# Nylon Nanocomposites in Flexible Packaging Applications

**Dr. Ying Liang**

**Nanocor, Inc.**

**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**

<u>Nylon 6 nanocomposite formation and production</u>

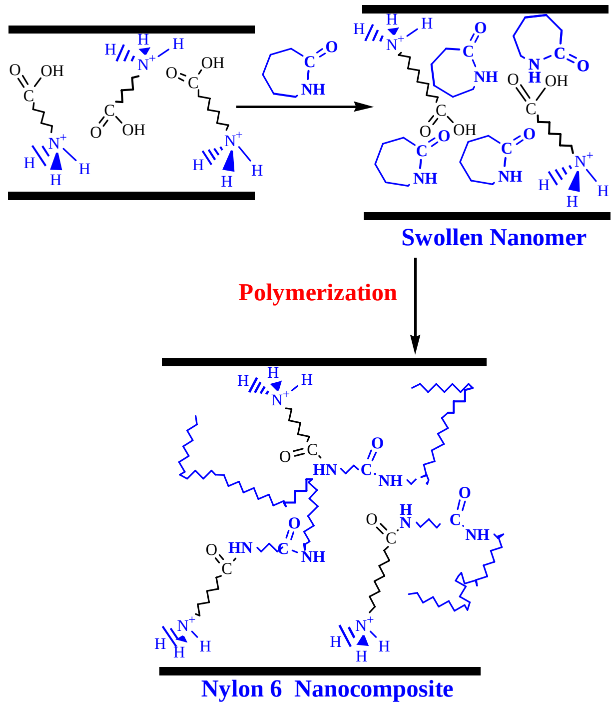
The type of nanoclay used for nylon 6 was montmorillonite surface treated with protonated 12-aminododecanoic acid (ADA). This was achieved by an ion-exchange process. Consequently, the protonated ADA is adhered to clay surface via electrostatic interaction. This nanoclay is named Nanomer® I.24TL(Nanoclay-A). After introducing Nanoclay-A to molten caprolactam, the clay gallery was swelled by caporlactam. 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.



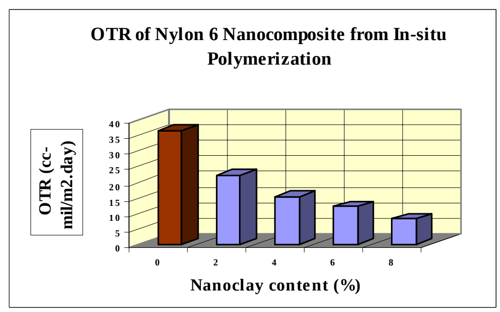




Figure 1. Nylon 6 Nanocomposite Formed through *in situ* Polymerization with ADA modified montmorillonite.

Figure 2. OTR of Nylon 6 Nanocomposite from *In situ* Polymerization (65% RH).

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$^{o}$C, comparing 60$^{o}$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.

Nylon 6 Nanocomposite Concentrate Development and Applications

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.[3] 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.[4]

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**

The author would like to thank Nanocor and CP Polymer (Mr. Orrin Addis) for their supports on attending/presenting this conference.

Reference:

1. Okada, A., Fukushima, Y., Kawasumi, M., Inagaki, S., Usuki, A., Sugiyama, S., Kurauchi, T., Kamigaito, O. Composite Material and Process for Manufacturing Same. U.S. Patent 4,739,007, 1988.
2. Lan, T.; Liang, Y.; Omachinski, S. Intercalates, Exfoliates, and Concentrates Thereof Formed with Protonated, Non-Carboxylic Swelling Agent and Nylon Intercalates Polymerized In-situ via Ring-Opening Polymerization. US Patent Appl. Publ. US2005256244 A1 20051117, 2005.
3. Liang, Y.; Lan, T.; Omachinski, S.; Cho, J. W. Intercalates, Exfoliates and Concentrates Thereof Formed with Low-Molecular-Weight Nylon Intercalants Polymerized in-situ via Ring-Opening Polymerization. U.S. Patent 6,906,127, 6/14/2005.
4. Lan, T.: Cruz, H.; Tomlin, A., Intercalates formed By Co-Intercalation Of Onium Ion Spacing/Coupling Agents and Monomer, Oligomer Or Polymer MXD6 Nylon Intercalants and Nanocomposites Prepared with the Intercalates. US Patent 6232388, 2001

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# Nylon Nanocomposites in Flexible Packaging Applications

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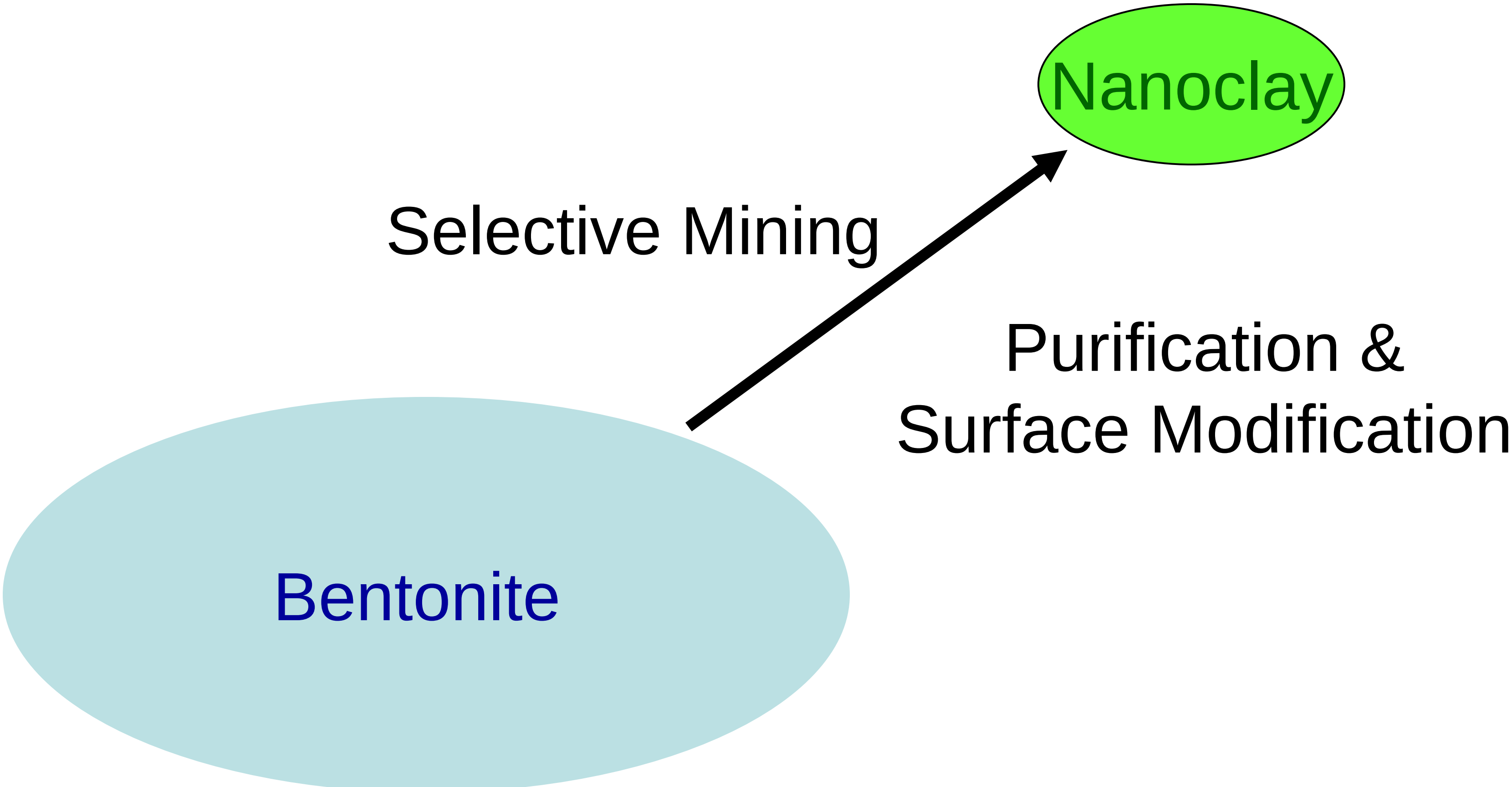
**Technical Sales Manager**
Nanocor

Sponsored by **CP Polymer**

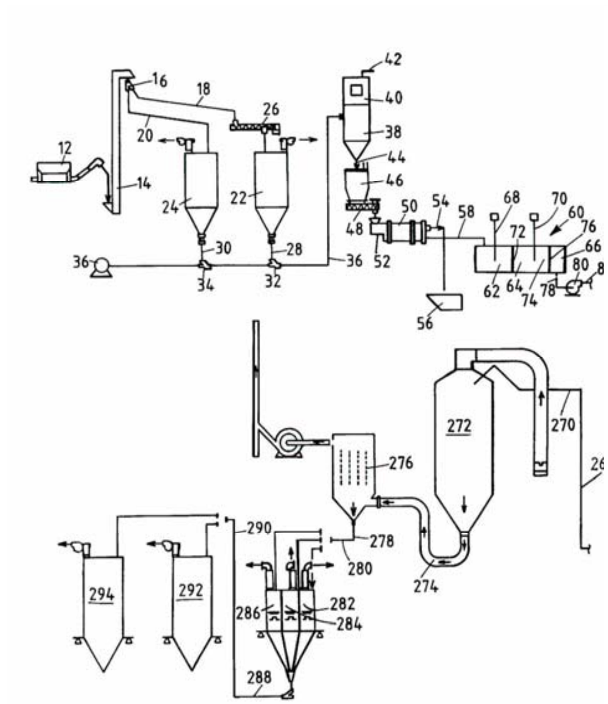
# Topics

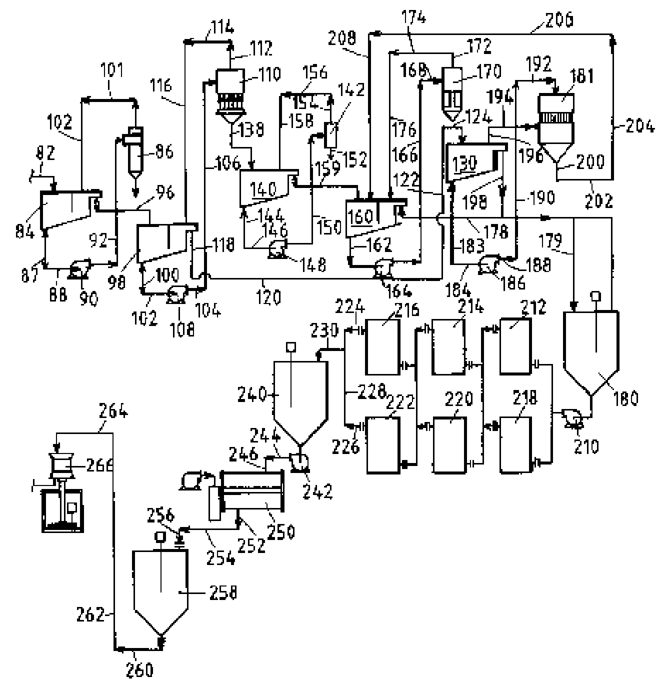
- **Nanoclay Technology and Preparation**
- **Nylon Nanocomposite**
  - **Nylon 6 Nanocomposites**
  - **Other nylon Nanocomposites**
- **Case Studies: Blend Different Nylon Nanocomposite to Balance Cost and Performance**
- **Applications**

# Nanoclay


Nanoclay
Selective Mining
Purification &
Surface Modification
Bentonite

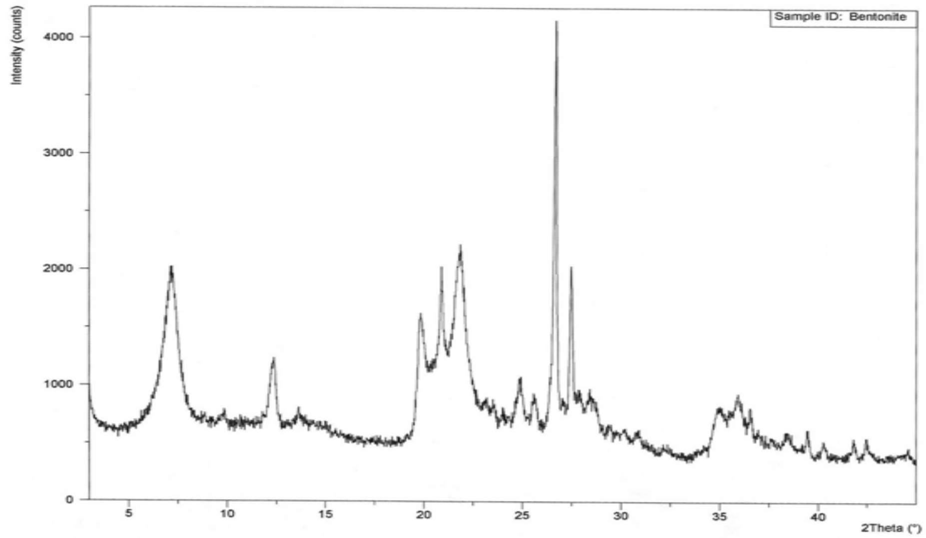
# Nanoclay



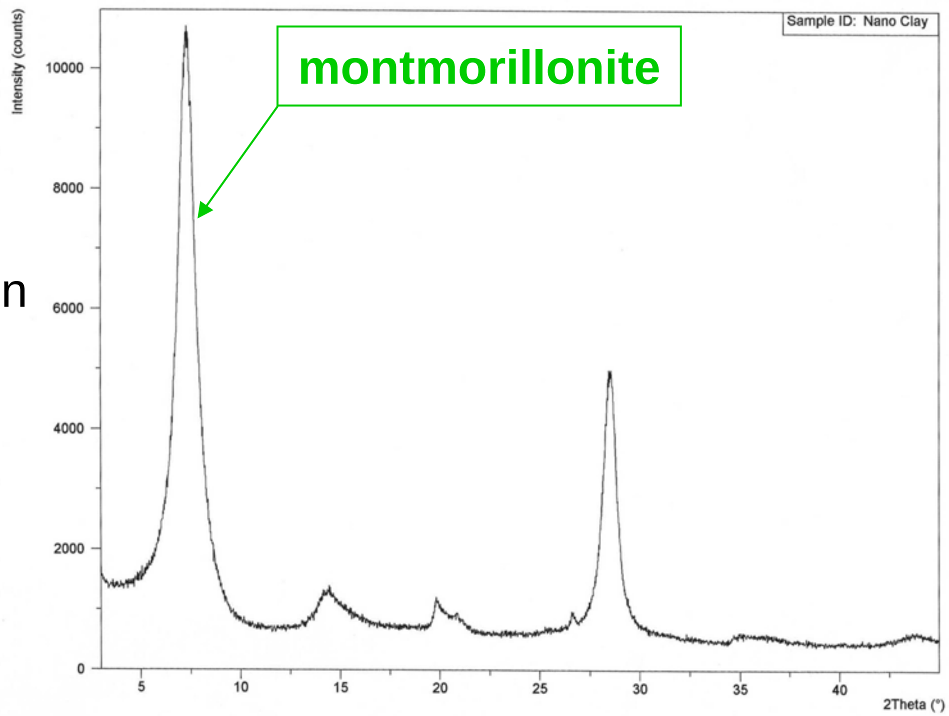


**US Patents, Amcol, 6,050,509 and 6,235,533**

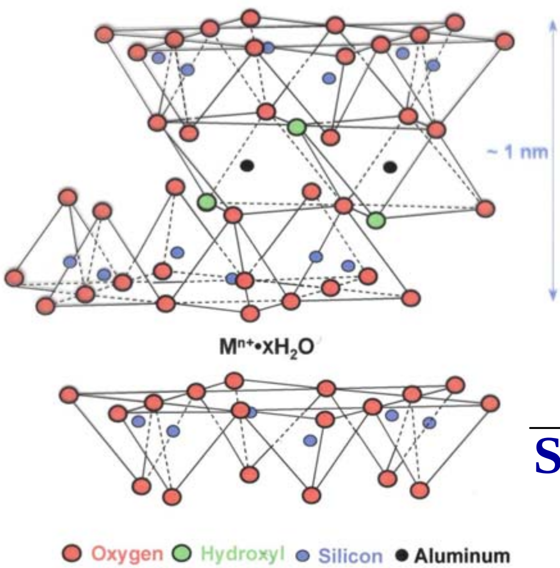
Clay as mined




Clay after purification



# Making a Nanoclay



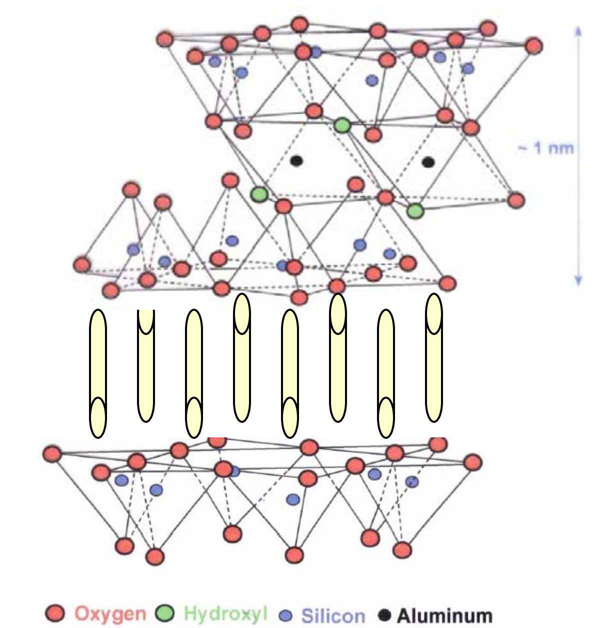

High
Aspect
Ratio

1st Step

**Surface Treatment**

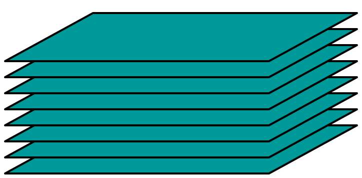
$Si^{4+} = Al^{3+} + Na^{+}$

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

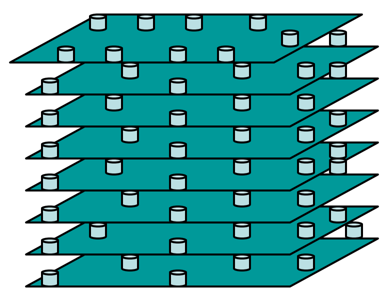



Hydrophi**l**ic

Hydroph**o**bic



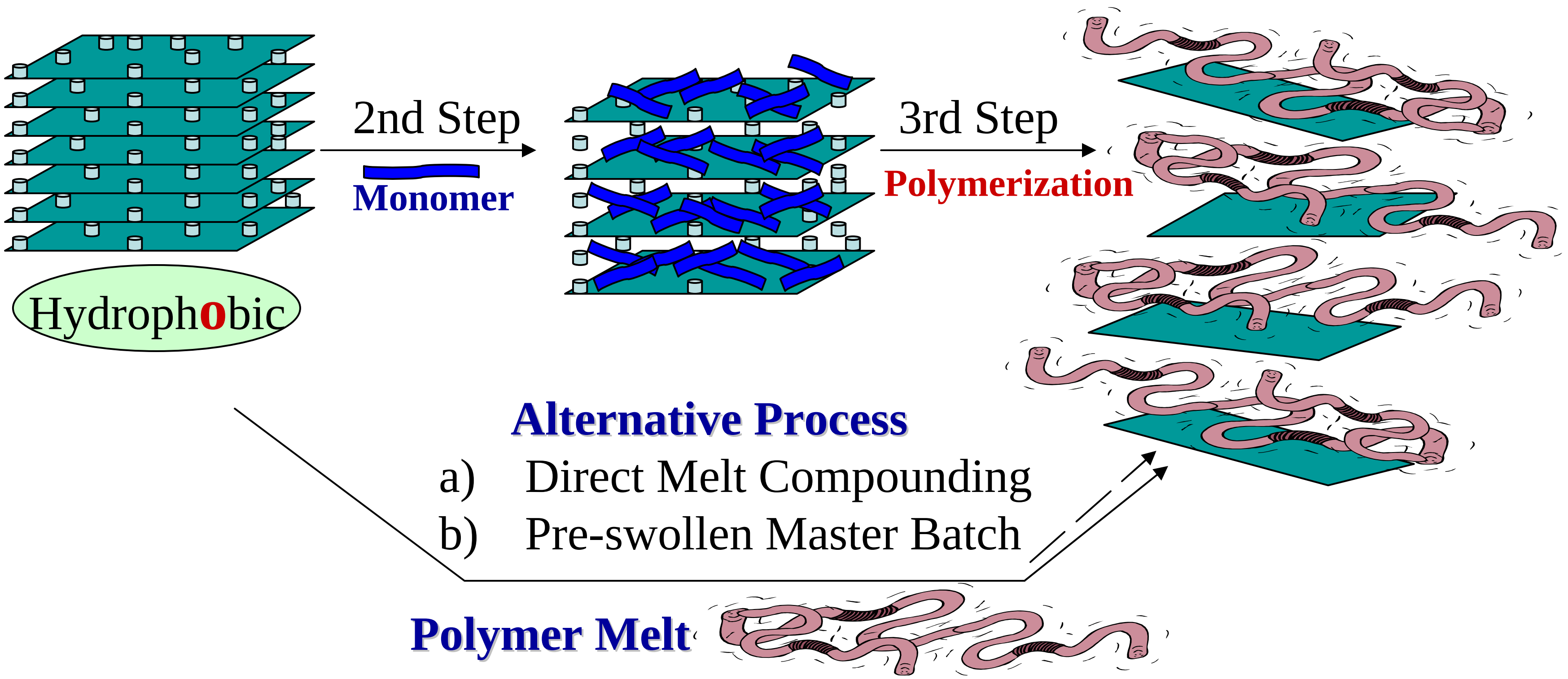
1st Step



**The Goal:**
**To Exfoliate the Individual Layer!**

# Making Nanocomposite

Nanomer® (Nanoclay) → Nanocomposite




**The Goal: To Exfoliate the Individual Layer!**

# Nylon 6 Nanocomposite: TEM

**TEM-2% Nanoclay**

Exfoliated Clay Platelets

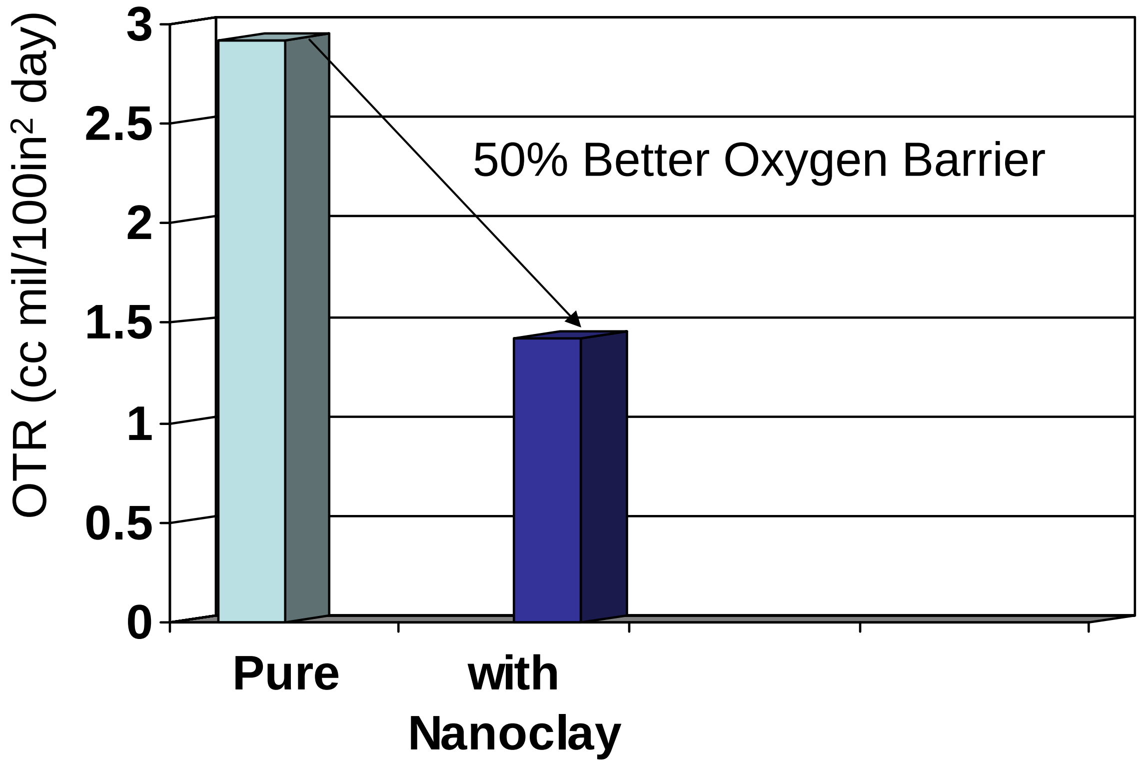

**TEM-8% Nanoclay**

# Why Exfoliation is Important?

To get 50% Barrier enhancement

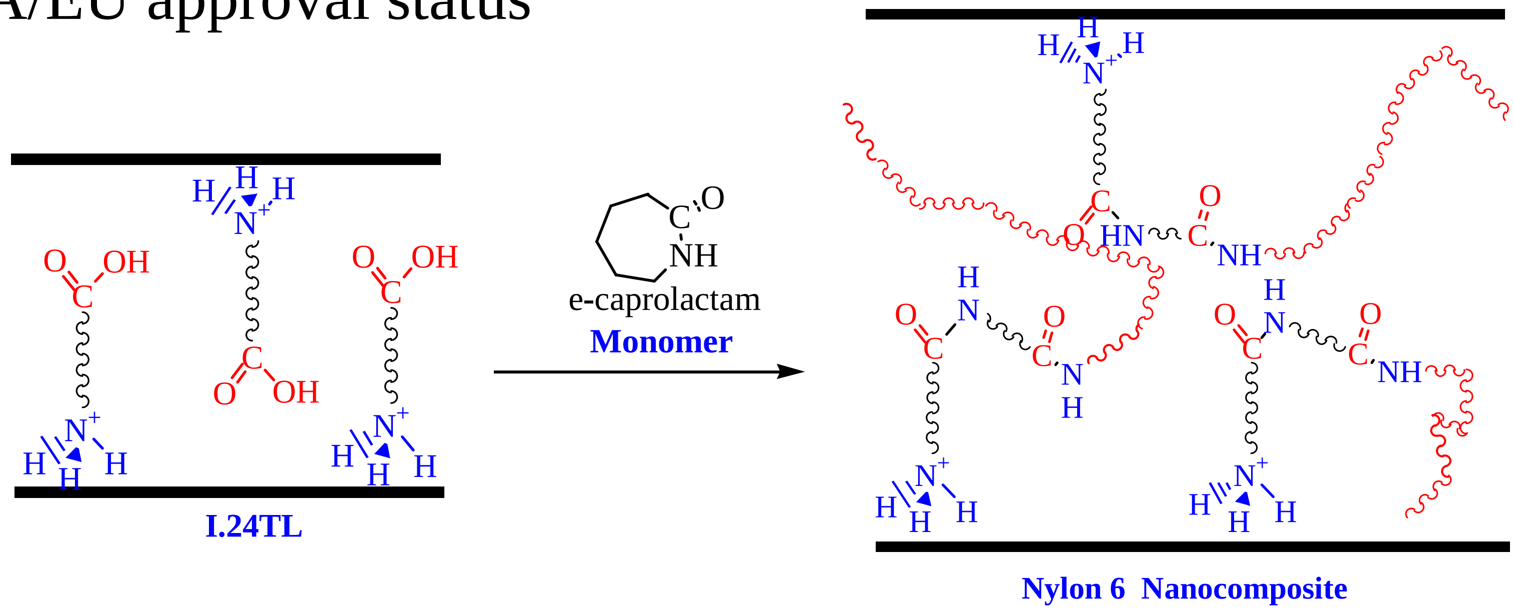
Melt-compounding: Need **5%** Nanoclay

Polymerization Route: Need **2-2.5%** Nanoclay



# Nylon 6 Nanocomposite: *in-situ* Polymerization

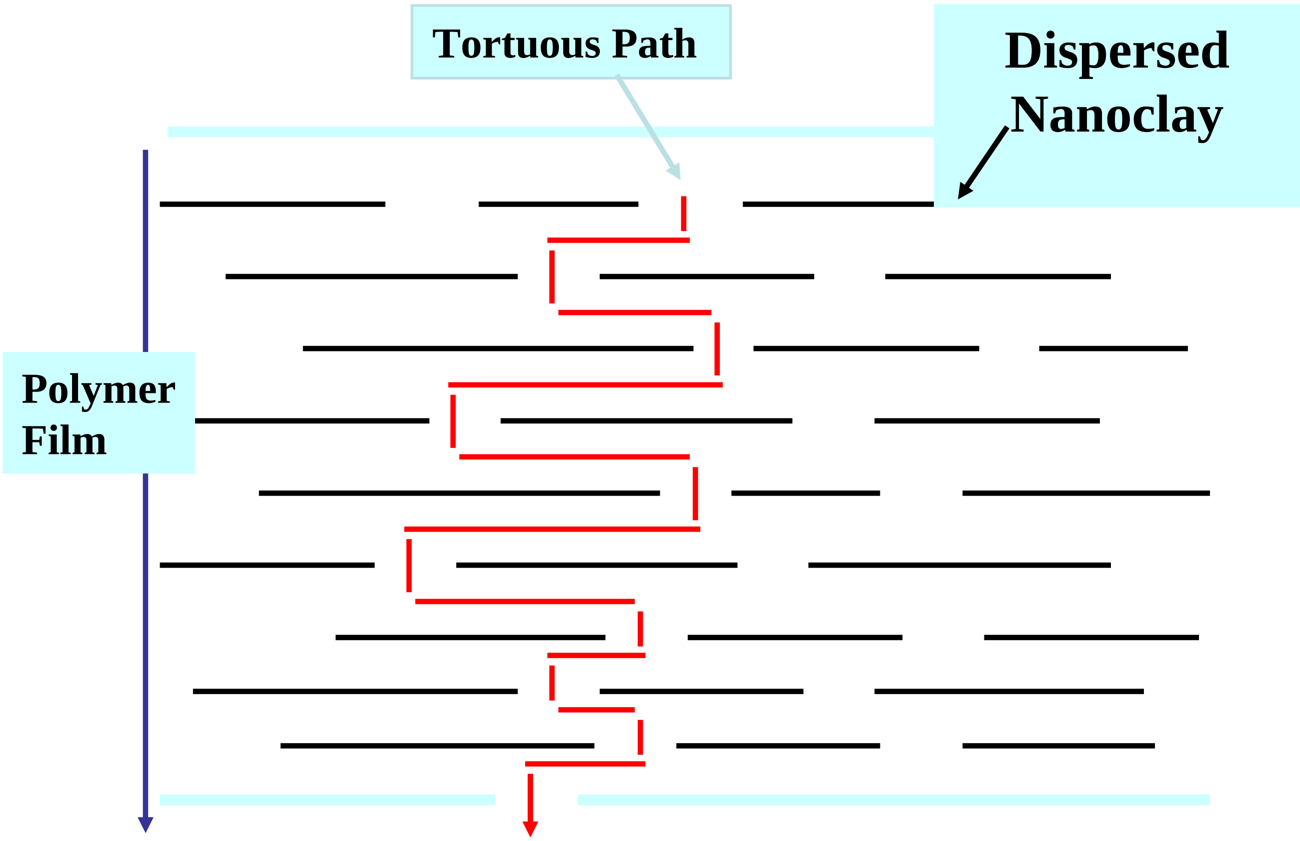
- Two Commercial Nanoclay products
- Both Nanoclay tether to the polymer chain after polymerization
- Patent coverage
- FDA/EU approval status





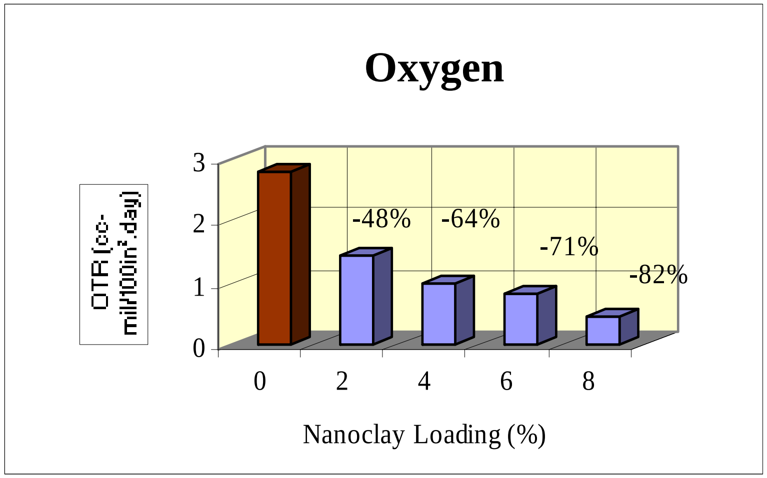
- Okada, A., Fukushima, et al U.S. Patent 4,739,007, 1988.
- Lan, T.; Liang, Y.; Omachinski, S. US Patent Appl. Publ. US2005256244 A1 20051117, 2005.

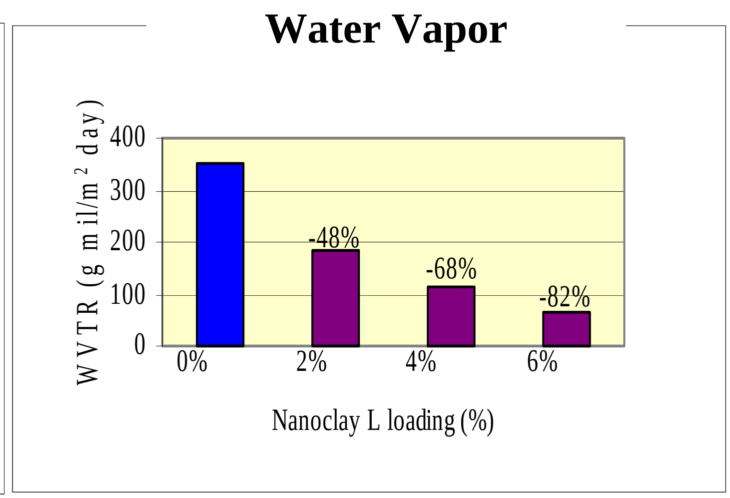
# Mechanism: Barrier Properties

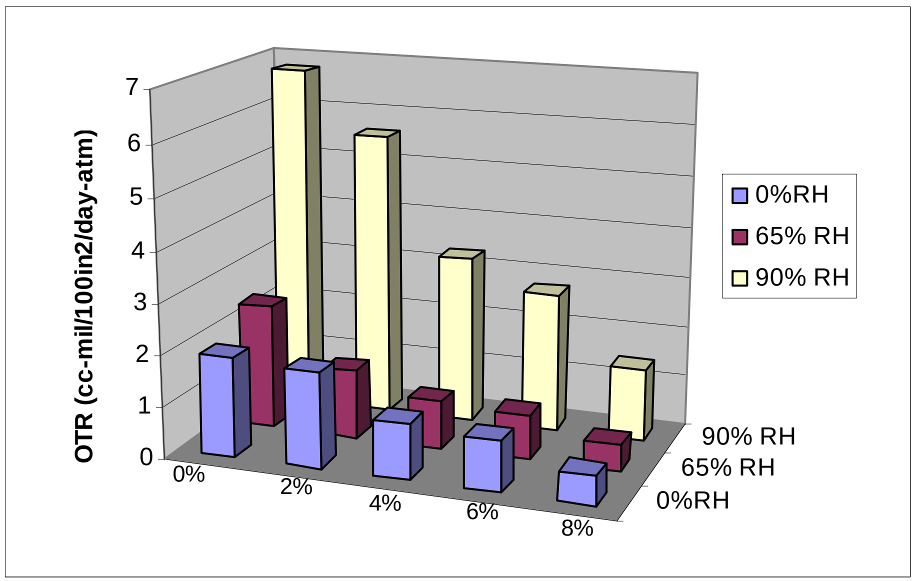


# Barrier of Nylon 6 Nanocomposite

Cast Film

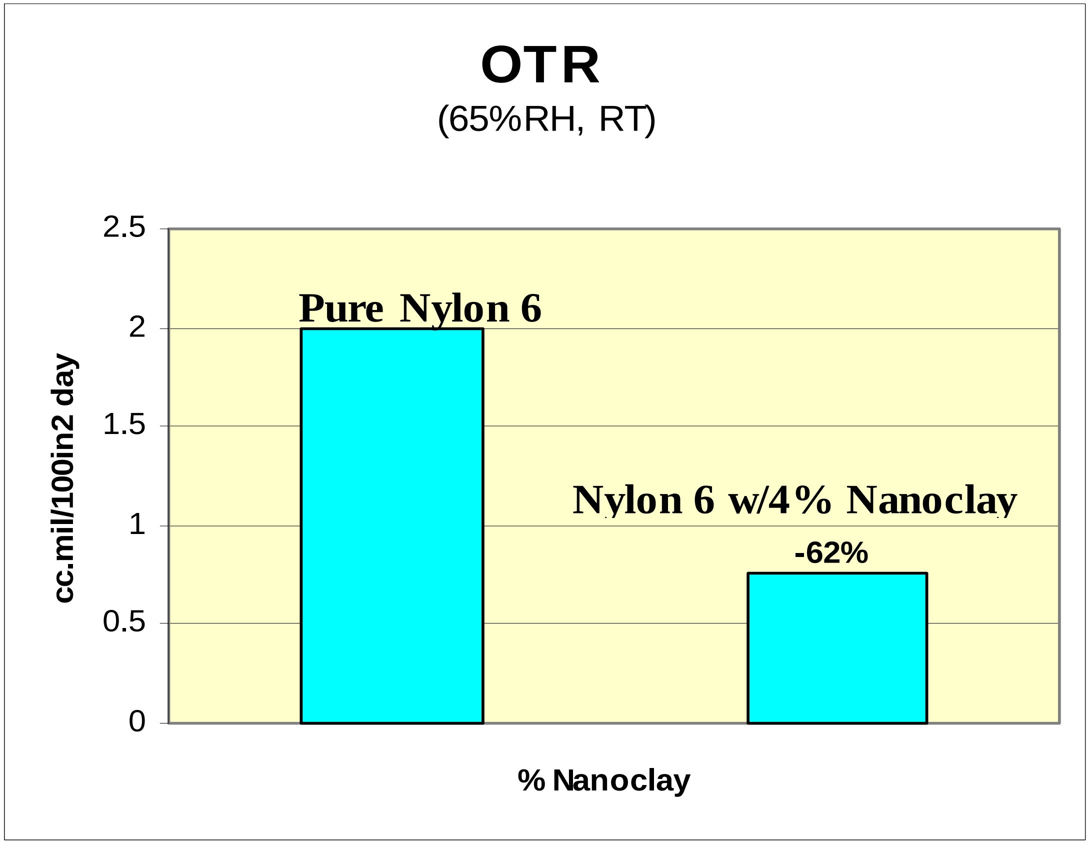


# Oxygen Barrier of Nylon 6 Nanocomposite

## *Blown Films*



# 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$^{o}$C to PA6 nanocomposite's 140$^{o}$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)

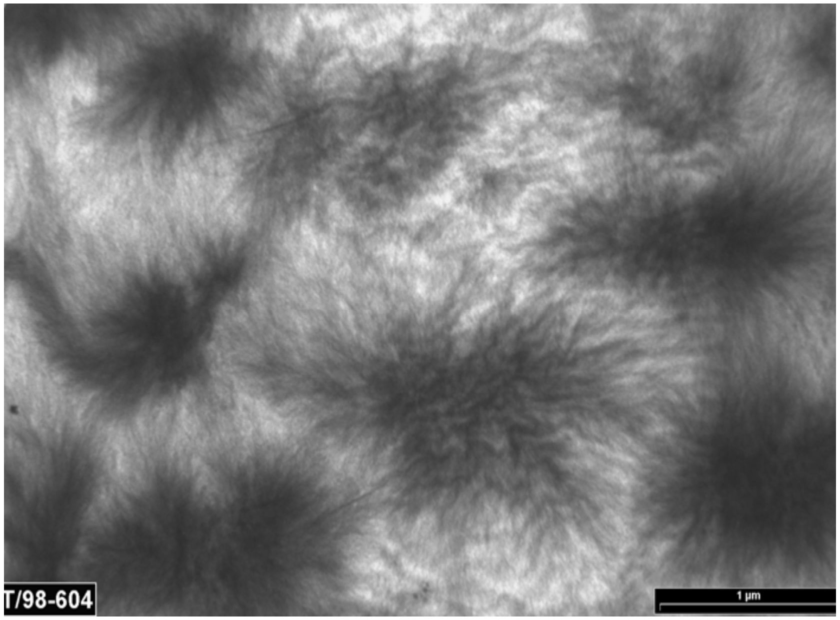
# Consideration for Packaging Applications

- **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

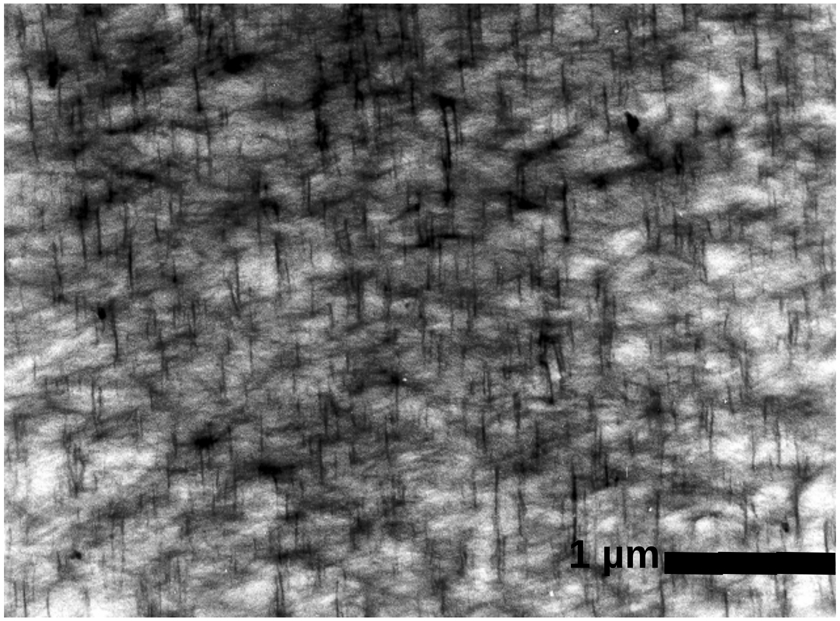
# Film Appearance

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

Nucleating effect!

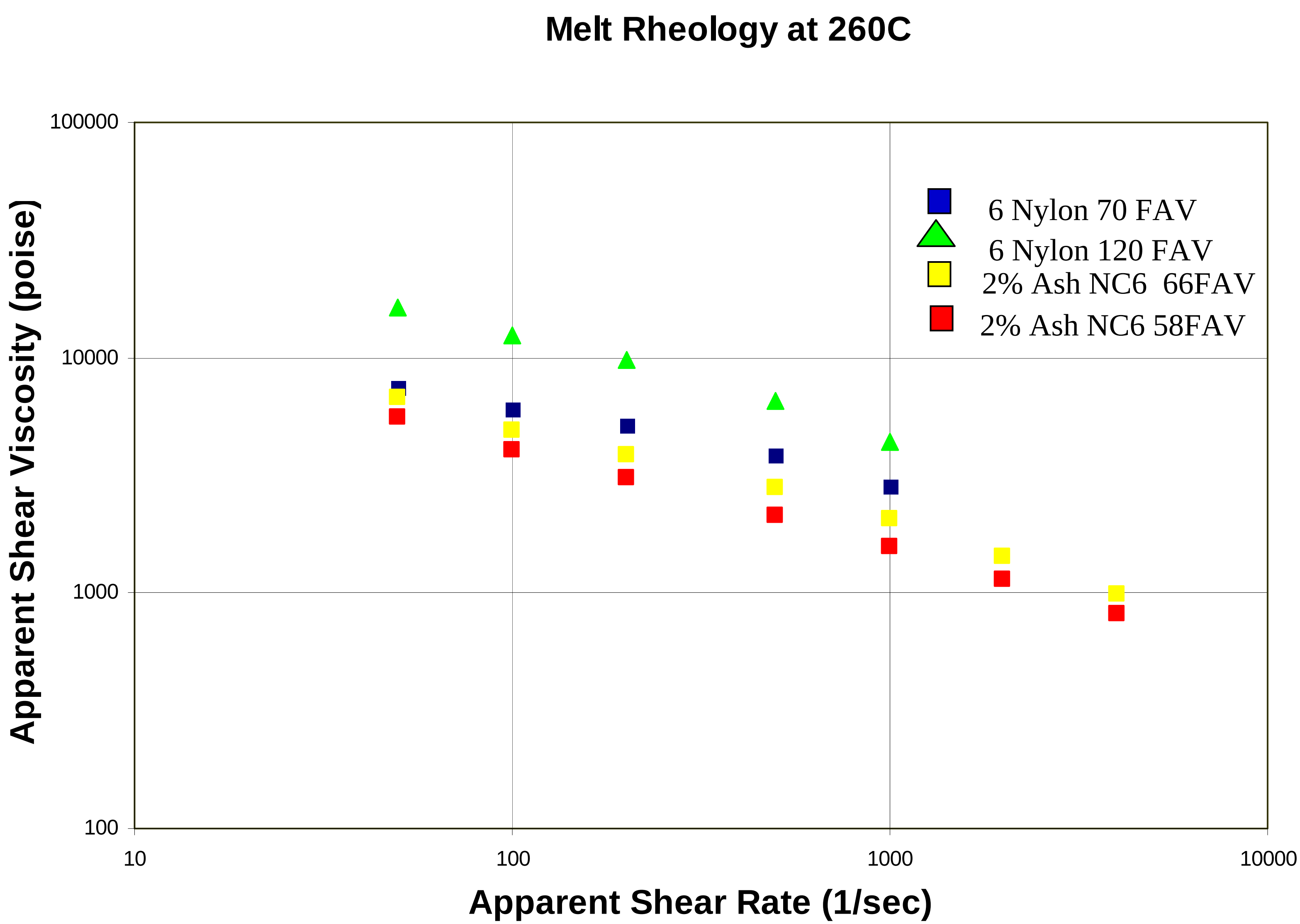



Standard PA (TEM, cross section)




Nylon Nanocomposite (TEM, cross section)

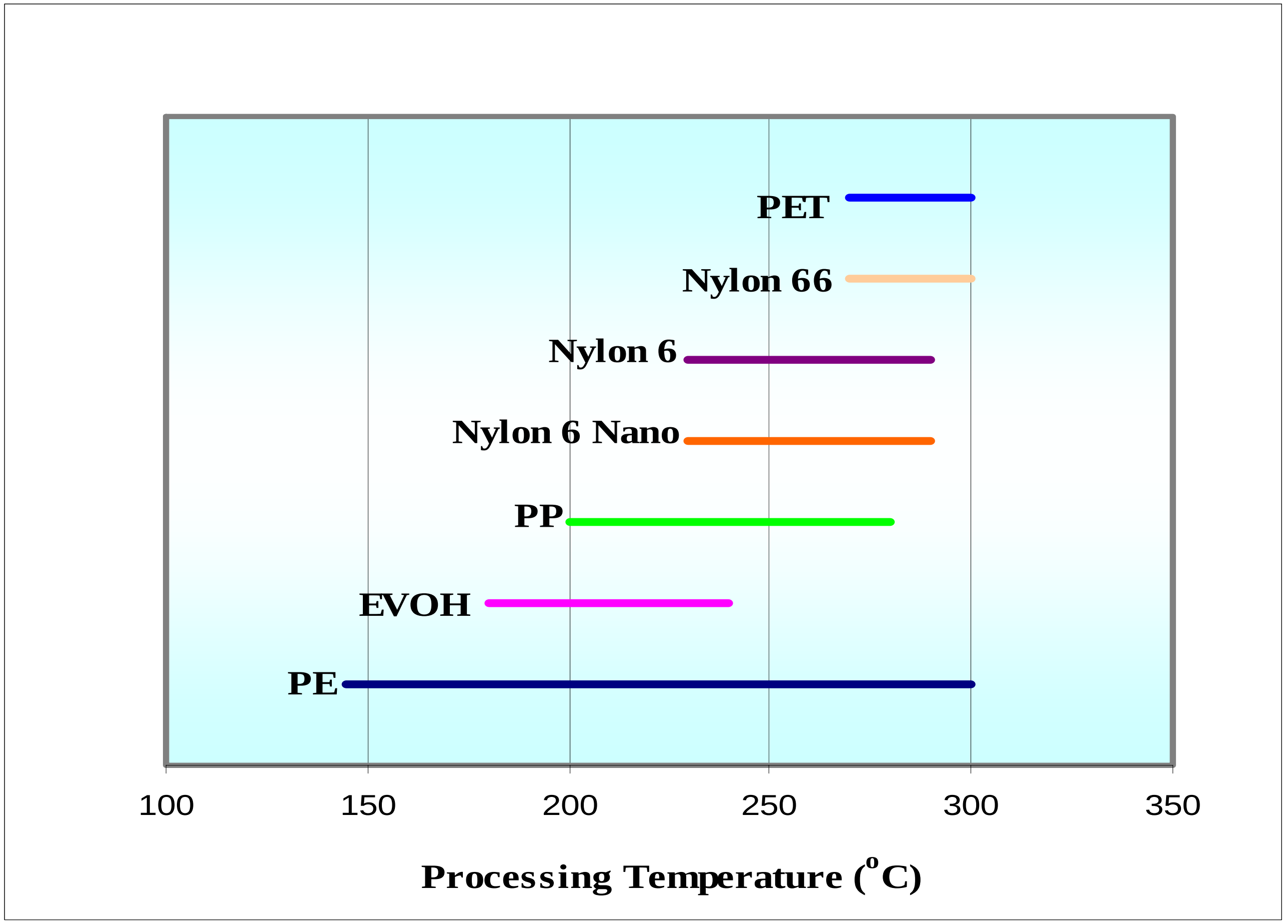
# Capillary Rheology of Nylon 6 Nanocomposite




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



# Effect of Nylon 6 Nanocomposite on 3-Layer Film Structures: Nylon 6/EVOH/Nylon 6

| **Property**<br>Stucture | | PA6/EVOH/PA6<br>0.7/0.4/0.7 (mil) | PA6NC/EVOH/PA6NC<br>0.7/0.4/0.7 (mil) |
|---|---|---|---|
| **Tensile Modulus (Kpsi)** | **MD** | **206** | **255** |
| | **TD** | **182** | **237** |
| Yield strength (Kpsi) | MD | 6.2 | 7.8 |
| | TD | 6.0 | 7.5 |
| Elongation at break (%) | MD | 390 | 350 |
| | TD | 380 | 330 |
| Tear Strength, Graves (G/mil) | | 560 | 640 |
| **Coefficient of Friction, Static (film to film)** | | **1.4** | **0.8** |
| Puncture Strength (gf) | | 1240 | 1347 |
| OTR (cc.mil/100in2/day-atm), 65%RH | | 0.036 | 0.030 |
| **Water vapor transmission rate (g.mil/100 $in^2$/day-atm, 100%RH)** | | **13.6** | **7.6** |

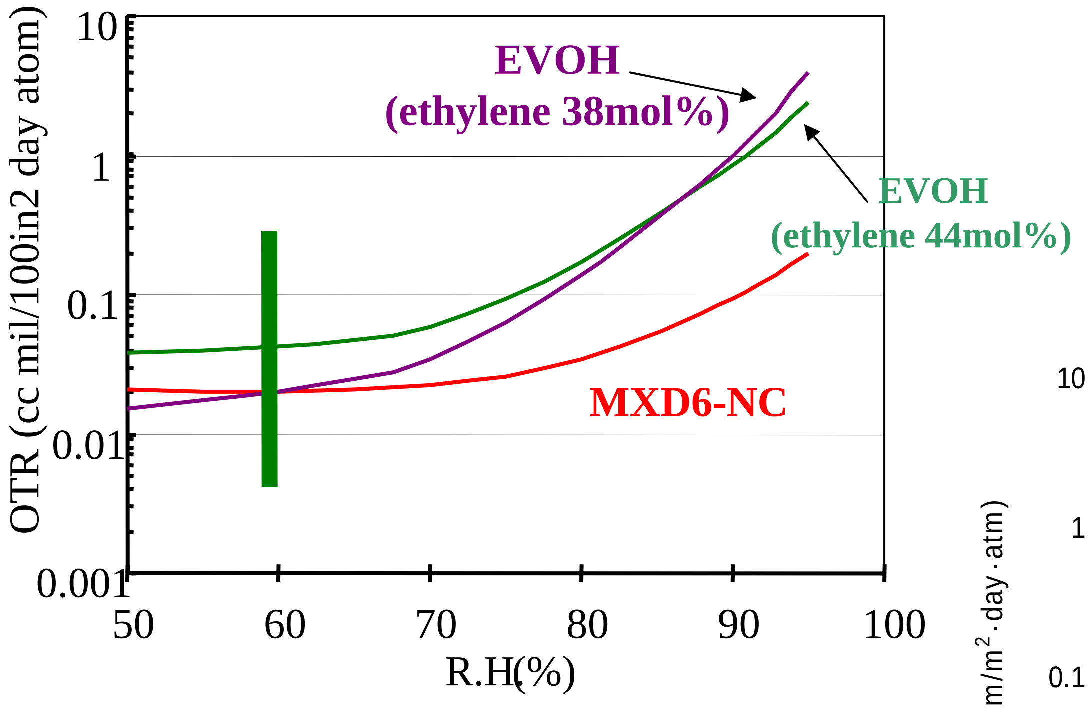
Dr. John Facinelli, Honeywell, 2006 Stand Up Pouches

# Nylon MXD6 Nanocomposite (MXD6-NC) Ultra Barrier System

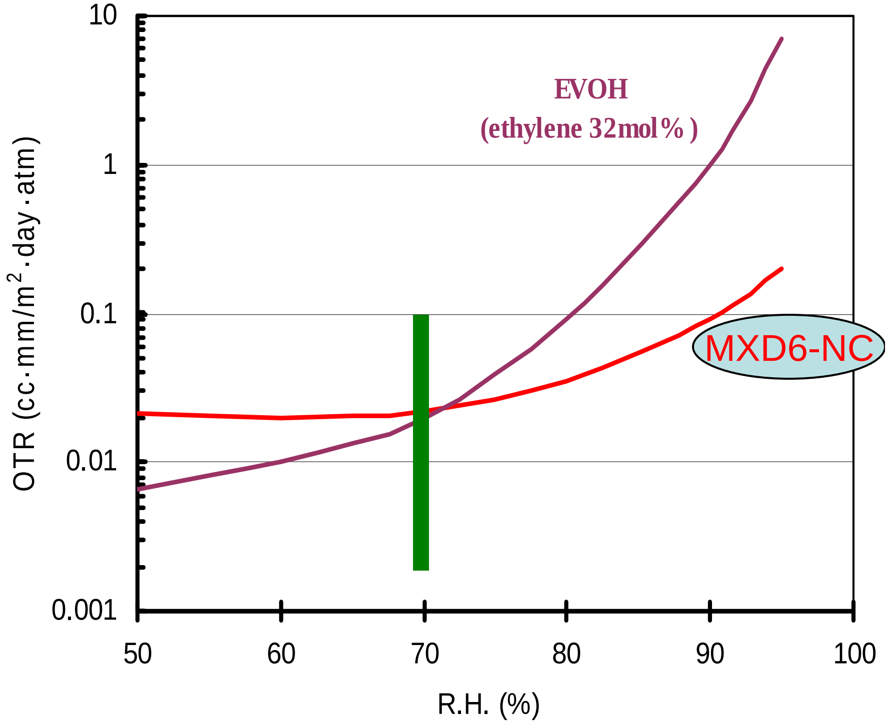
- **Patented technology**
- **MXD6-NC is fully cleared for use as non-food contact layers All food group and Condition-of-Use A**
- **Easy processing**
- **Excellent $O_2$ barrier**
- **Superb $CO_2$ barrier**

Lan, T.: Cruz, H.; Tomlin, A., US Patent 6232388, 2001

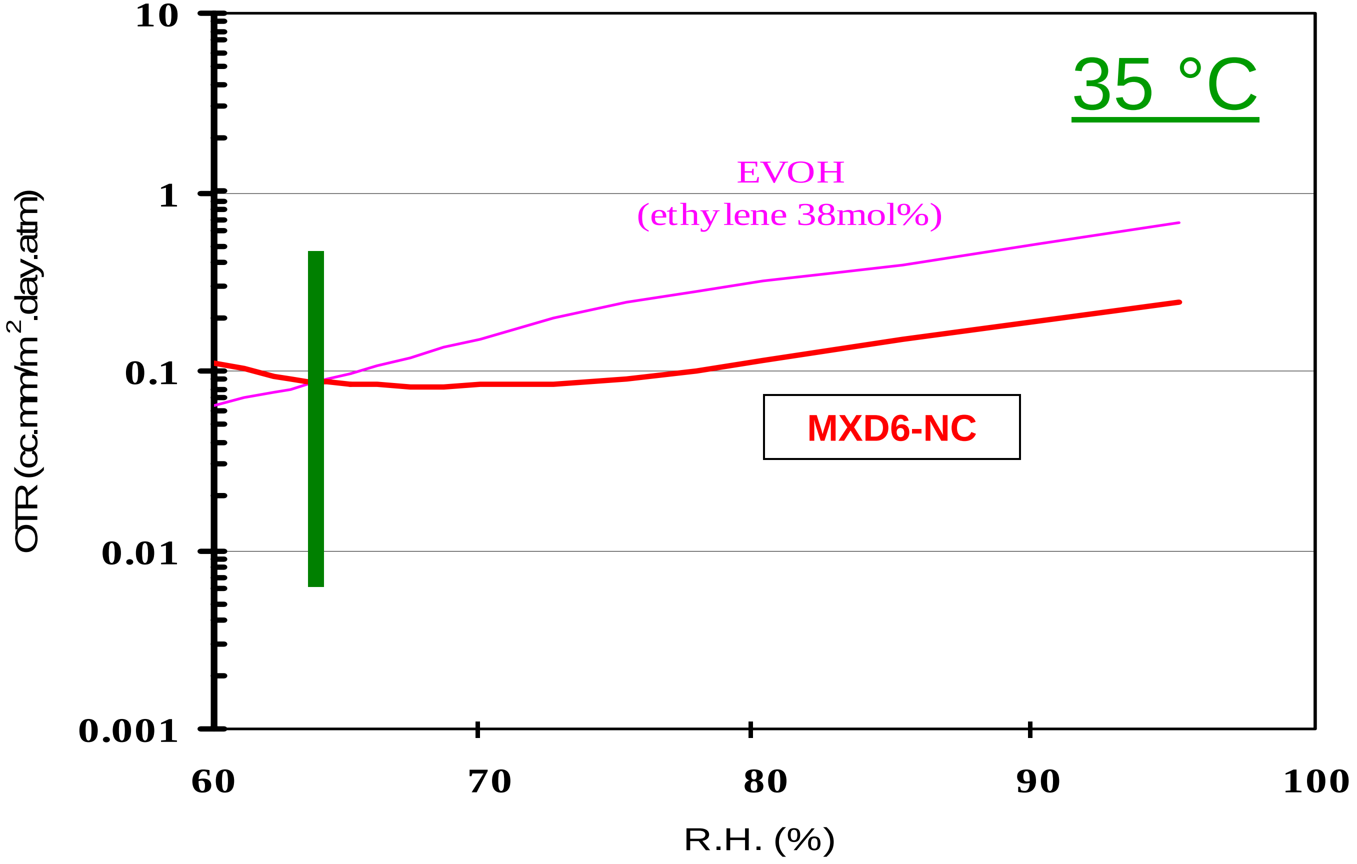
# MXD6-NC: Oxygen Barrier



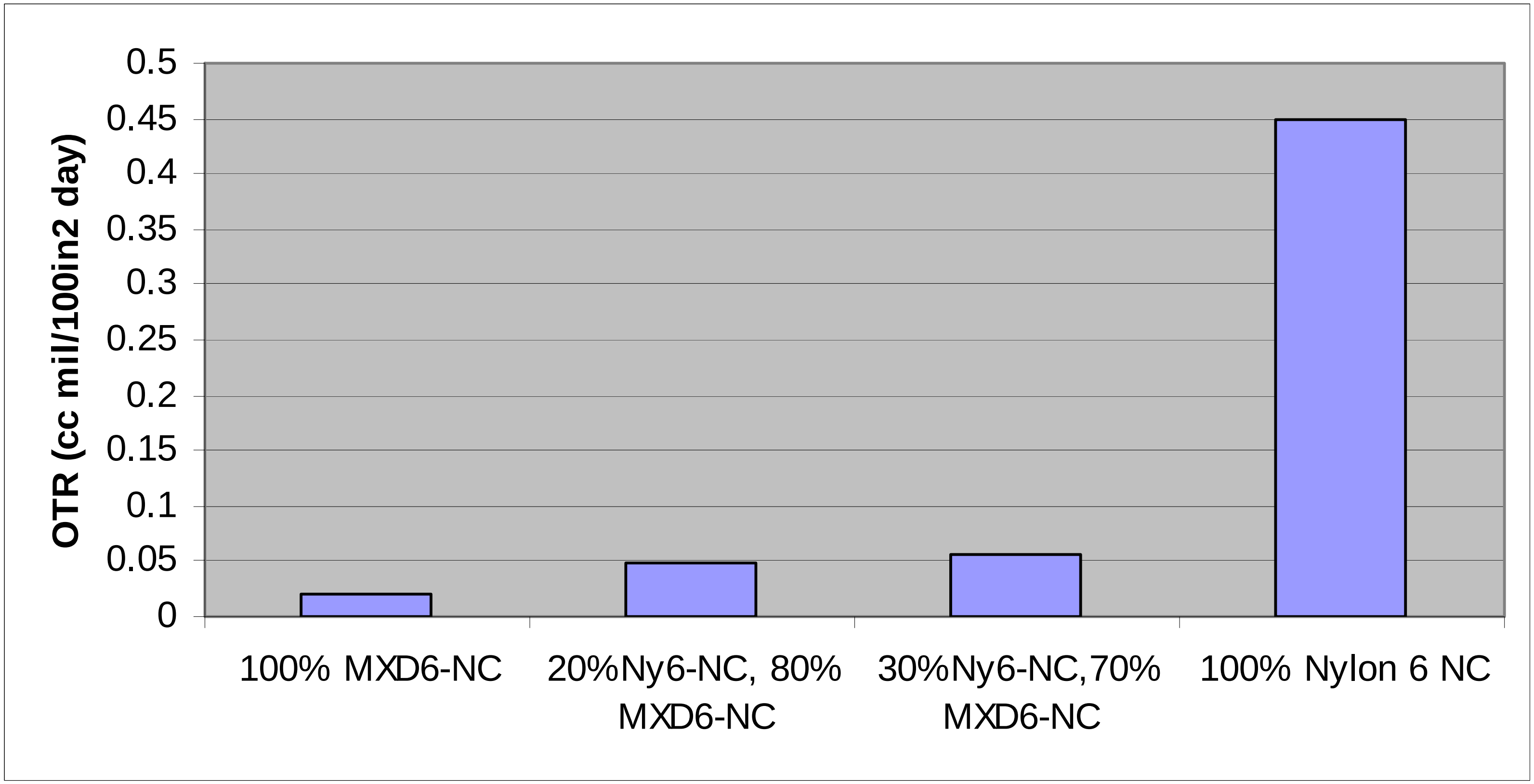

23 °C



# MXD6-NC: Oxygen Barrier



# Blend Nano Nylon 6 Nanocomposite with MXD 6 NC



# Amorphous Nylon Nanocomposite

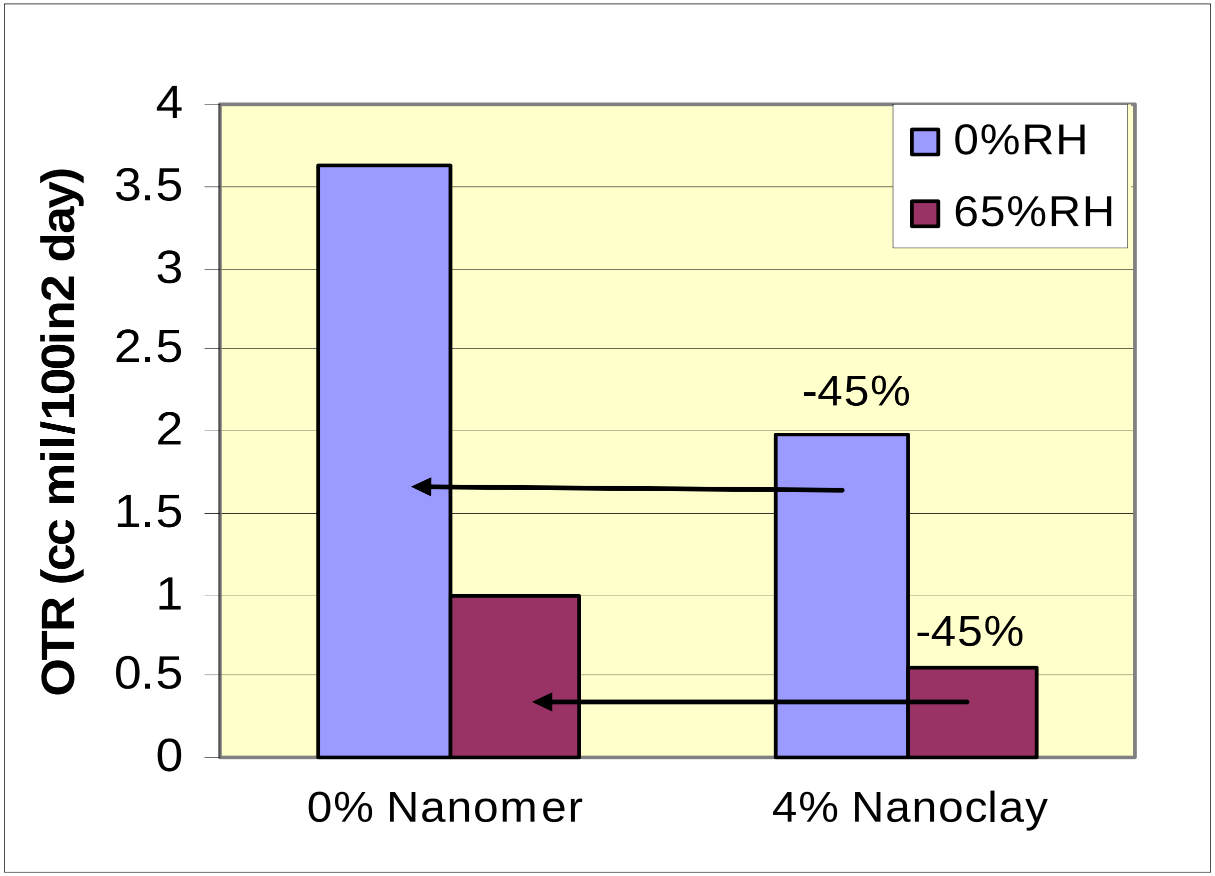
- Amorphous Nylon is 6I/6T type (Selar from DuPont and G21 from EMS)
- Can make the nanocomposite through direct melt-compounding or blending with nylon 6 nanocomposite
- Advantage of tethering effect from blending with nylon 6 nancomposite
- Barrier increases with the addition of Nanoclay

# 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**

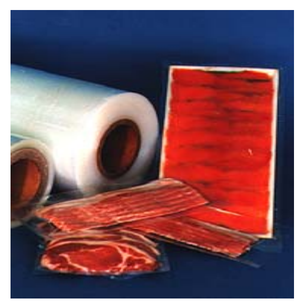
Liang, Y.; Lan, T.; Omachinski, S.; Cho, J. W. U.S. Patent 6,906,127, 6/14/2005.

# 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

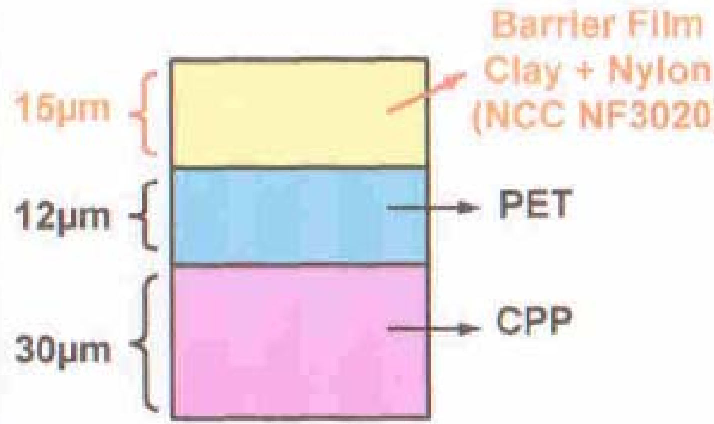
- Flexible Packaging: Multi-layer Polyolefin/nano PA films
- Extrusion Coating of Paperboard: Juice Packaging, Milk Cartons
- Single Layer Film: Down Gauging to Save Cost
- Stand-up Pouches: Barrier, Strength
- Crystallization: clear film
- Retort and cooking bag: High temperature application

# 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
  - 90/128/EEC and Commission Directive 97/48/EEC (amendment of 90/128/EEC) and 2004/19/EC (amendment of 2002/72/EC).
- Free of BBP (Benzyl Butyl Phthalate) and BPA (Bisphenol A).

Film before shaping

Finish Product

# 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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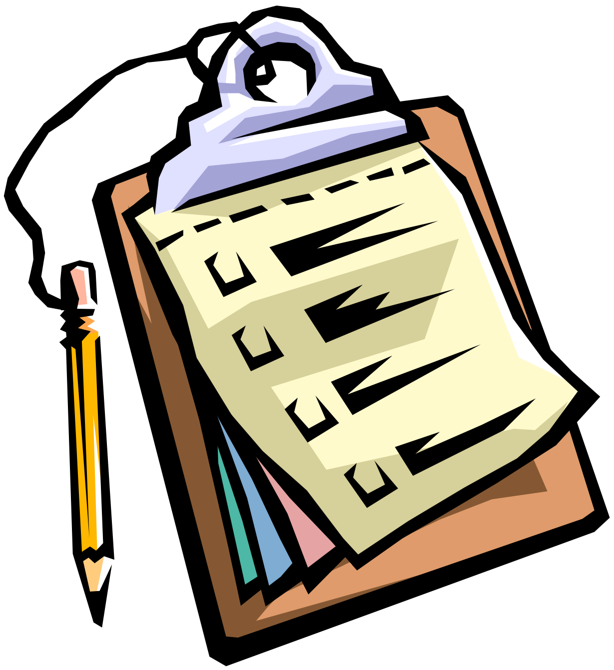

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