cost
- Stand-up Pouches: Barrier, Strength
- Crystallization: clear film
- Retort and cooking bag: High temperature application
Airtight Self-Venting Microwaveable Film

Description:

Airtight Self-Venting Microwaveable Film is a multilayer laminated film with a heat-sealing layer. Manufactured with patented pressure regulating film, it allows the package to stay hermetically sealed for storage and during microwave heating; the top barrier film separates or delaminates automatically from the self-venting film, regulating the excessive buildup pressure without rupturing the film.
Airtight Self-Venting Microwaveable Film

Food Status:
- Airtight Self-Venting Microwaveable Film complies with all the requirements of:
  - C-Nylon (Clay + Nylon): FDA 21 CFR 176.170
  - PET: FDA 21 CFR 177.1630
  - CPP: FDA 21 CFR 177.1520
- Free of BBP (Benzyl Butyl Phthalate) and BPA (Bisphenol A).
Thermoplastic Nanocomposite Summary

- Nanocomposite offers improved barrier properties on OTR, WVTR and CO$_2$TR, etc
- Increased stiffness
- High temperature applications
- Can tailor cost and performance by blending different types of nylon nanocomposites
- Can be included as one or more components in smart packaging design
Thank You

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