Nanocomposite Materials for Packaging Film Applications

Tie Lan
General Manager
Nanocor, Inc.
Outline

• Concept of Nanocomposites
• Manufacturing and Processing Technologies
• Enhanced Barrier Properties
• Applications in Packaging
Nanoclay As Passive Barrier materials

Montmorillonite

High aspect ratio impermeable silicate layers, 200-300 nm

Chemical reactivity for inner surface modification

100 to 500 nm

Nanoclay platelets are one-ten thousandth the diameter of a human hair!!
Nanoclay

Na-montmorillonite

- H2O

Nanos

Water Dispersion

BEST DISPERSED NANOCLAY
It is **impossible** to supply single layer nanoclay particles.
Nanoclay

Resin Solvation  Nanocomposite

15~25 Microns  Nanos  Nanos
Nanoclay: Barrier Enhancement

Clay Platelets Create Tortuous Path

\[
P_{\text{nanocomposite}} = \frac{(\text{Matrix Volume Fraction}) \times (P_{\text{matrix}})}{1 + (\text{Clay Volume Fraction}) \times (\text{Clay Aspect Ratio}) / 2}
\]

Nanoclay: Barrier Enhancement

What does it take to reduce 50% permeability?

<table>
<thead>
<tr>
<th>Aspect ratio</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>9%</td>
</tr>
<tr>
<td>200</td>
<td>1%</td>
</tr>
<tr>
<td>400</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

\[
P_{\text{nanocomposite}} = \frac{(\text{Matrix Volume Fraction}) \times (P_{\text{matrix}})}{1 + (\text{Clay Volume Fraction}) \times (\text{Clay Aspect Ratio})/2}
\]

Nanocomposites

- Low addition level of nanoclay enhances the barrier of the base resin
- Development from lab to pilot to production
Nanoclay

Selective Mining

Bentonite

Nanoclay

Purification & Surface Modification
Nanomer® Formation

High Aspect Ratio

Surface Treatment

Hydrophilic → Hydrophobic

Surface treatment
Requirement For Food Packaging
Regulatory Compliance of all materials/processes

- Montmorillonite is considered GRAS
  (Generally Recognized As Safe, 21CFR184.1155)
- Clay surface treatment agents have various FDA status.
- Migration of the surface modifier is the concern
- Minimize surface treatment is the key to obtain good regulatory status.
- Detailed information on package film structure, packed food, storage condition, pack conditions, etc...
- KH letter, FCN with FDA, etc....
Making Nanocomposites

- Hydrophobic Monomer
- Polymerization
  a) Direct Melt Compounding
  b) Pre-swollen Master Batch

Nanomer® → Nanocomposite
Nanocomposite Formation

In Situ Polymerization

Monomer intercalation into clay inner layer regions
Anchor polymerization catalyst into the clay layer resin
Initiate polymerization via heat or UV
PA6, epoxy, urethane, PP and PE
Nanocomposite Processing

**In situ polymerization: Nano-PA6**

- In situ polymerization process with patented technology
- No extractable surface modifiers
- FDA/EU approval status for direct food contact

![Chemical structures](image)
Nanoclay Phase Change in nano-PA6
Formation process
Nanoclay Morphology-PSD

- Produced nanoclay
- Fully Dispersed nanoclay in plastics
- Burning of plastic resin
- Char of nanocomposite
Typical Nanoclay Particle size (I.24TL) DRY

Mean=17 micron

We do NOT supply nano-sized powers.
Nanocomposite

Nanoclay platelets are one-ten thousandth the diameter of a human hair!!
NANO-PA6                   AFTER BURNING (950°C)
                           FOR 30 MINS
PARTICLE SIZE OF RESIDUAL ASH AFTER BURING OF NANO-PA6 (MECHANICALLY GROUND)

Mean = 100 micron
Nanocomposite Processing
Melt Compounding

15 µm Particle >1 Million Platelets

We do NOT supply nano-sized powers.
Nanocomposite Processing
Melt Compounding

It is easy for polymer to enter clay interlayer region

It is difficult to break the clay agglomerates

Edge-surface chemistry
Polymer shear stress is more important in clay dispersion.
Nanocomposite Processing
Melt Compounding

Screw Design-Twin Screw Extruder (27 mm, 36 L/D)
Nanocomposite Processing
Melt Compounding

High Shear Stress Processing Equipments

TSE-JSW

SUPERTEXCI NIC TKR-F

STRATEK PLASTIC LTD

Tek-Mix: an Extensional flow Mixer that attaches to any extruder
Tek-Mix: an Extensional flow Mixer that attaches to any extruder
Nanocomposite Processing

Nanomers I.30P, I.44PA
Compatibilizer
Polyolefin Pellets

Twin Screw Compounding
nanoMax®

Twin Screw Compounding
Polyolefin Pellets

Single Screw Extruder Injection Molder
Nanocomposite
(Engineering, FR Only)

Nanocomposite
(Film, Engineering & FR)

Nanomer® Powder

Compatibilizer
Polymers Laminations Adhesives Coatings Extrusions
2009 Symposium on Nanomaterials for Flexible Packaging
Nanocomposite Processing
Melt Compounding

Elimination of Polyolefin Compatibilizers (PP-g-Ma, PE-g-Ma):

• In favor for food contact applications

• Remove additional cost to the formulation

• Reduce negative effect on melt rheology
Nanocomposite Processing
Melt Compounding

Regular MB with Ma-PE,  Tek-Mix MB without Ma-PE

5% Nanoclay in LLDPE

30-140 µm  13-22 µm
Barrier Improvement of nanocomposites

- Nano-PA6
- Nano-Nylon MXD6
- Nano-PP and nano-PE
Barrier Improvement of nano-PA6

Oxygen

Water Vapor

I.24TL Loading (%)
Barrier Improvement of nano-PA6
## Film Mechanical Properties of Nano-PA6

### Cast Monolayer Films (20-30 micron)

#### Flow Direction

<table>
<thead>
<tr>
<th>Testing Sample</th>
<th>%Nano Loading</th>
<th>Young’s Modulus (Mpa)</th>
<th>Yield Strength (Mpa)</th>
<th>Strain @ break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6 B135WP</td>
<td>n/a</td>
<td>150</td>
<td>12</td>
<td>700</td>
</tr>
<tr>
<td>Nano-PA6</td>
<td>3%</td>
<td>270</td>
<td>35</td>
<td>650</td>
</tr>
</tbody>
</table>

#### Perpendicular Direction

<table>
<thead>
<tr>
<th>Testing Sample</th>
<th>%Nano Loading</th>
<th>Young’s Modulus (Mpa)</th>
<th>Yield Strength (Mpa)</th>
<th>Strain @ break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon 6 B135WP</td>
<td>n/a</td>
<td>200</td>
<td>16</td>
<td>600</td>
</tr>
<tr>
<td>Nano-PA6</td>
<td>3%</td>
<td>380</td>
<td>28</td>
<td>550</td>
</tr>
</tbody>
</table>
Nanocomposites

• Same Tm, Tg ---Same processing
• Smart design

Use less resin ---same strength and barrier

PE//PA6//PE = 40//20//40
PE//nano-PA6// = 40//10//40
10% saving in film weight

Nanocomposites can save cost!
Nanocomposites

Extruder with barrier nanofilm counts chickens

By Dan Hockensmith
PLASTICS NEWS STAFF

Next Generation Films Inc. is applying nanotechnology literally on top of the chickens lying in grocers' meat aisles.

The Lexington, Ohio-based extruder of three-layer films is marketing a new ultrathin oxygen barrier for food packaging that consists of a layer of nanonylon sandwiched between two layers of polyethylene.

The 14-year-old company has made three-layer bags using nanotechnology for more than a year, founder and Chief Executive Officer David Freckka said in an pending technology, those com-

“The bio-based films, you can’t recycle,” “With nano [film], you can use fewer layers – it’s still as strong and it can be recycled.”

- David Freckka, CEO, Next Generation Films

Windmoeller & Hoelscher Varex three-layer blown film line running in one of its four bays, cranking out as much as 2,100 pounds of film per hour. An 87-inch W&H Varex three-layer line is scheduled to be installed this summer.

Once that machine — the company's third W&H line — is in he said.

Next Generation's sales are about $80 million, Freckka said, though he wouldn't give the actual amount. He said he gets "a phone call a day" from private equity investors that want to buy the company. But he's not ready to sell — in

IFT 08
## Nano-Nylon MXD6 Barrier Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>MXD6 $^a$</th>
<th>Imperm $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTR (23°C, 60%RH)</td>
<td>cc · mm/m² · day · atm</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>CO₂TR (23°C, 60%RH)</td>
<td>cc · mm/m² · day · atm</td>
<td>0.30</td>
<td>0.15</td>
</tr>
<tr>
<td>WVTR (40°C, 90%RH)</td>
<td>g · mm/m² · day</td>
<td>1.36</td>
<td>0.58</td>
</tr>
</tbody>
</table>

$a$) Non-oriented monolayer film
PP and HDPE Nanocomposites

OTR of HDPE and PP nanocomposite

<table>
<thead>
<tr>
<th>Material</th>
<th>OTR (cc mm/m2 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE 9608XD</td>
<td>60</td>
</tr>
<tr>
<td>3.5% Nanomer in HDPE</td>
<td>30</td>
</tr>
<tr>
<td>PP 4772 (Exxon)</td>
<td>57</td>
</tr>
<tr>
<td>3.5% Nanomer in PP 4772</td>
<td>20</td>
</tr>
</tbody>
</table>
Summary

- Nanoclays are effective additives to plastics to enhance barrier properties.

- Plastic nanocomposites are the same class of plastics but with better properties

- Nanocomposites offer material saving option and higher performance product design

- It is possible and practical to have regulatory approval to use nanocomposite plastic as food packaging materials
Thank You