**Nylon Nanocomposites in Flexible Packaging Applications**

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**ABSTRACT**  
Since the first patent by Toyota on nylon 6 nanocomposite\(^1\), significant progresses have been made in understanding the nature of nanoclay exfoliation and property reinforcement. More significantly, commercial scale productions based on the original Toyota nylon 6 nanocomposite technologies have been achieved. One significant attribute of nanoclay is barrier enhancement. In addition, the tethering between nanoclay and nylon 6 enables its approval for food package applications. Other nylon systems, such as amorphous nylon and nylon MXD6 nanocomposite, deliver barrier improvement as well. Blending at different ratio of these nylon nanocomposites offers wide spectrum of performance for packaging applications.

**INTRODUCTION**  
There are generally three methods of making a nanocomposite: 1) in-situ polymerization; 2) direct melt compounding, and 3) master batch let down. Nylon 6 nanocomposite is able to be produced by in-situ polymerization. This approach offers the best exfoliation of nanoclay platelet. At 2 wt% nanoclay addition, the barrier property is equal to a PA6 nanocomposite made from direct melt compounding with 5 wt% nanoclay. Currently, only PA6 nanocomposite is produced from in-situ polymerization at commercial scale. Nylon 11 and nylon 12 can be produced from in situ polymerization as well. However, no commercial production of these nanocomposites has been achieved yet. UBE reported that Nylon 666 was made from in situ polymerization as well. Other nylon systems, such as nylon 66, amorphous and MXD 6 nanocomposite can not be made by reaction route, but can be produced by melt-compounding, either direct or master batch let down.

**DISCUSSION**

**Nylon 6 nanocomposite formation and production**  
The type of nanoclay used for nylon 6 was montmorillonite surface treated with protonated 12-aminododecanoic acid (ADA). This was achieved by an ion-exchange process. Consequently, the protonated ADA is adhered to clay surface via electrostatic interaction. This nanoclay is named Nanomer® I.24TL(Nanoclay-A). After introducing Nanoclay-A to molten caprolactam, the clay gallery was swelled by caprolactam. Polymerization under standard condition formed the PA 6 nanocomposite. Since the polymerization took many hours to complete, the force generated from chemical bond formation helped to separate and eventually exfoliate the clay platelet into individual layers. TEM and XRD proved this is a fully exfoliated product.

During the polymerization, ADA was reacted with caprolactam and formed covalent bonds. This phenomenon is referred as tethering effect. After polymerization, each ADA on clay surface is chemically bonded to one nylon 6 chain. Due to the tethering effect, the individual protonated ADA was no longer exist after polymerization (Figure 1). Therefore, ADA molecules can not be extracted by ethanol or ethanol/water mixture. Lab results confirmed this. As a result, nylon 6 nanocomposite made with ADA-MONT has FDA approval and EU approval for direct food contact applications. There is another type of Nanoclay-B that works like Nanoclay-A. It is covered in a recent patent application.\(^2\) It also has tethering effect after polymerization, with FDA approval for direct food contact applications.

Currently, many resin producers are able to produce nylon 6 nanocomposite from their reactors. They can add different weight percentage of nanoclay, such as 2%, 4%, 5%, 8% and 10% into the reactor. Today, nylon 6 nanocomposite is available at commercial quantity with a reasonable value proposition. This is a very important milestone, since many film converters can now get enough quantity to evaluate a material that can be produced at commercial scale. For packaging application, the most important grade is nylon 6-NC with 4% nanoclay. This grade is produced by one producer from continuous nylon 6 reactor.
Optimal loading level of nanoclay

In order to answer the question what the optimal nanoclay loading levels are, different amount of nanoclay was introduced to PA 6 polymerization process. A nanoclay loading level of 2%, 4%, 6% and 8% was examined. The trend was not a straight line that was proportional to nanoclay loading. As the nanoclay loading level increased, the property enhancement gradually approached a plateau. Figure 2 demonstrated the oxygen barrier improvement at different nanoclay loading. We conclude that the optimal nanoclay loading level to achieve the best cost/performance balance is 3-4 wt%. At 4 wt% nanoclay, the barrier properties were enhanced by 64% over the pure nylon 6.

At 65% relative humidity at room temperature, the absolute OTR of a nylon 6 nanocomposite containing 4 wt% ADA-MONT is superior to amorphous nylons based on hexamethylene diamine, isophthalic acid and terephthalic acid. In addition, the water vapor barrier followed similar trend as oxygen barrier. At 4 wt% of ADA-MONT, WVTR reduced by 68%, thus barrier was enhanced by 68%. Reduced water permeation allows nanocomposites to maintain better performance compared with neat resin under prolonged moisture exposure conditions.

Tensile strength on cast and blown film increased 80%-160% on both machine and transverse directions, with only slight reduction on elongation, from 280% for pure to 220% for nanocomposites. One more properties that needed to mention is the heat resistance. Following test standard (ASTM D 648), the heat deflection temperature of PA 6 nanocomposite with 4% ADA-MONT is 140°C, comparing 60°C for the pure. This helps its application in packaging application that requires high heat resistance.

With excellent barrier performance, mechanical properties and regulatory clearance, nylon 6 nanocomposites have wide applications in food packaging, ranging from single layer and multi layers film to rigid plastic containers. Its applications are exampled by flexible packaging in multi-layer polyolefin/nano-PA films; extrusion coating of paperboard: juice packaging, milk cartons and retort and cooking bag: high temperature application.
As discussed earlier that nanocomposites for other types of nylon other than nylon 6 cannot be produced via in-situ polymerization. Accordingly, the nanocomposite made from melt-compounding have no chemical bond between clay’s organic modifier and polymer chain. This organic modifier thus is susceptible to be extracted. The challenge was how a tethered system can be introduced to these nylon systems, thus boost their chances for FDA approval for food application.

Nylon 6 nanocomposite concentrate was developed to meet the requirement. It contains 20-30 wt% of nanoclay made in the polymerization process. It is a tethered system. For example, when letting down into amorphous nylon, the nanoclay is still chemically bonded to nylon 6. Oxygen barrier at 0% RH and 65% RH has increase by 45% when nylon 6 nanocomposite concentrate was letting down to final 4 wt% nanoclay containing nanocomposite.

**Nylon MXD 6 Nanocomposite (MXD6-NC) Technology**

MXD6-NC is a family of superior gas barrier resins particularly useful in extending package shelf life. The base resin for MXD6-NC is Nylon MXD6, a proven gas barrier with 25 years of industry acceptance. MXD6-NC is designed for multilayer films/sheet in combination with polyethylene, polypropylene, Polyamides, and PET.

MXD6-NC products are fully approved for use as a non-contact barrier layer in multilayer structures up to retort applications for all types of foods. MXD6-NC is created by dispersing proprietary nanoclay into MXD6 to form a nanocomposite with significantly enhanced barrier, while processing characteristics remain similar to MXD6 itself. The dispersion technology is patented.

**Blending different nanocomposites**

All nylon nanocomposite discussed above can blend with each other to provide certain property and processing advantage. It also offers cost performance balance to best match the packaging design requirement.

**CONCLUSION**

Nylon nanocomposite offers barrier, mechanical properties enhancement as well as boost heat resistance. It can deliver great solutions for packaging applications.

**ACKNOWLEDGMENTS**

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Reference:

Nylon Nanocomposites in Flexible Packaging Applications

Presented by:
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Technical Sales Manager

Sponsored by CP Polymer
Topics

• Nanoclay Technology and Preparation
• Nylon Nanocomposite
  Nylon 6 Nanocomposites
  Other nylon Nanocomposites
• Case Studies: Blend Different Nylon Nanocomposite to Balance Cost and Performance
• Applications
Nanoclay

Selective Mining

Bentonite

Nanoclay

Purification & Surface Modification
Nanoclay

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

Clay after purification

montmorillonite
Making a Nanoclay

The Goal: To Exfoliate the Individual Layer!

1st Step

Surface Treatment

High Aspect Ratio

$\text{Si}^{4+} = \text{Al}^{3+} + \text{Na}^+$

$\text{Al}^{3+} = \text{Mg}^{2+} + \text{Na}^+$

Hydrophilic

Hydrophobic
The Goal: To Exfoliate the Individual Layer!

Making Nanocomposite

Nanomer® (Nanoclay) → Nanocomposite

2nd Step: Monomer

Hydrophobic

3rd Step: Polymerization

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

Polymer Melt

The Goal: To Exfoliate the Individual Layer!
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

![Bar Graph]

- Pure
- with Nanoclay

**50% Better Oxygen Barrier**
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](image)

![Nylon 6 Nanocomposite](image)

Mechanism: Barrier Properties

- Polymer Film
- Tortuous Path
- Dispersed Nanoclay
Barrier of Nylon 6 Nanocomposite

Cast Film

**Oxygen**

![Oxygen Graph](image)

**Water Vapor**

![Water Vapor Graph](image)
Blown Films

Oxygen Transmission Rate (OTR)
(65% RH, RT)

- Pure Nylon 6
- Nylon 6 w/4% Nanoclay

% Nanoclay

cc.mil/100in² day

-62%
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
Flexible Packaging Market Needs

Life Style Change Raises New Material Demands in Flexible Packaging

– Consumer convenience
  • Single serve portions
  • Cooking bags (high temperature application)

– Visual Effects (First Moment of Truth)
  • Appeal to customer – sustainable packaging
  • See through (clarity)
  • Package integrity (pinhole resistance)
  • Designed rigidity (stand up pouches, rigidity at different humidity)
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
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
Capillary Rheology of Nylon 6 Nanocomposite

Melt Rheology at 260°C

Dr. John Facinelli, Honeywell, 2006 Stand Up Pouches
Polyamide Processing

- Coextrude with PP, PE, PET for multilayer applications
- Blend with other polymers, especially other types of PAs

![Graph showing processing temperatures for different polymers]
## Effect of Nylon 6 Nanocomposite on 3-Layer Film Structures: Nylon 6/EVOH/Nylon 6

<table>
<thead>
<tr>
<th>Property</th>
<th>Structure</th>
<th>PA6/EVOH/PA6 0.7/0.4/0.7 (mil)</th>
<th>PA6NC/EVOH/PA6NC 0.7/0.4/0.7 (mil)</th>
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<tbody>
<tr>
<td>Tensile Modulus (Kpsi)</td>
<td>MD</td>
<td>206</td>
<td>255</td>
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<tr>
<td></td>
<td>TD</td>
<td>182</td>
<td>237</td>
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<tr>
<td>Yield strength (Kpsi)</td>
<td>MD</td>
<td>6.2</td>
<td>7.8</td>
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<td></td>
<td>TD</td>
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<td>Elongation at break (%)</td>
<td>MD</td>
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<td>350</td>
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<tr>
<td></td>
<td>TD</td>
<td>380</td>
<td>330</td>
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<td>Coefficient of Friction, Static (film to film)</td>
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<td>Puncture Strength (gf)</td>
<td></td>
<td>1240</td>
<td>1347</td>
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<tr>
<td>OTR (cc.mil/100in2/day-atm)</td>
<td>, 65%RH</td>
<td>0.036</td>
<td>0.030</td>
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<tr>
<td>Water vapor transmission rate (g.mil/100 in²/day-atm, 100%RH)</td>
<td></td>
<td>13.6</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Dr. John Facinelli, Honeywell, 2006 Stand Up Pouches
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 O₂ barrier
Superb CO₂ barrier

MXD6-NC: Oxygen Barrier

OTR (cc mil/100 in² day atom)

MXD6-NC

23 °C
MXD6-NC: Oxygen Barrier

35 °C

OTR (cc.mm/m².day.atm)

EVOH (ethylene 38mol%)

MXD6-NC
Blend Nano Nylon 6 Nanocomposite with MXD 6 NC

![Graph showing OTR (cc mill/100in² day) for different blends of MXD6-NC and Nylon 6 NC]
Amorphous Nylon Nanocomposite

• Amorphous Nylon is 6I/6T type (Selar from DuPont and G21 from EMS)

• Can make the nanocomposite through direct melt-compounding or blending with nylon 6 nanocomposite

• Advantage of tethering effect from blending with nylon 6 nanocomposite

• Barrier increases with the addition of Nanoclay
Amorphous PA Nanocomposite: Containing nanoclay-Nylon 6 Masterbatch

Blend of 80% amorphous nylon and 20% of Nylon 6 master batch (NPC)

(NPC: in-situ master batch with 20% Nanoclay)

- Tethered
- FDA

Nanocomposite: Packaging Applications

• The blends of Nylon 6 nanocomposite with either amorphous or MXD6-NC boost the performance and processability.

• In multilayer application: the middle layer containing nylon nano blends can be further down gauged.

• Application for high temperature.

• Cost saving.
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).

Film before shaping

Finish Product
• 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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